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枪支射击残留物现场快速检测技术研究进展

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摘要: 射击残留物(GSR)是子弹发射过程中形成的微量颗粒,作为法庭科学的重要研究对象,在涉枪案件侦查中具有关键作用。目前,常规的GSR检测主要依赖于大型实验室仪器,但由于样品前处理复杂、送检流程耗时较长,难以快速提供分析结果,从而影响了现场侦查工作的决策效率。近年来,GSR现场快速检测技术因其操作简便、成本低、便于携带等特点受到广泛关注。该类技术无需依赖大型精密仪器,可在案发现场直接实施,并能够快速输出检测结果,既适用于GSR的初步筛查,也可作为最终确认的检测手段,已成为该领域的研究热点。因此,针对GSR现场快速检测技术的研究进展进行系统综述,重点介绍比色法、光谱法、质谱法、电化学法以及荧光标记法五类方法,对其优势与局限性充分分析,并与实验室检测技术的实际应用进行对比,最后提出未来的研究方向,以期在现场技术人员在实际检测工作中提供理论依据与方法参考。

关键词: 射击残留物(GSR);现场快速检测;比色法;光谱法;质谱法;电化学法;荧光标记法

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0 引言

枪支常被视为威胁公共安全的重要因素之一。据统计,全球每年都有大量人员因枪支的使用或滥用而丧生^[1]。在涉枪案件中,射击残留物(GSR)具有重要的证据价值。当开枪射击时,GSR会附着在射击者的手部、面部以及衣物上,并可能沉积在枪击现场周围的各种物体表面^[2-5]。因此,通过对GSR进行检测,能够为枪击案件重建提供重要线索,并有助于判断射击行为的发生。

GSR主要来源于击发过程中燃烧与部分燃烧的底火中的击发药、弹壳中的发射药,以及弹头与枪管摩擦产生的金属颗粒^[6-8]。根据成分差异,GSR可分为无机射击残留物(IGSR)和有机射击残留物(OGSR)两

类^[9-10]。其中,IGSR主要来自击发药,其常见组分为斯蒂酚酸铅、三硫化二锑和硝酸钡等^[11]。因此,IGSR中通常含有铅(Pb)、锑(Sb)和钡(Ba)等金属元素^[12-13]。而OGSR则主要来源于发射药,包含硝化纤维素(NC)、硝化甘油(NG)、二乙基二苯胺(EC)、二甲基二苯胺(MC)、邻苯二甲酸二丁酯(DBP)以及二苯胺(DPA)及其硝化衍生物等成分^[14-15]。近年来,出于对传统含铅弹药在健康与环保方面潜在影响的担忧,无毒无重金属弹药受到了广泛关注。目前大多数国家中这类弹药的实际使用比例仍然较低^[16]。此类弹药产生的IGSR主要包含硫(S)、铝(Al)、硅(Si)、钾(K)和锌(Zn)等环境中常见的元素^[17]。与含Pb、Sb和Ba等重金属成分的传统IGSR相比,更易与环境背景颗粒物相混淆,从而增加了识别和区分的难度^[18]。因此,在实际GSR的现场检测中,应注重IGSR与OGSR的联合分析,以提高检测结果的准确性与可靠性。

常规的GSR检测通常基于实验室分析,尽管实验室检测结果准确可靠,但其流程较为繁琐耗时,难以在短时间内提供检测结果,因而会影响枪击案件现场侦查人员的即时判断与决策。近年来,随着现场快速检测技术的不断发展,GSR分析技术的应用正逐步从实验室走向案发现场。该技术能够实现对GSR的现场

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快速检测,帮助技术人员在枪击案件现场迅速、准确地完成检验工作。办案人员不仅能够高效判断涉案人员近期是否接触或使用过枪支,大幅缩短排查周期、指引后续侦查方向,还能通过提供关键线索缩小侦查范围,形成从嫌疑人锁定、现场重建到证据固定的全流程技术支持,为案件及时侦破提供有力支撑。

目前,国内外研究大多针对于GSR的实验室检测技术进行综述^[19-24],而对于GSR现场快速检测技术的总结却少有报道。因此,区别于既有的综述,本研究首次从GSR可现场实施检测的视角,聚焦于GSR的现场快速检测技术,系统梳理了比色法、光谱法、质谱法、电化学法以及荧光标记法在该领域的研究进展。深入探究了各类方法的优势与局限性,并与GSR的实验室检测技术比

较分析,旨在为GSR现场检测工作提供帮助。

1 GSR的实验室检测技术简述

目前常用的GSR实验室检测技术摘要如表1~2所示。针对IGSR的检测,扫描电子显微镜-能量色散X射线光谱(SEM-EDX)凭借其非破坏性、高分辨率成像及元素同步分析能力,是检测的标准方法,但其分析时间较长。激光诱导击穿光谱(LIBS)和电感耦合等离子体发射光谱(ICP-OES)检测速度快,其中LIBS还兼具高分辨率成像与元素同步分析优势,但灵敏度不如SEM-EDX。中子活化分析(NAA)和原子吸收光谱(AAS)可实现高灵敏度定性定量分析,但NAA无法检

表1 IGSR的实验室检测技术摘要

Table 1 IGSR's laboratory testing techniques summary

detection technology	detection site	component	detection limit	ref
SEM-EDX	hand	Pb	particles with a diameter of 0.5 μm	[25]
		Ba		
		Sb		
		Sn		
SEM-EDX	various substrate surfaces	Pb	particles with a diameter of 0.5 μm	[26-27]
		Ba		
		Sb		
SEM-EDX	clothing	Pb	particles with a diameter of 1 μm	[28]
		Ba		
LIBS	hand	Pb	50 ng	[29]
		Ba	0.2 ng	
		Sb	220 ng	
		Cu	20 ng	
LIBS	clothing	Pb	30 ng	[30]
		Ba	0.2 ng	
		Sb	220 ng	
ICP-OES	various substrate surfaces	Pb ²⁺	50 ng·mL ⁻¹	[31]
		Ba ²⁺	10 ng·mL ⁻¹	
		Sb ³⁺	50 ng·mL ⁻¹	
		Cu ²⁺	10 ng·mL ⁻¹	
ICP-OES	hand	Pb ²⁺	1.49 ng·mL ⁻¹	[32]
		Ba ²⁺	0.15 ng·mL ⁻¹	
		Sb ³⁺	4.79 ng·mL ⁻¹	
NAA	nasal mucus	Ba	2 ng	[33]
		Sb	5 ng	
AAS	hand	Pb ²⁺	56.22 ng·mL ⁻¹	[34]
		Ba ²⁺	11.94 ng·mL ⁻¹	
		Sb ³⁺	3.30 ng·mL ⁻¹	
AAS	nasal mucus	Pb ²⁺	0.11 ng·mL ⁻¹	[35]
		Ba ²⁺	0.5 ng·mL ⁻¹	
		Sb ³⁺	0.4 ng·mL ⁻¹	

表2 OGSr的实验室检测技术摘要

Table 2 OGSr's summary of laboratory testing techniques

detection technology	detection site	component	detection limit	ref
ROMAN	skin clothing	NC	—	[36-37]
		EC		
		DPA		
		2-NDPA		
		4-NDPA		
ROMAN	clothing propellant	NC	—	[38-39]
		EC		
		DPA		
		DBP		
ATR-FTIR	clothing	NC	particles with a diameter of 4.7 μm	[40]
		NG		
		2,4-DNT		
MS	hand clothing	NG	12 ng	[41]
		EC	0.15 ng	
		MC	0.12 ng	
		DPA	0.075 ng	
		2-NDPA	0.62 ng	
		4-NDPA	0.66 ng	
MS	hand clothing	NG	187 $\text{ng}\cdot\text{mL}^{-1}$	[42]
		EC	94.9 $\text{ng}\cdot\text{mL}^{-1}$	
		DPA	223 $\text{ng}\cdot\text{mL}^{-1}$	
		2-NDPA	104 $\text{ng}\cdot\text{mL}^{-1}$	
		2,4-DNT	128 $\text{ng}\cdot\text{mL}^{-1}$	
GC-MS	hand	NG	110 $\text{ng}\cdot\text{mL}^{-1}$	[43]
		EC	60 $\text{ng}\cdot\text{mL}^{-1}$	
		MC	40 $\text{ng}\cdot\text{mL}^{-1}$	
		DPA	60 $\text{ng}\cdot\text{mL}^{-1}$	
		2-NDPA	60 $\text{ng}\cdot\text{mL}^{-1}$	
SPME/GC-MS	cartridge case	EC	—	[44]
		DPA		
		DPB		
HSSE/GC-MS	cartridge case	EC	0.05 ng	[45]
		MC	0.05 ng	
		DPA	0.005 ng	
		DPB	0.5 ng	
LC-MS	hand	EC	0.013 ng	[46]
		MC	0.04 ng	
		DPA	22.40 ng	
		2-NDPA	1.84 ng	
LC-MS	hand	4-NDPA	0.39 ng	[43]
		EC	1.0 $\text{ng}\cdot\text{mL}^{-1}$	
		MC	0.3 $\text{ng}\cdot\text{mL}^{-1}$	
		DPA	3.4 $\text{ng}\cdot\text{mL}^{-1}$	
		2-NDPA	2.7 $\text{ng}\cdot\text{mL}^{-1}$	
4-NDPA	3.0 $\text{ng}\cdot\text{mL}^{-1}$			

测主要成分Pb,易导致假阴性结果。因此,SEM-EDX仍是IGSR检测的首选方法。

对于OGSR的检测,气相色谱-质谱联用(GC-MS)和液相色谱-质谱联用(LC-MS)技术具备优异的分选鉴定性能,成为复杂OGSR成分检测的核心技术。相比之下,拉曼光谱(ROMAN)、衰减全反射傅里叶变换红外光谱(ATR-FTIR)和质谱(MS)技术虽然分析速度快,但灵敏度不及GC-MS和LC-MS。其中,GC-MS通常需要结合固相微萃取(SPME)或顶空吸附萃取(HSSE)预浓缩样品以提升检测限。而LC-MS无需复杂前处理即可实现高灵敏度检测,在OGSR分析中是更优的选择。

2 GSR的现场快速检测技术

2.1 比色法

比色法在GSR现场快速检测中主要包括化学试剂显色法和纳米材料增强法。化学试剂显色法基于目标成分与特定试剂发生显色反应,形成有色复合物,通过其颜色变化实现定性和半定量分析^[47-48]。纳米材料增强法则通过与比色传感器结合,利用金属纳米颗粒的局部表面等离子体共振(LSPR)效应^[49]。当纳米颗粒与目标成分相互作用时,会发生聚集,导致LSPR吸收峰位移和溶液颜色变化,实现对目标成分的高灵敏检测^[50]。比色法具有诸多优势,主要体现在操作简便和经济实用两方面。该方法通常仅需少量设备与试剂,且成本相对较低^[51]。此外,比色法的分析过程响应迅速,能够在短时间内提供检测结果,适合现场快速筛查的需求^[52]。另一个显著的优势是比色法适用于各种分析物,在各种类型样本中都具有广泛的应用性^[53-54]。

在针对皮肤创口内的IGSR检测时,Andreola等^[55]通过切片法并利用亚铁氰化钠-盐酸试剂对Pb进行显色,使Pb呈现出蓝紫色。Geusens等^[56]则将15%醋酸溶液润湿的滤纸置于衣物弹着点处,经热压机压缩使IGSR转移至滤纸上,随后向滤纸喷洒罗丹明酸钠-缓冲液混合溶液,使Pb呈现出粉红色。在该实验中,传统的热熨斗转移方法被改进为使用热压机通过精确控制温度、压力和时间,实现了更均匀和高效的IGSR模式转移,使得显色效果更好。Henrique Braz Garcia等^[57]则研究了一种更为可靠的定性比色方法,实现对IGSR中Pb、Ba和Cu这3种成分的显色。该方法首先使用40%醋酸润湿采集后的胶带样本,随后喷洒罗丹明酸钠溶液,使得Pb形成紫色或酒红色络合

物,而Ba出现橙色或橙红色络合物。对于Cu的检测,则利用其与二硫代草酰胺在乙醇溶液中的显色反应,生成绿色或深绿色络合物进行识别。

除了上述传统的比色法之外,微流控纸基分析装置(μ -PADs)也是一种有效的比色检测手段。其以纤维素为基础构建纸基底,通过疏水材料构筑微通道和检测区域。待测样本在毛细作用下沿微通道流动,与

预置在检测区域的化学试剂发生反应,产生颜色变化。Buking等^[58]和Wongpakdee等^[59]通过 μ -PADs实现了对Pb的快速、便捷的比色检测。其原理是Pb与罗丹宁酸钠反应生成粉红色络合物。此外,通过测量该络合物条带的长度进行定量分析,并将其应用于射击距离的推断(图1)。但该方法的有效检测范围有限,仅适用于60 cm以内的射击距离。

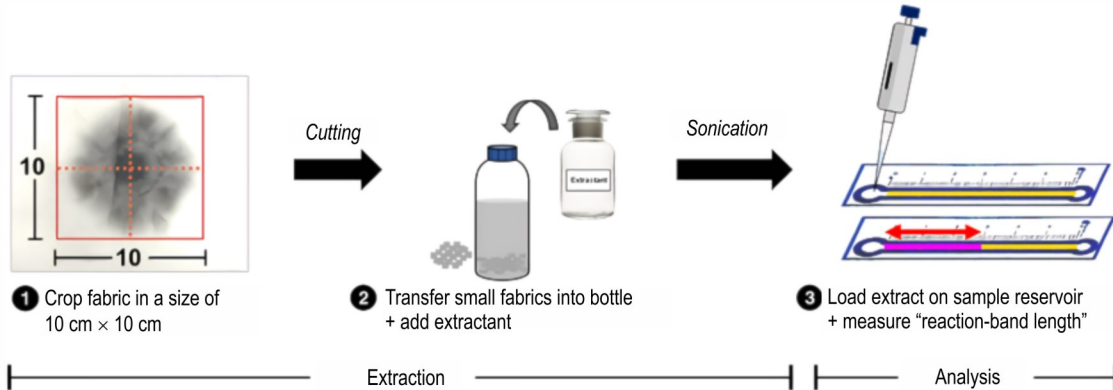


图1 基于 μ -PADs推断射击距离的实验过程图^[59]

Fig.1 Experimental process diagram of inferring shooting distance based on μ -PADs^[59]

为了简化前处理流程,并提高对IGSR的现场检测效率与灵敏度,Shrivastava等^[60-61]开发出一款手持式检测设备。该设备基于比色传感原理,采用聚乙烯醇修饰的银纳米粒子和金纳米粒子分别特异性识别Pb和Ba这两种成分。该设备内部集成LED光源、光电探测器、微处理器和显示屏,具备信号采集、数据处理和浓度显示一体化功能,可实现Pb与Ba这两种成分的现场快速检测。其中,金纳米粒子检测Ba的机制如图2所示。

然而,比色法也存在着一定的局限性。在检测过程中,该方法容易受到交叉反应或复杂样本基质的干

扰,可能导致假阳性或假阴性的结果,影响检测的准确性^[62-63]。此外,在分析物浓度较低时,比色法的检测效果通常不理想。因此,该方法仅适用于GSR的初步筛查,为获得更可靠的分析结果,仍需借助仪器分析技术进行进一步检测确认。近年来,基于比色传感的手持式检测设备结合纳米材料的应用,有效提升了对GSR的检测灵敏度,并简化了前处理流程。在未来,研究的重点工作应聚焦于开发基于新型纳米材料的手持式比色传感设备,以实现IGSR和OGSR的高特异性联合识别。其中,比色法在GSR现场快速检测中的摘要如表3所示

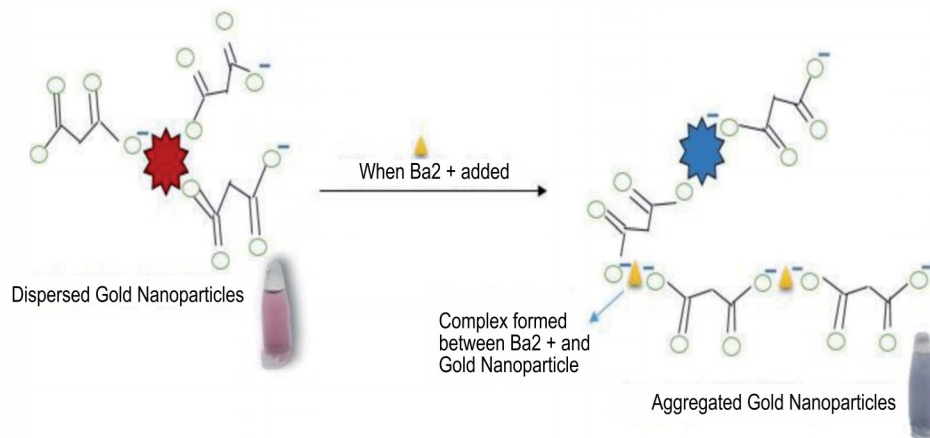


图2 金纳米粒子检测Ba的机制^[61]

Fig.2 Mechanism of Gold Nanoparticles Detection for Ba^[61]

表3 比色法在GSR现场快速检测中的摘要

Table 3 Summary of colorimetric method in on-site rapid detection of GSR

detection technology	detection site	component	color	detection limit	ref
Sodium Ferrocyanide - Hydrochloric Acid	skin wound	Pb ²⁺	blue-violet	—	[55]
15% Acetic Acid	clothing	Pb ²⁺	pink	—	[56]
Sodium Rhodanine					
40% Acetic Acid	hand	Pb ²⁺	purple or burgundy	—	[57]
Rodan Sodium Ascorbate		Ba ²⁺	orange or orange-red		
40% Acetic Acid	hand	Cu ²⁺	green or dark green	—	[57]
Dithiocarbamide					
μ-PADs	clothing	Pb ²⁺	pink	—	[58-59]
Silver Nanoparticle	clothing	Pb ²⁺	red and yellow	1.02 μg·mL ⁻¹	[60]
Gold Nanoparticle	clothing	Ba ²⁺	blue	200 μg·mL ⁻¹	[61]

2.2 光谱法

2.2.1 表面增强拉曼光谱法

表面增强拉曼光谱(SERS)是一种能够显著增强分子拉曼散射信号的技术,其原理主要基于金属表面或纳米结构的特性^[64-65]。当待测分子吸附在金和银等特定金属表面或纳米结构上时,会显著增强拉曼散射信号,从而实现信号的大幅提升^[66-67]。SERS在检测OGSR具有高灵敏度和高选择性,使得极少量的OGSR也能被可靠检测^[68]。

Shafirovich等^[69]首次利用便携式SERS,实现了对OGSR中DPA和EC等多种成分的痕量检测。该方法采用金纳米颗粒作为SERS基底,以半胱胺修饰提高稳定性。该研究证明了SERS与便携设备联用检测OGSR的可行性,相较于传统的便携式拉曼光谱仪,SERS检测限展现出了最高约7倍的信号增强。Thayer等^[70]则通过SERS分别比较了在丙酮、乙腈、乙醇和甲醇这4种溶剂中对DPA和EC检测效果影响。研究指出,丙酮和乙腈因其背景干扰低、目标物信号强度高,被证明是检测DPA和EC的最佳溶剂。相比之下,甲醇和乙醇则由于自身的溶剂峰与DPA、EC的特征峰存在重叠,严重降低了检测的灵敏度。

便携式SERS技术集成了表面增强拉曼散射的高灵敏性与便携式设备的现场快速检测优势。但该技术在实际应用中仍存在一定的局限性。一方面,复杂样品基质中的共存成分可能竞争SERS纳米颗粒表面的吸附位点或引入荧光背景,从而干扰目标信号;另一方面,受限于便携式仪器的紧凑设计,其在信噪比控制和信号采集效率上不及台式设备,往往需借助复杂的数据处理算法以增强特征信号,消除背景噪音。

2.2.2 激光诱导击穿光谱法

激光诱导击穿光谱(LIBS)是一种基于激光烧蚀与

等离子体发射光谱的原子光谱技术,其原理为高能脉冲激光聚焦于样品表面烧蚀产生微等离子体,冷却过程中激发态原子/离子发射特征光,即可实现元素组成的定性与定量分析^[71-72]。LIBS技术具有分析速度快、可多元素同步检测以及对样品微损等显著优势,因此被广泛用于痕量IGSR的高灵敏度检测与识别^[73-74]。此外,LIBS技术还具备高空间分辨率的特点,能够实现IGSR分布的可视化,对弹孔周围IGSR的空间分布进行高分辨率成像^[75-77]。

Rodriguez-Pascual等^[78]评估了便携式LIBS设备在建筑材料、织物和车辆等多种表面现场检测IGSR的效果。该设备能够在射击后表面中有效识别多种IGSR特征成分,并可检测到直径大于1 μm的颗粒。实验结果表明,便携式LIBS技术在多种实际射击场景下表现出良好的应用潜力,且无需采样即可实现现场快速、可靠的IGSR检测。

为验证便携式LIBS应用于IGSR现场检测的可靠性,Pyl等^[79]通过实验对比了便携式与实验室LIBS检测IGSR的能力。以300份手部IGSR样品为实验对象,分析对象为Pb、Ba、Sb,所有样品先由便携式LIBS分析,再经实验室LIBS复测。研究结果表明,便携式LIBS总体准确率为98.8%,实验室LIBS总体准确率为99.0%。其中,便携式与实验室LIBS的比较如图3所示。Doña-Fernández等^[80]则系统比较了便携式LIBS与SEM-EDX在检测IGSR方面的性能。研究结果表明,便携式LIBS对直径小于1 μm的IGSR颗粒检测能力有限,可能存在漏检风险。而SEM-EDX可检测到直径0.4 μm的颗粒。

Thomas等^[81]进一步利用了便携式LIBS的高分辨率成像能力,对多种物体表面进行IGSR现场分析。该技术同时结合了高分辨率成像与光谱分析,能够观察

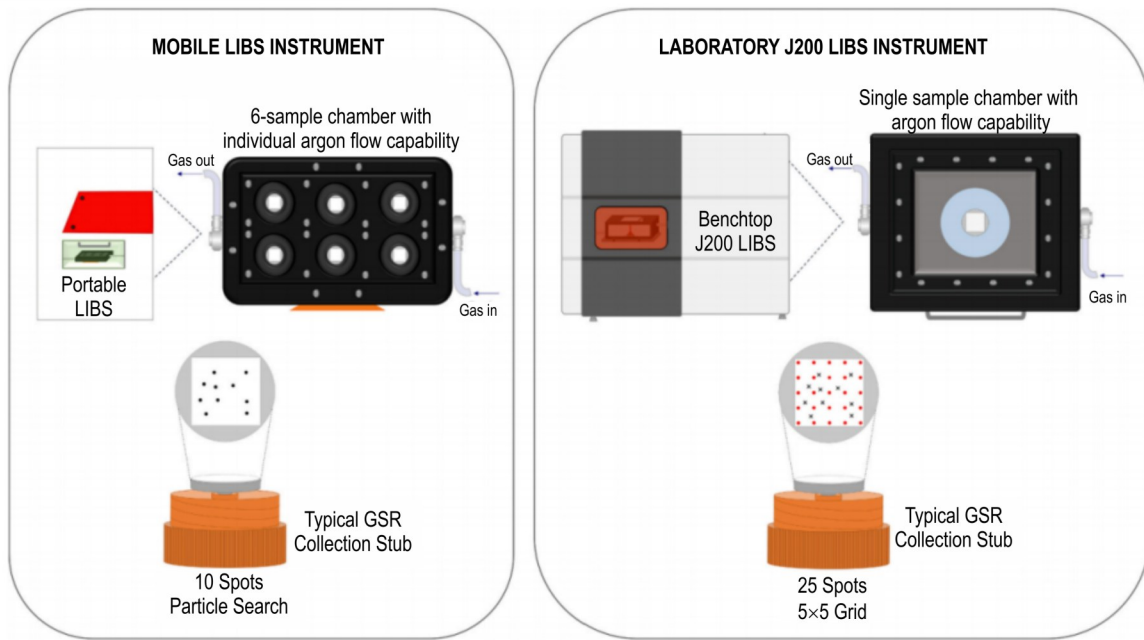


图3 便携式与实验室 LIBS 的仪器差异以及采样模式比较^[79]

Fig.3 Instrument differences between portable and laboratory LIBS and comparison of sampling modes^[79]

到 IGSR 颗粒的微观形态, 并实现对单个颗粒的定点识别分析(图 4)。在 260 个测试样本中, 射击者手部及弹孔处样本的 GSR 检出率达到 95%。该方法分析速度快, 单个样品测量时间不足 1 min, 展现出了便携式 LIBS 高效、灵敏的多元素检测与高分辨率成像的综合分析能力。Lazic 团队^[82]则开发了一种新型便携式 LIBS 传感器, 可直接进行手持式 IGSR 的现场快速检测。该传感器头内置高分辨率彩色相机和指示激光

器, 用于 IGSR 样品的可视化和精确定位, 单次激光脉冲即可检测到 Pb、Ba、Sb 等多种成分。

便携式 LIBS 技术在 IGSR 分析中具有显著优势, 能够实现快速实时检测, 单次分析时间通常仅需数十秒至几分钟, 远快于传统的 SEM-EDS 方法。该技术无需复杂样品前处理, 可直接对多种表面进行分析, 有效保持物证的原始状态与完整性。因此, 便携式 LIBS 非常适用于现场的 IGSR 快速筛查。然而, 受限于检测灵

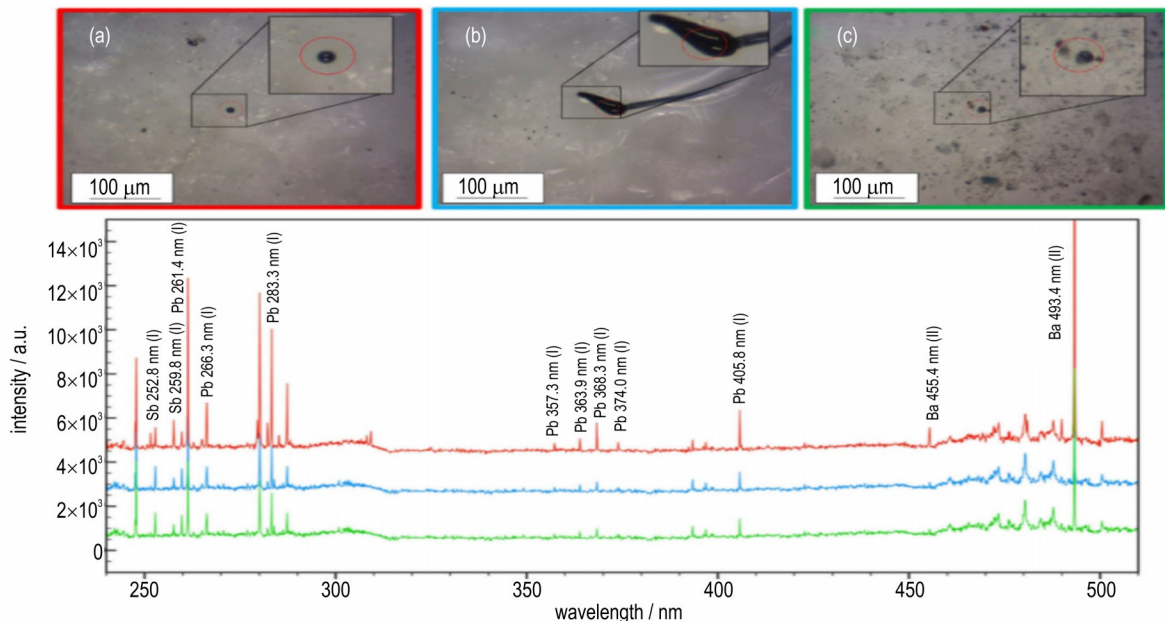


图4 便携式 LIBS 在三种基质上的高分辨率图像及光谱谱图: (a) 射击者手部; (b) 汽车挡泥板; (c) 石膏板^[81]

Fig.4 High-resolution images and spectra of portable LIBS on three substrates: (a) shooter's hand; (b) car fender; (c) gypsum board^[81]

灵敏度,该技术对于直径小于1 μm 的IGSR颗粒可能因信号较弱而出现漏检。因此,在实际应用中,便携式LIBS更适合作为IGSR初步筛查工具,仍需结合SEM-EDX进行后续结果验证,以有效排除假阴性风险,确保检测结果的准确性与可靠性。

2.3 质谱法

MS技术通过电离源将样品分子或原子转化为气态离子,依据离子质荷比的差异,利用电磁场实现分离,结合质荷比与丰度的对应关系,获取样品分子量、组成及结构信息^[83-84]。MS技术凭借其高灵敏度和高特异性,已成为检测OGSR的重要工具^[85-87]。但其仪器的现场应用受限于大型的设备,样品前处理复杂且分析耗时,限制了其在现场快速检测中的应用。而便携式喷雾电离质谱技术结合采样工具和离子化探头一体化,能够实现无需复杂样品前处理的直接采样和分析,大幅简化了操作流程,从采样到获得结果仅需几分钟,特别适用于现场快速检测^[88-89]。

Fedick等^[90]创新性地提出拭子触碰喷雾电离质谱法,简化了分析流程,用于现场快速检测人体及各种表面上的OGSR。首先使用铝柄拭子擦拭目标区域,然后利用甲醇喷雾结合高压电喷雾直接解吸样本,并通过便携式质谱仪能够实现对OGSR特征成分EC和MC的即时分析。

为了能够实现在地毯、衣物、玻璃等多种复杂基质中快速收集并检测痕量OGSR,Bondzie等^[91]利用3D打印技术设计出锥形喷雾电离质谱的新型离子源并结合真空收集装置,能够在单一容器内完成对OGSR的收集、提取、过滤和喷雾离子化,大幅简化了操作流程(图5)。这一创新方法不仅提高了便携式质谱仪的检测灵敏度,同时大幅缩短了前处理时间。

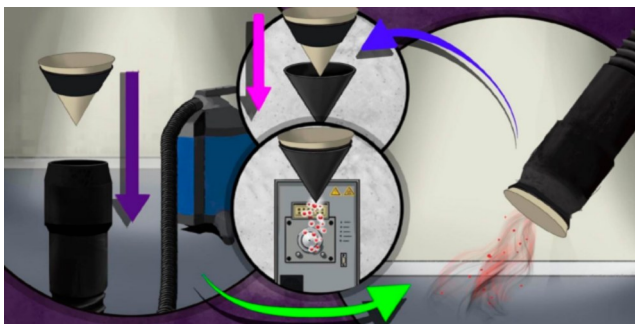


图5 基于集成真空收集的3D打印锥形喷雾电离源前处理过程^[91]

Fig.5 3D printed cone spray ionization source pretreatment process based on integrated vacuum collection^[91]

便携式质谱仪结合喷雾电离技术,可在数分钟内完成OGSR从采样到质谱检测的全过程,展现出了较好的现场检测分析能力。该技术灵敏度高,能够有效检测痕量OGSR。其前处理流程也因采用3D打印技术而大幅简化。然而,在面对地毯等复杂基质时,OGSR的采集效率较低,未来仍需进一步优化采样方法以提高检测效果。此外,受限于便携式设备的设计,其碰撞能量与分辨率通常低于台式质谱仪,会对定量分析的准确性产生一定影响。上述光谱法和质谱法在GSR现场快速检测中的摘要如表4所示。

表4 光谱法和质谱法在GSR现场快速检测中的摘要

Table 4 Summary of spectroscopic and chromatographic methods in on-site rapid detection of GSR

detection technology	detection site	component	detection limit	ref
SERS	—	EC	72.46 $\mu\text{g}\cdot\text{mL}^{-1}$	[69]
		DPA	28.77 $\mu\text{g}\cdot\text{mL}^{-1}$	
		2-NDPA	38.25 $\mu\text{g}\cdot\text{mL}^{-1}$	
		4-NDPA	6.43 $\mu\text{g}\cdot\text{mL}^{-1}$	
		N-NODPA	7.08 $\mu\text{g}\cdot\text{mL}^{-1}$	
SERS	—	EC	—	[70]
		DPA	—	
LIBS	various substrate surfaces	Pb	particles with a diameter of 1 μm	[78]
		Ba	2.0 ng	
		Sb	0.2 ng	
LIBS	hand	Ba	2.0 ng	[79]
		Sb	2.0 ng	
		Pb	particles with a diameter of 1 μm	
LIBS	various substrate surfaces	Pb	particles with a diameter of 1 μm	[80]
		Ba	2.0 ng	
		Sb	2.0 ng	
LIBS	various substrate surfaces	Pb	particles with a diameter of 1 μm	[81]
		Ba	2.0 ng	
		Sb	2.0 ng	
LIBS	various substrate surfaces	Pb	—	[82]
		Ba	—	
MS	hand clothing cartridge case	EC	50 ng	[90]
		MC	50 ng	

2.4 电化学法

电化学检测是一种基于电化学反应的分析技术,其基本原理是通过在电极表面施加控制电位,使目标电活性物质发生氧化或还原反应,并测量产生的电流信号,该电流大小与目标物浓度成正比,从而实现定性和定量检测^[92-93]。电化学法因其响应速度快、操作简便、设备成本低以及灵敏度高等优势,已成为检测

GSR 的重要技术之一^[94-97]。该方法可在数分钟内同时完成对 IGSR 和 OGSR 的检测,并表现出良好的选择性以及较低检测限^[98]。传统的电化学装置及其工作电极体积大且需要大量的电解质溶液,这限制了其在现场检测中的应用。丝网印刷碳电极 (SPCE) 因其使用便捷、低成本、结构简单以及响应迅速,常被用作便携式电化学传感器的工作电极^[99]。然而,SPCE 存在比表面积有限和催化能力不足的问题,限制了其对目标成分高灵敏度检测的能力^[100]。因此,通常采用具有

催化活性的导电纳米材料对 SPCE 进行修饰,以增大电极表面积和提升催化效率,从而提高检测的性能^[101]。

Promsuwan 等^[102]研制了一种新型便携式电化学传感器,该传感器以银纳米棱柱 (AgNPrs) 与磷掺杂碳纳米管 (P-CNTs) 复合形成的 AgNPr@P-CNT 修饰 SPCE,并结合便携式流动注射安培检测系统,实现了 GSR 中亚硝酸盐的高灵敏现场快速检测 (图 6)。此外,该方法通过滴铸法修饰电极,有效克服了传统丝网印刷电极催化活性不足和稳定性差的问题。

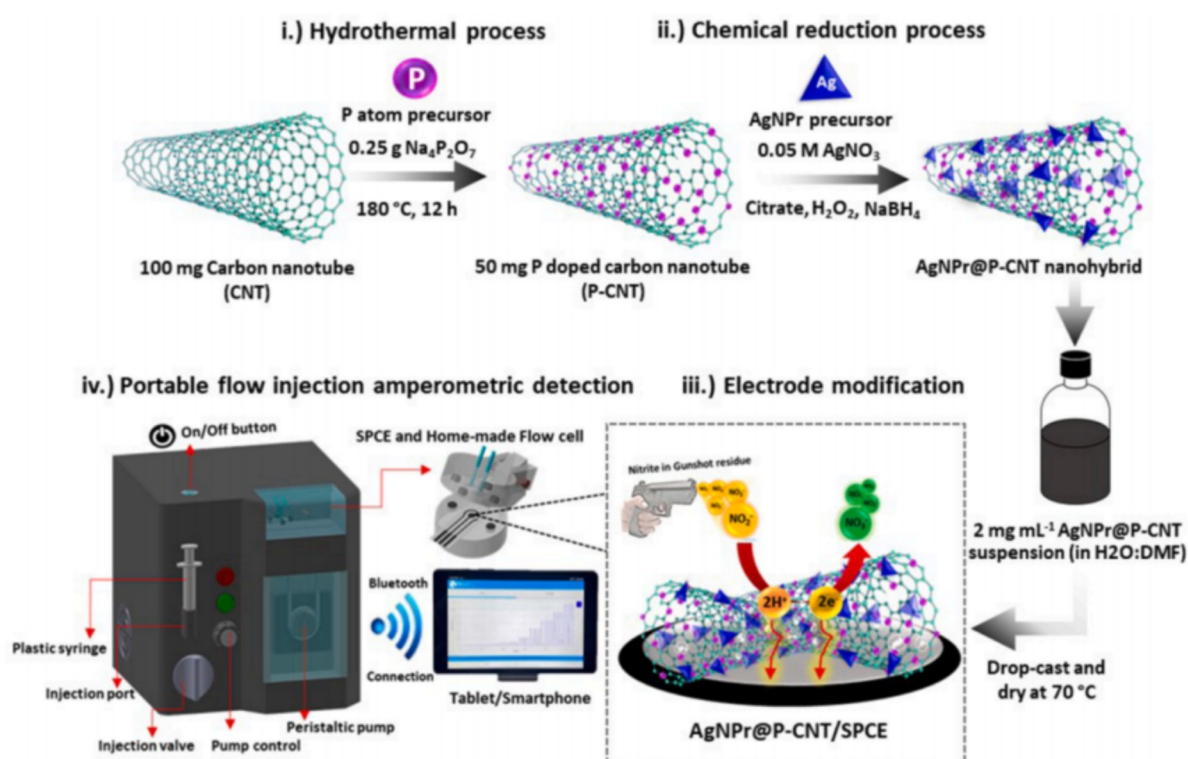


图 6 AgNPr@P-CNT 纳米杂化物的制备过程、纳米杂化物修饰的丝网印刷电极工作机理、以及便携式流动注射安培检测系统示意图^[102]

Fig.6 Preparation process of AgNPr@P-CNT nanohybrid, working mechanism of screen-printed electrode modified with nanohybrid, and schematic diagram of portable flow injection amperometric detection system^[102]

Wongpakdee 等^[103]基于金纳米结构修饰的 SPCE,通过方波阳极溶出伏安法 (SWASV),实现了对 IGSR 多种成分在现场快速检测。该方法利用电沉积金纳米结构增强了电极的导电性和活性面积,显著提高了对 IGSR 的检测灵敏度。此外,在另一项研究中,该团队基于金箔伏安传感器开发了射击距离分析方法^[104]。实验采用方波阳极溶出伏安法 (SWASV),通过对比不同射击距离条件下采集的 Pb 信号特征,成功构建了射击距离与伏安响应信号强度间的定量关系。研究结果显示,随着射击距离的增加,Pb 信号强度呈

现显著的指数衰减趋势。

随着微型化技术的成熟,便携式电化学仪器也能达到台式仪器检测 GSR 的要求。Dalzell 等^[105]比较了便携式与台式电化学仪器检测 GSR 的效果,利用 SPCE 通过 SWASV 同时检测出 Pb、Sb、DPA 和 EC 等 IGSR 和 OGSR 成分,且检测准确率都超过 95% (图 7)。这一研究证明了便携式电化学仪器的可靠性,为其现场快速检测 GSR 的应用提供了理论支撑。其中,台式和便携式电化学传感器检测 GSR 的实验参数差异如表 5 所示。

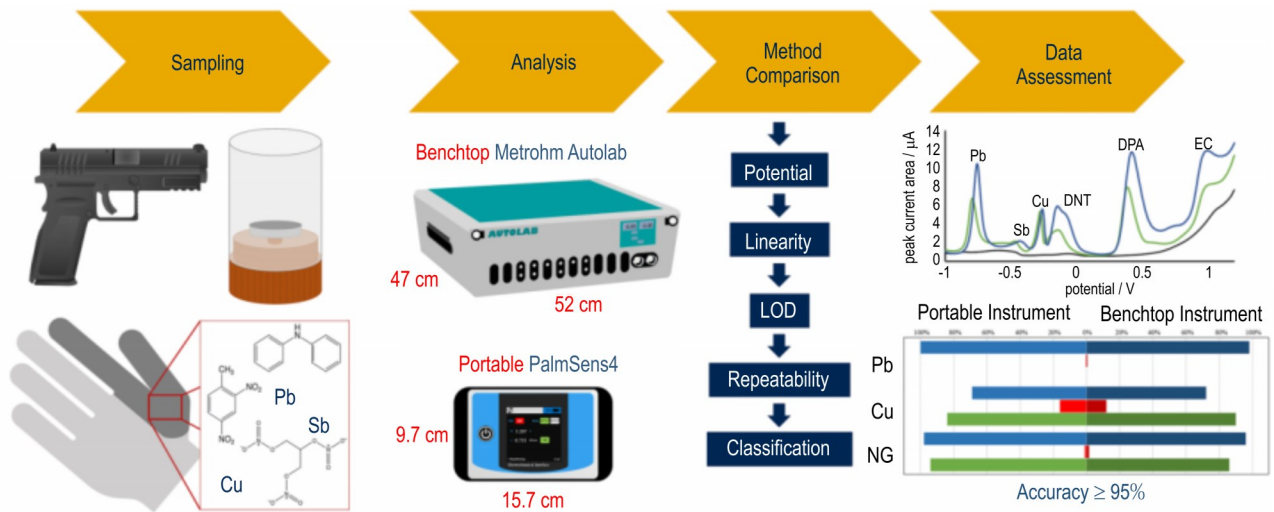


图7 便携式与台式电化学仪器在GSR检测中的比较^[105]

Fig.7 Comparison of portable and benchtop electrochemical instruments in GSR detection^[105]

表5 台式和便携式电化学传感器检测GSR的实验参数^[105]

Table5 Experimental parameters for detecting GSR using desktop and portable electrochemical sensors^[105]

parameter	benchtop instrument	portable instrument
deposition time	120 s	120 s
deposition potential	-0.95 V	-0.95 V
start potential	-1.0 V	-1.0 V
end potential	1.2 V	1.2 V
potential step	0.004 V	0.005 V
amplitude	0.025 V	0.025 V
frequency	8 Hz	11 Hz

Torrarit等^[106]则首次研究了基于环保型氧化铁/废弃咖啡渣的复合材料修饰玻碳电极(GCE)的新型电化学传感器,通过差分脉冲阳极溶出伏安法(DPASV)实现对IGSR中的Pb和Cu现场快速检测(图8)。该复合材料充分利用了废弃咖啡渣的大比表面积与多孔结构^[107-108],以及铁氧化物颗粒优良的电化学活性和吸附能力^[109-110],二者协同作用显著提高了GCE的导电性与吸附性能。

此外,3D打印技术在便携式电化学仪器中具有重要应用价值,能够快速制造出兼具采样与检测双重功能的柔性器件,其表面具有较高的粗糙度,可直接从多种物体表面高效采集痕量残留物,实现快速、集成的现场检测分析^[111]。Castro等^[112]开发了一种基于熔融沉积建模3D打印技术的低成本便携式电化学传感器,用于同步检测IGSR中的Pb和Sb。该传感器采用石墨烯-聚乳酸(G-PLA)复合材料打印而成,其电极兼具采样与传感功能。使用时,G-PLA电极直接接触射击者

的手部或衣物表面,即可完成样品采集。随后将电极置于电解质溶液中,通过SWASV进行检测。该方法避免了复杂的样品前处理过程,以及有效减少了样品损失,显著提高了检测效率。

便携式电化学传感器结合SPCE等工作电极在GSR检测中具备便携、快速响应和低成本等优势,非常适用于现场筛查,可在数分钟内完成检测。通过纳米材料修饰工作电极可显著提升检测灵敏度,但修饰后的电极在环境中易发生性能衰减,例如Cu/Au-SPCE中的铜层容易氧化,往往需要现场电沉积或密封保存。此外,3D打印电极集采样与传感功能于一体,无需复杂前处理过程,并能在复杂基质中高效采集GSR,有助于进一步提高检测灵敏度,在未来GSR现场检测中具有良好的应用前景。然而,便携式电化学传感器的性能易受沉积时间、电位等参数影响,这增加了现场操作的复杂性,也对操作人员提出了较高要求。目前,便携式电化学传感器多集中于IGSR的检测,未来有必要进一步拓展OGSR的检测,以实现IGSR与OGSR的联合分析。其中,便携式电化学传感器在GSR现场快速检测中的应用总结如表6所示。

2.5 荧光标记法

荧光标记法是一种在弹药中添加荧光标记物的技术。当子弹被击发后,荧光标记物会掺杂在GSR中。在现场检测时,只需使用便携式紫外线灯进行照射,这些荧光标记物便会在紫外光激发下发出独特的荧光,从而实现对目标物的可视化检测^[113-114]。荧光标记法不仅简化了现场分析和样本采集过程,还在复杂环境中显著提高GSR的可识别性。

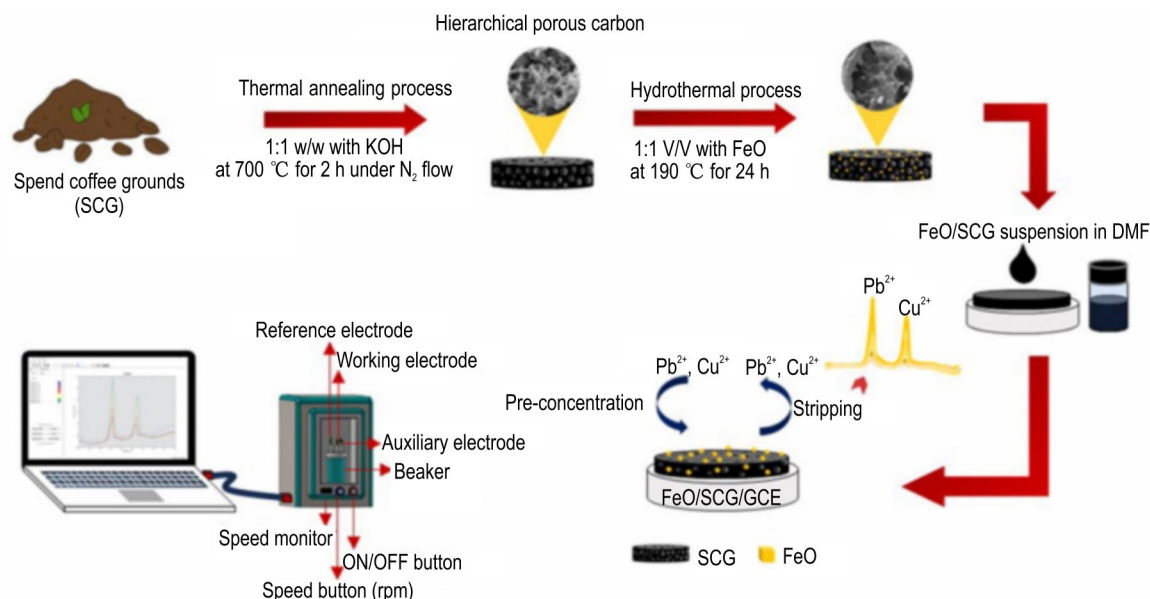


图8 氧化铁/废弃咖啡渣复合材料制备过程以及便携式电化学传感器系统示意图^[106]

Fig.8 Schematic diagram of iron oxide/waste coffee grounds composite preparation process and portable electrochemical sensor system^[106]

表6 便携式电化学传感器在GSR现场快速检测中的应用总结

Table 6 Summary of the application of portable electrochemical sensor in on-site rapid detection of GSR

working electrode	decorative material	electrode technology	detection site	component	detection limit	ref
SPCE	AgNPr@P-CNT	AMP	various substrate surfaces	NO_2^-	$0.147 \text{ ng} \cdot \text{mL}^{-1}$	[102]
SPCE	Cu/Au	SWASV	cartridge case	Pb^{2+}	$51 \text{ ng} \cdot \text{mL}^{-1}$	[103]
				Sb^{3+}	$29 \text{ ng} \cdot \text{mL}^{-1}$	
				Zn^{2+}	$67 \text{ ng} \cdot \text{mL}^{-1}$	
GLE	—	SWASV	clothing	Pb^{2+}	—	[104]
				Pb^{2+}	$278 \text{ ng} \cdot \text{mL}^{-1}$	
				Sb^{3+}	$235 \text{ ng} \cdot \text{mL}^{-1}$	
SPCE	—	SWASV	hand	Cu^{2+}	$9 \text{ ng} \cdot \text{mL}^{-1}$	[105]
				NG	$438 \text{ ng} \cdot \text{mL}^{-1}$	
				EC	$566 \text{ ng} \cdot \text{mL}^{-1}$	
				DPA	$152 \text{ ng} \cdot \text{mL}^{-1}$	
GCE	FeO/SCG	DPASV	target paper	Pb^{2+}	$1.0 \text{ ng} \cdot \text{mL}^{-1}$	[106]
				Cu^{2+}	$2.4 \text{ ng} \cdot \text{mL}^{-1}$	
G-PLA	—	SWASV	hand	Pb^{2+}	$10 \text{ ng} \cdot \text{mL}^{-1}$	[112]
			clothing	Sb^{3+}	$40 \text{ ng} \cdot \text{mL}^{-1}$	

目前,在GSR荧光标记材料的研究中,镧系金属有机框架(Ln-MOFs)因制备简便、对分析物无损,以及具备优异发光性能而受到广泛关注^[115-118]。Ln-MOFs具有独特的发光特性和良好的热稳定性,是一种理想的荧光标记材料。此外,镧系元素在环境中较为罕见,特别是在识别来自无铅弹药残留颗粒时,Ln-MOFs能有效提高GSR检测的准确性。

镱(Eu)和铽(Tb)凭借其高亮度的发光特性,通常被用作GSR荧光标记物的发光中心,在实际检测中具

有较高的应用价值。Lucena等^[119]采用以钇(Y)为基质,以及均苯三酸(BTC)为有机配体,构建了两种Ln-MOFs,分别为 $\text{Y}_{0.95}\text{Eu}_{0.05}(\text{BTC})$ 和 $\text{Y}_{0.85}\text{Yb}_{0.10}\text{Tb}_{0.05}(\text{BTC})$ 。在射击实验中,研究人员将这两种荧光标记物掺入弹药内部。在紫外线照射下,标记物分别发出绿色和红色的荧光。实验结果表明,在射击者手部、枪支及弹壳等表面均可观察到清晰的荧光痕迹(图9),且荧光颗粒的分布范围最远可达8 m。此外,作者进一步通过毒性实验,初步证明了Eu-MOFs作为荧光标

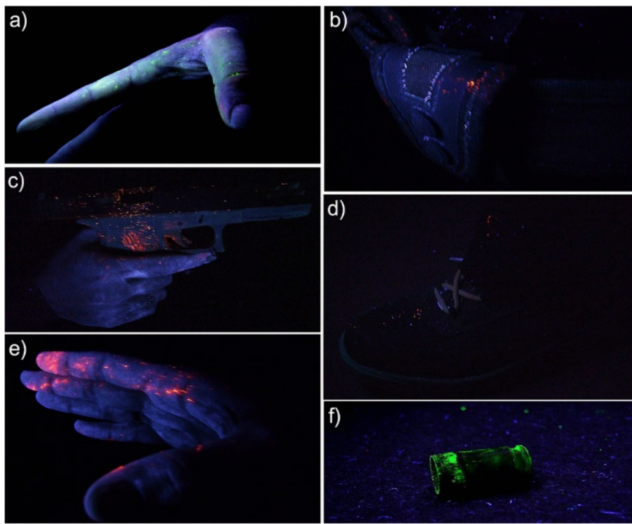


图9 荧光标记物在射击者的手部(a、e)、射击者的腰带(b)、枪支的表面(c)、射击者的鞋(d)以及弹壳的表面(f)所呈现出的紫外照射发光现象^[119]

Fig. 9 The fluorescence of the fluorescent marker on the shooter's hands (a, e), the shooter's belt (b), the surface of the firearm (c), the shooter's shoes (d), and the surface of the cartridge case (f) are shown in the ultraviolet light emission phenomenon^[119]

记物的低毒性与安全性^[120]。

在针对GSR转移行为的研究中,Arouca等^[121]通过握手链实验结合紫外照射可视化表征,验证了Eu-MOFs荧光标记物在人际接触中的二次及三次转移潜在风险。研究发现,荧光标记物颗粒可在握手过程中实现2~3次转移,且转移至第三人手部时荧光强度显著减弱。为研究荧光标记物的添加比例对子弹发射速度的影响,Weber等^[122]以Eu和Tb作为发光中心,合成了两种Ln-MOFs,并按照弹药质量的2、5、10%掺入其中。实验结果表明,当标记物添加比例为2%时,子弹速度仅略有下降,仍处于正常范围;当比例提高至5%时,子弹速度出现明显下降趋势;而进一步增加至10%时,速度下降幅度达到30%。

基于GSR中不同荧光标记物产生的独特发光信

号,能够追溯至弹药来源,从而建立起射击者、枪支与射击现场之间的关联。Lucena等^[123]研究了基于Ln-MOFs共掺杂的弹药编码与GSR溯源的新方法。该方法利用微波辅助水热法合成了8种掺杂不同镧系离子的Ln-MOFs作为荧光标记物。Carneiro等^[124]则针对不同的有机配体,合成了3种发光特性不同的Eu-MOFs荧光标记物,以此实现不同类型弹药的差异化编码。此外,作者进一步建立了基于荧光与拉曼光谱联用的分析方法,并结合主成分分析(PCA)与偏最小二乘判别分析(PLS-DA),以检测和区分射击后产生的这3种标记残留物。在另一个实验中,作者通过视频光谱比较仪与PCA和PLS-DA相结合,也实现了两种Eu-MOFs标记残留物的有效区分^[125]。

作为荧光标记物的Ln-MOFs因高镧系元素含量而导致成本较高。因此,可采用其他低成本金属部分掺杂替代镧系金属。Serwy等^[126]采用锌离子部分替代镧系金属的策略,通过室温沉淀法成功合成了不同Zn/Ln比例的MOFs。与使用纯Ln-MOFs荧光标记物相比,该方法将成本降低了约7倍。

Ln-MOFs凭借其优异的发光性能以及诸多优势,是当前GSR的主流荧光标记材料。近年来,研究人员也进一步发现了兼具优异发光性能和高稳定性的新型荧光标记材料,有望成为其潜在的替代品。Gomes等^[127]研究发现,Eu³⁺β-二酮配合物能够很好代替传统的Ln-MOFs。该研究首次将此类配合物应用于GSR标记,证实其不仅具备高发光强度与良好的热稳定性。弹道测试数据显示,子弹速度仅出现轻微下降,手枪约为1.28%~2.80%,步枪约为6.95%,这表明Eu³⁺β-二酮配合物与发射药之间无显著的物理化学相互作用^[128]。此外,Filho等^[129]采用乙醇回流法,成功合成了以噻苯达唑(TBZ)为配体的Eu和Tb发光配合物Eu(TBZ)与Tb(TBZ)。Silva等^[130]则以1,2,4-苯四羧酸(H₄btec)和Tb为原料,通过水热法合成了一种新型配

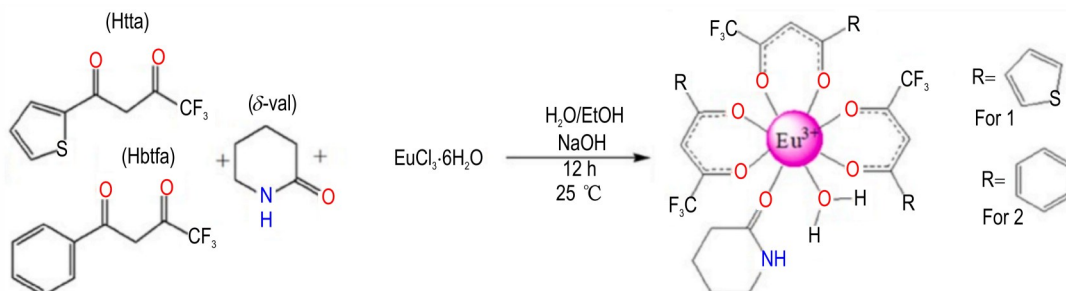


图10 Eu³⁺β-二酮配合物的合成路线^[128]

Fig. 10 The synthesis route of Eu³⁺β-dicyclopentadienone complexes^[128]

位网络 Tb(Hbtec)_n 标记物。

Lucena 等^[131]首次证明了镧系金属无机材料作为 GSR 荧光标记物的可行性。该研究打破了以往使用有机物配体的局限性,为 GSR 荧光标记物的合成提供了全新视角。实验采用燃烧法成功合成了铈/铽共掺钒酸铋(YVO₄:Er³⁺,Yb³⁺),并系统评估了其光学性能。实验结果表明,YVO₄:Er³⁺,Yb³⁺材料具备双模式发光特性。在便携式紫外灯与红外灯的照射下,该标记物均可激发出明亮的绿色荧光。

作为一种新兴的 GSR 现场检测技术,荧光标记法通过在弹药中引入 Ln-MOFs 等荧光标记材料,能够实现 GSR 的高效识别。该技术的核心优势在于其独特的发光特性与低环境背景干扰能力。此外,通过调节镧系元素比例或更换配体,设计具有不同荧光响应模式的标记物,可对荧光标记物进行化学编码,形成特

异性标识,从而追溯弹药来源。

然而,该技术目前仍面临一些挑战。例如,荧光标记物的引入可能影响子弹的射击性能,不同添加比例可能导致初速度下降甚至射击失败,因此需系统研究标记物种类和添加比例对弹道性能的影响。其次,荧光标记物可能经接触发生二次转移,在实际检测中需注意区分二次污染,以避免假阳性结果。此外,荧光标记物的生物毒性及其对人体健康的潜在影响也有待进一步评估。在应用层面,荧光信号易受户外强光干扰,弱发光信号可能被掩盖,通常需在遮光条件下观察,这限制了其在明亮环境下的现场适用性。虽然目前荧光标记物尚未在弹药中普及应用,但随着未来研究的深入与技术的完善,其在实际中的应用前景将十分广阔。可以预见,荧光标记技术有望发展成为 GSR 现场快速检测的重要手段之一。其中,GSR 荧光标记技术总结如表 7 所示。

表 7 GSR 荧光标记技术总结

Table 7 Summary of GSR fluorescent labeling technology

fluorescent material	luminous center	ligand	excitation wavelength	addition amount	ref
Y _{0.95} Eu _{0.05} (BTC)	Eu ³⁺ , Tb ³⁺	BTC	254 nm	5%	[119]
Y _{0.85} Yb _{0.10} Tb _{0.05} (BTC)					
Eu(BTC)	Eu ³⁺	BTC	254 nm	5、10%	[121]
Eu(DPA)(HDPA)		(DPA)(HDPA)			
[Eu ₂ (BDC) ₃ (H ₂ O) ₂] _n	Eu ³⁺ , Tb ³⁺	BDC	254 nm	2、5、10%	[122]
Eu(DPA)(HDPA)		(DPA)(HDPA)			
Tb(DPA)(HDPA)					
Y _{0.95} Eu _{0.05} (BTC)	Eu ³⁺ , Tb ³⁺	BTC	302 nm	5%	[123]
Y _{0.90} Eu _{0.10} (BTC)					
Y _{0.90} Eu _{0.05} Sm _{0.05} (BTC)					
Y _{0.80} Eu _{0.10} Sm _{0.10} (BTC)					
Y _{0.95} Tb _{0.05} (BTC)					
Y _{0.90} Tb _{0.10} (BTC)					
Y _{0.85} Yb _{0.10} Tb _{0.05} (BTC)					
Y _{0.80} Yb _{0.10} Tb _{0.05} Eu _{0.05} (BTC)					
Eu(BTC)	Eu ³⁺	BTC	293 nm	5%	[124]
Eu(DPA)(HDPA)		(DPA)(HDPA)			
[Eu ₂ (BDC) ₃ (H ₂ O) ₂] _n	Eu ³⁺ , Tb ³⁺	BDC	323 nm	4%	[126]
[Eu ₂ (BDC) ₃ (H ₂ O) ₂] _n					
[Tb ₂ (BDC) ₃ (H ₂ O) ₂] _n					
Eu(tta) ₃ (ε-cap)(H ₂ O)	Eu ³⁺	tta	380 nm	30 mg	[127]
Eu(btfa) ₃ (ε-cap)(H ₂ O)		btfa			
		ε-cap			
Eu(tta) ₃ (δ-val)(H ₂ O)	Eu ³⁺	tta	380 nm	30 mg	[128]
Eu(btfa) ₃ (δ-val)(H ₂ O)		btfa			
		δ-val			
Eu(TBZ)	Eu ³⁺ , Tb ³⁺	TBZ	254 nm	5%	[129]
Tb(TBZ)					
Tb(Hbtec) _n	Tb ³⁺	Hbtec	322 nm	30 mg	[130]
YVO ₄ :Er ³⁺ ,Yb ³⁺	Er ³⁺ ,Yb ³⁺	YVO ₄	254 nm、980 nm	10%	[131]

3 总结与展望

本研究综述了当前现场快速检测技术在 GSR 检测中的应用,涵盖比色法、光谱法、质谱法、电化学法及荧光标记法 5 种方法,并对比分析了各方法的研究现状、优势与局限性。

比色法以其操作简便、成本低的优势,成为大范围初步筛查的理想选择。其中,基于纳米材料增强的手持式比色传感器,通过提升检测灵敏度和简化前处理步骤,进一步拓展了其应用潜力。然而,与 IGSR 实验室检测技术相比,其检测灵敏度仍显不足。光谱法中,便携式 SERS 适用于 OGSR 的高灵敏度检测,但易受基质干扰和荧光背景影响,且依赖算法进行信号提取和降噪;便携式 LIBS 适用于 IGSR 的快速检测,具备高空间分辨率,可实现分布可视化,但灵敏度不如 SEM-EDS,仍需结合后者验证以避免假阴性结果。质谱法方面,喷雾电离技术与 3D 打印相结合的便携质谱装置,在痕量 OGSR 的高效检测中表现出一定的应用前景。但该装置的检测效能与实验室质谱技术相比仍存在明显不足,特别是在复杂基质样品的分析中,其采样效率与准确定量能力均有待进一步优化和提升。电化学法通过采用纳米材料修饰电极或 3D 打印集成电极,显著提升了 GSR 的检测灵敏度。但修饰电极在实际应用中通常需进行复杂处理,或依赖严格密封的保存条件,对操作人员的专业技能也提出了较高要求。目前,采用 GCE 和 G-PLA 的电化学方法能够达到 IGSR 的实验检测标准,但对 OGSR 的检测需进一步研究完善。荧光标记法利用便携紫外灯激发荧光以实现 GSR 的可视化检测,但其后续仍需对成分作进一步检测分析。此外,荧光标记物可能对弹道性能产生影响,并且在户外强光环境下存在信号识别困难的问题,这些因素均限制了该技术的现场应用。目前,大多数 GSR 现场快速检测技术在检测性能方面仍与实验室技术存在一定差距。当现场检测结果为阴性时,须结合实验室仪器分析进行二次确证,才能确保结果的可靠性。针对当前 GSR 现场快速检测技术的研究现状,未来可重点从以下几个方向展开深入研究:

(1) 开发基于新型纳米材料的手持式比色传感装置,以实现 IGSR 和 OGSR 的高特异性联合识别。进一步可将比色传感器与便携式光谱仪集成,在发生颜色反应后直接于设备内部进行光谱定量与定性分析,提升检测的准确性。

(2) 针对便携式 SERS 技术,可设计具备选择性富集和净化功能的采样贴片,或开发能特异性吸附 OGSR 成分的 SERS 基底,从而在检测前实现目标物的分离与纯化,在富集目标物的同时有效排除干扰物质,降低基质干扰。在实际现场检测中,还可结合便携式 SERS 与 LIBS 技术,分别对 IGSR 和 OGSR 进行检测,以提高结果的可靠性。

(3) 针对便携式质谱技术,利用 3D 打印技术定制具有高吸附效率的采样器,或结合新型微萃取材料构建采样探头,提升对复杂基质中痕量 OGSR 成分的选择性吸附与富集能力,以进一步提高检测灵敏度。

(4) 借助 3D 打印技术批量制备具备固有高活性微纳结构的工作电极,避免现场电沉积步骤,简化操作流程。同时拓展纳米材料修饰工作电极在 OGSR 检测中的应用,为实现 IGSR 与 OGSR 的联合分析提供新途径。

(5) 系统研究发光性能更优的荧光标记物,并深入探讨不同标记物及其添加比例对弹道性能的影响,推动建立安全可靠的行业标准。在检测手段上,可采用配备特定滤光片及便携式暗箱或护目镜式探测器,有效抑制环境光干扰,实现对微弱荧光信号的高信噪比捕捉与成像,增强在户外现场的适用性。

参考文献:

- [1] SEROL M, AHMAD S M, QUINTAS A, et al. Chemical analysis of gunpowder and gunshot residues[J]. *Molecules*, 2023, 28(14): 5550.
- [2] HARLES S, JONCKHEERE A. The use and understanding of forensic reports by judicial actors—The field of gunshot residue expertise as an example [J]. *Forensic Science International*, 2022, 335: 111312.
- [3] EL KHOURY MOUSSA C, PAYRÉ B, ARIES S, et al. Effects of carbonization on gunshot residue detection in an animal model [J]. *Forensic Imaging*, 2024, 39: 200612.
- [4] OBERENKO A V, SAGALAKOV S A, KACHIN S V. Current approaches for sampling to study the traces of gunshot residue [J]. *Sudebno-meditsinskaya ekspertiza*, 2023, 66(6): 55–58.
- [5] REDOUTÉ MINZIERE V, WEYERMANN C. Organic and inorganic gunshot residues on the hands, forearms, face, and nostrils of shooters 30 min after a discharge [J]. *Science & Justice*, 2024, 64(5): 557–571.
- [6] YÜKSEL B, ŞEN N, ÖGÜNÇ G I, et al. Elemental profiling of toxic and modern primers using ICP-MS, SEM-EDS, and XPS: an application in firearm discharge residue investigation [J]. *Australian Journal of Forensic Sciences*, 2022, 55 (4): 529–546.
- [7] CHARLES S, GEUSENS N, VERGALITO E, et al. Interpol review of gunshot residue 2016–2019 [J]. *Forensic Science International: Synergy*, 2020, 2: 416–428.
- [8] ISRAELSOHN AZULAY O, ZIDON Y, MALIHI L, et al. Preva-

- lence of gunshot residue particles on back seats of police vehicles [J]. *Journal of Forensic Sciences*, 2024, 69(5): 1880–1886.
- [9] VANDER PYL C, DALZELL K, MENKING-HOGGATT K, et al. Transfer and persistence studies of inorganic and organic gunshot residues using synthetic skin membranes [J]. *Forensic Chemistry*, 2023, 34: 100498.
- [10] BLAKEY L, SHARPLES G P, CHANA K, et al. Environmental assessment of gunshot residue particles in the public domain of the United Kingdom [J]. *Journal of Forensic Sciences*, 2023, 68(4): 1330–1334.
- [11] BROŽEK-MUCHA Z. Trends in analysis of gunshot residue for forensic purposes [J]. *Analytical and bioanalytical chemistry*, 2017, 409(25): 5803–5811.
- [12] PIEGARI G, D’AQUINO I, SALANTI G V, et al. Pathological changes and sodium rhodizonate test as tools for investigating gunshot wounds in veterinary forensic pathology [J]. *Animals*, 2024, 14(19): 2913.
- [13] ISRAELSOHN Azulay O, ZIDON Y, KOHALSKY E. Investigation of the impact of a sound suppressor on the weapon’s memory effect and gunshot residue formation [J]. *Journal of Forensic Sciences*, 2025, 70(3): 1–7.
- [14] KRISHNA S, AHUJA P. A chronological study of gunshot residue (GSR) detection techniques: A narrative review [J]. *Egyptian Journal of Forensic Sciences*, 2023, 13(1): 51.
- [15] PEREZ J J, WATSON D A, LEVIS R J. Classification of gunshot residue using laser electrospray mass spectrometry and offline multivariate statistical analysis [J]. *Analytical Chemistry*, 2016, 88(23): 11390–11398.
- [16] CHARLES S, GEUSENS N, NYS B. Interpol review of gunshot residue 2019 to 2021 [J]. *Forensic Science International: Synergy*, 2023, 6: 100302.
- [17] ROMANÒ S, DE-GIORGIO F, D’ONOFRIO C, et al. Characterisation of gunshot residues from non-toxic ammunition and their persistence on the shooter’s hands [J]. *International Journal of Legal Medicine*, 2020, 134(3): 1083–1094.
- [18] BENDER R, NEIMKE D, NIEWOEHNER L, et al. Discrimination of SINTOX® GSR against environmental particles and its automated investigation by SEM/EDS [J]. *Forensic Chemistry*, 2021, 24: 100338.
- [19] 南策, 赵鹏程, 张祉悦, 等. 枪支有机射击残留物痕量检测技术研究进展 [J]. 含能材料, 2024, 32(07): 772–783.
NAN Ce, ZHAO Peng-cheng, ZHANG Zhi-yue, et al. Research progress of trace detection technology of organic gunshot residue in firearms [J]. *Chinese Journal of Energetic Materials (Hanneng Cailiao)*, 2024, 32(7): 772–783.
- [20] FEENEY W, VANDER PYL C, BELL S, et al. Trends in composition, collection, persistence, and analysis of IGSR and OGSR: A review [J]. *Forensic Chemistry*, 2020, 19: 100250.
- [21] VACHON C R, MARTINEZ M V. Understanding gunshot residue evidence and its role in forensic science [J]. *American Journal of Forensic Medicine & Pathology*, 2019, 40(3): 210–219.
- [22] TONIN P, MOURA S. Exploring analytical chemistry in gunshot residue: Innovations and obstacles in organic and inorganic analysis [J]. *Critical Reviews in Analytical Chemistry*, 2025: 1–12.
- [23] SHRIVASTAVA P, JAIN V K, NAGPAL S. Gunshot residue detection technologies—a review [J]. *Egyptian Journal of Forensic Sciences*, 2021, 11(1): 11.
- [24] SACCO M A, GUALTIERI S, SANTOS A, et al. Scanning electron microscopy techniques in the analysis of gunshot residues: A literature review [J]. *Applied Sciences*, 2025, 15(5): 2634.
- [25] BONNAR C, MOULE E C, LUCAS N, et al. Tandem detection of organic and inorganic gunshot residues using LC-MS and SEM-EDS [J]. *Forensic Science International*, 2020, 314: 110389.
- [26] ONETTO M A, CARIGNANO E, PREGLIASCO R G. False-negative probability in the SEM/EDS automated discovery of IGSR particles: A Bayesian approach [J]. *Journal of Forensic Sciences*, 2023, 68(5): 1792–1799.
- [27] ESHUN J, LAMAR N C, AKSOY S G, et al. Identifying sample provenance from SEM/EDS automated particle analysis via few-shot learning coupled with similarity graph clustering [J]. *Microscopy and Microanalysis*, 2024, 30(4): 741–750.
- [28] BROŽEK-MUCHA Z, WAŚ-GUBAŁA J. Effects of the interaction of gunshot residue plume and cotton fabrics—an empirical study towards extensive assessment of close-range shooting distance [J]. *The Analyst*, 2022, 147(10): 2141–2155.
- [29] TREJOS T, VANDER PYL C, MENKING-HOGGATT K, et al. Fast identification of inorganic and organic gunshot residues by LIBS and electrochemical methods [J]. *Forensic Chemistry*, 2018, 8: 146–156.
- [30] PYL C V, OVIDE O, HO M, et al. Spectrochemical mapping using laser induced breakdown spectroscopy as a more objective approach to shooting distance determination [J]. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2019, 152: 93–101.
- [31] MERLI D, AMADASI A, MAZZARELLI D, et al. Comparison of different swabs for sampling inorganic gunshot residue from gunshot wounds: Applicability and reliability for the determination of firing distance [J]. *Journal of Forensic Sciences*, 2018, 64(2): 558–564.
- [32] VANINI G, SOUZA R M, DESTEFANI C A, et al. Analysis of gunshot residues produced by 38 caliber handguns using inductively coupled plasma-optical emission spectroscopy (ICP OES) [J]. *Microchemical Journal*, 2014, 115: 106–112.
- [33] MERLI D, BRANDONE A, AMADASI A, et al. The detection of gunshot residues in the nasal mucus of suspected shooters [J]. *International Journal of Legal Medicine*, 2016, 130(4): 1045–1052.
- [34] YUEKESL, BAYRAM, OZLER-YIGITER, et al. GFAAS determination of antimony, barium, and lead levels in gunshot residue swabs: An application in forensic chemistry [J]. *Atomic Spectroscopy*, 2016, 37(4): 164–169.
- [35] ALISTE M, CHÁVEZ L G. Analysis of gunshot residues as trace in nasal mucus by GFAAS [J]. *Forensic Science International*, 2016, 261: 14–18.
- [36] KHANDASAMMY S R, RZHEVSKII A, LEDNEV I K. A novel two-step method for the detection of organic gunshot residue for forensic purposes: Fast fluorescence imaging followed by raman microspectroscopic identification [J]. *Analytical Chemistry*, 2019, 91(18): 11731–11737.
- [37] KARAHACANE D S, DAHMANI A, KHIMECHE K. Raman spectroscopy analysis and chemometric study of organic gun-

- shot residues originating from two types of ammunition [J]. *Forensic Science International*, 2019, 301: 129–136.
- [38] KHANDASAMMY S R, BARTLETT N R, HALÁMKOVÁ L, et al. Hierarchical modelling of raman spectroscopic data demonstrates the potential for manufacturer and caliber differentiation of smokeless powders[J]. *Chemosensors*, 2022, 11(1): 11.
- [39] KHANDASAMMY S R, HALÁMKOVÁ L L, BAUDELET M, et al. Identification and highly selective differentiation of organic gunshot residues utilizing their elemental and molecular signatures[J]. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2023, 291: 122316.
- [40] BUENO J, LEDNEV I K. Attenuated total reflectance - FT-IR Imaging for rapid and automated detection of gunshot residue[J]. *Analytical Chemistry*, 2014, 86(7): 3389–3396.
- [41] LEDERGERBER T D, FEENEY W, ARROYO L, et al. A feasibility study of direct analysis in real time-mass spectrometry for screening organic gunshot residues from various substrates[J]. *Analytical Methods*, 2023, 15(36): 4744–4757.
- [42] TAUDTE R V, ROUX C, BISHOP D P, et al. High-throughput screening for target compounds in smokeless powders using online-SPE tandem mass spectrometry[J]. *Australian Journal of Forensic Sciences*, 2019, 53(1): 16–26.
- [43] VANDER PYL C, FEENEY W, ARROYO L, et al. Capabilities and limitations of GC-MS and LC-MS/MS for trace detection of organic gunshot residues from skin specimens [J]. *Forensic Chemistry*, 2023, 33: 100471.
- [44] GALLIDABINO M D, BYLENGA K, ELLIOTT S, et al. Comparison of four commercial solid-phase micro-extraction (SPME) fibres for the headspace characterisation and profiling of gunshot exhausts in spent cartridge casings[J]. *Analytical and Bioanalytical Chemistry*, 2022, 414(17): 4987–4998.
- [45] GALLIDABINO M, ROMOLO F S, WEYERMANN C. Time since discharge of 9 mm cartridges by headspace analysis, part 1: Comprehensive optimisation and validation of a headspace sorptive extraction (HSSE) method[J]. *Forensic Science International*, 2017, 272: 159–170.
- [46] BELL S, FEENEY W. Single shot, single sample, single instrument detection of IGSR and OGSR using LC/MS/MS[J]. *Forensic Science International*, 2019, 299: 215–222.
- [47] ÇEKEM B K, ÜZER A, APAK R. Direct colorimetric detection of triacetone triperoxide explosive by hydroxylamine-mediated Fenton chemistry catalyzed by goethite nanoparticles[J]. *Microchemical Journal*, 2024, 207: 111853.
- [48] DHAKA G, JINDAL G, KAUR R, et al. Multianalyte azo dye as an on-site assay kit for colorimetric detection of Hg²⁺ ions and electrochemical sensing of Zn²⁺ ions [J]. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2020, 229: 117869.
- [49] SHRIVAS K, NIRMALKAR N, THAKUR S S, et al. Experimental and theoretical approaches for the selective detection of thymine in real samples using gold nanoparticles as a biochemical sensor[J]. *RSC advances*, 2018, 8(43): 24328–24337.
- [50] TAEFI Z, GHASEMI F, HORMOZI-NEZHAD M R. Selective colorimetric detection of pentaerythritol tetranitrate (PETN) using arginine-mediated aggregation of gold nanoparticles [J]. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2020, 228: 117803.
- [51] MCGANN P T, HOPPE C. The pressing need for point-of-care diagnostics for sickle cell disease: A review of current and future technologies [J]. *Blood Cells, Molecules, and Diseases*, 2017, 67: 104–113.
- [52] COSTANZO H, GOOCH J, FRASCIONE N. Nanomaterials for optical biosensors in forensic analysis [J]. *Talanta*, 2023, 253: 123945.
- [53] KANGAS M J, BURKS R M, ATWATER J, et al. Colorimetric sensor arrays for the detection and identification of chemical weapons and explosives [J]. *Critical Reviews in Analytical Chemistry*, 2016, 47(2): 138–153.
- [54] SOH J H, LIN Y, RANA S, et al. Colorimetric detection of small molecules in complex matrixes via target-mediated growth of aptamer-functionalized gold nanoparticles [J]. *Analytical Chemistry*, 2015, 87(15): 7644–7652.
- [55] ANDREOLA S, GENTILE G, BATTISTINI A, et al. Forensic applications of sodium rhodizonate and hydrochloric acid: A New histological technique for detection of gunshot residues [J]. *Journal of Forensic Sciences*, 2011, 56(3): 771–774.
- [56] GEUSENS N, NYS B, CHARLES S. Implementation and optimization of the sodium -rhodizonate method for chemographic shooting distance estimation [J]. *Journal of Forensic Sciences*, 2019, 64(4): 1169–1172.
- [57] HENRIQUE BRAZ GARCIA A M, DANIELE SILVA DOS SANTOS P, DE LIMA FIGUEIREDO A, et al. Método Qualitativo para Coleta de Resíduos de Disparo de Arma de Fogo (GSR) das Mãos do Atirador e Análise Colorimétrica [J]. *Revista Virtual de Química*, 2024, 16(6): 812–820.
- [58] BUKING S, SAETEAR P, TIYAPONGPATTANA W, et al. Microfluidic paper-based analytical device for quantification of lead using reaction band-length for identification of bullet hole and its potential for estimating firing distance [J]. *Analytical Sciences*, 2018, 34(1): 83–89.
- [59] WONGPAKDEE T, BUKING S, RATANAWIMARNWONG N, et al. Simple gunshot residue analyses for estimating firing distance: Investigation with four types of fabrics [J]. *Forensic Science International*, 2021, 329: 111084.
- [60] SHRIVASTAVA P, JAIN S, KUMAR N, et al. Handheld device for rapid detection of lead (Pb²⁺) in gunshot residue for forensic application [J]. *Microchemical Journal*, 2021, 165: 106186.
- [61] SHRIVASTAVA P, SINGH B P, JAIN S K, et al. A novel approach to detect barium in gunshot residue using a handheld device: a forensic application [J]. *Analytical Methods*, 2021, 13(38): 4379–4389.
- [62] CHEN S, YANG X, FU S, et al. A novel AuNPs colorimetric sensor for sensitively detecting viable *Salmonella typhimurium* based on dual aptamers [J]. *Food Control*, 2020, 115: 107281.
- [63] 唐乐, 胡辰辰, 马艺宁, 等. 爆炸物的现场快速检测技术研究进展 [J]. *含能材料*, 2025, 33(10): 1228–1254.
- TANG Yue, HU Chen-chen, MA Yi-ning, et al. Research progress on rapid on-site detection technology of explosives [J]. *Chinese Journal of Energetic Materials (Hanneng Cailiao)*, 2025, 33(10): 1228–1254.
- [64] LANGER J, ABERASTURI D J D, AIZPURUA J, et al. Present and future of surface enhanced Raman scattering [J]. *ACS Nano*, 2020, 14(1): 28–117.
- [65] CHAUHAN S, GUPTA L, SHARMA S. A systematic review on

- the analysis of trace materials via Raman spectroscopy: Advancements and forensic implications[J]. *Forensic Science International*, 2025: 112609.
- [66] KIM S, JOO J-H, KIM W, et al. A facile, portable surface-enhanced Raman spectroscopy sensing platform for on-site chemometrics of toxic chemicals[J]. *Sensors and Actuators B: Chemical*, 2021, 343: 130102.
- [67] REESE T, SUAREZ C, PREMASIRI W, et al. Surface enhanced Raman scattering specificity for detection and identification of dried bloodstains [J]. *Forensic science international*, 2021, 328: 111000.
- [68] LÓPEZ-LÓPEZ M, MERK V, GARCÍA-RUIZ C, et al. Surface-enhanced Raman spectroscopy for the analysis of smokeless gunpowders and macroscopic gunshot residues[J]. *Analytical and Bioanalytical Chemistry*, 2016, 408 (18) : 4965–4973.
- [69] SHAFIROVICH T, ALIGHOLIZADEH D, JOHNSON M, et al. Point-and-shoot: portable Raman and SERS detection of organic gunshot residue analytes [J]. *Vibrational Spectroscopy*, 2024, 131: 103669.
- [70] THAYER E, TURNER W, BLAMA S, et al. Signal detection limit of a portable Raman spectrometer for the SERS detection of gunshot residue [J]. *MRS Communications*, 2019, 9 (3) : 948–955.
- [71] ZHANG R, HU S, MA C, et al. Laser-induced breakdown spectroscopy (LIBS) in biomedical analysis[J]. *TrAC Trends in Analytical Chemistry*, 2024, 181: 117992.
- [72] ZHANG Y, ZHANG T, LI H. Application of laser-induced breakdown spectroscopy (LIBS) in environmental monitoring [J]. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2021, 181: 106218.
- [73] DOÑA-FERNÁNDEZ A, RODRIGUEZ-PASCUAL J A, DE ANDRES-GIMENO I, et al. Assessing the shooting distance of lead-free ammunition regardless of composition using Laser Induced Breakdown Spectroscopy [J]. *Forensic Sciences Research*, 2023, 8(3): 256–264.
- [74] CIOCCIA G, WENCESLAU R, RIBEIRO M, et al. Probabilistic-based identification of gunshot residues (GSR) using Laser-Induced Breakdown Spectroscopy (LIBS) and Support Vector Machine (SVM) algorithm[J]. *Microchemical Journal*, 2024, 207: 112142.
- [75] MENKING-HOGGATT K, OTT C, VANDER PYL C, et al. Prevalence and probabilistic assessment of organic and inorganic gunshot residue and background profiles using LIBS, electrochemistry, and SEM-EDS [J]. *Forensic Chemistry*, 2022, 29: 100429.
- [76] LÓPEZ-LÓPEZ M, ALVAREZ-LLAMAS C, PISONERO J, et al. An exploratory study of the potential of LIBS for visualizing gunshot residue patterns [J]. *Forensic Science International*, 2017, 273: 124–131.
- [77] RODRIGUEZ-PASCUAL J A, DOÑA-FERNÁNDEZ A, HERNÁNDEZ-CRESPO F J, et al. Preliminary study of gunshot residues in entry holes at different angles: Feasibility of using LIBS to support trajectory estimation[J]. *Forensic Science International*, 2025, 367: 112349.
- [78] RODRIGUEZ-PASCUAL J A, DOÑA-FERNÁNDEZ A, LOARCE-TEJADA Y, et al. Assessment of gunshot residue detection on a large variety of surfaces by portable LIBS system for crime scene application[J]. *Forensic Science International*, 2023, 353: 111886.
- [79] VANDER PYL C, MENKING-HOGGATT K, ARROYO L, et al. Evolution of LIBS technology to mobile instrumentation for expediting firearm-related investigations at the laboratory and the crime scene[J]. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2023, 207: 106741.
- [80] DOÑA-FERNÁNDEZ A, DE ANDRES-GIMENO I, SANTIAGO-TORIBIO P, et al. Real-time detection of GSR particles from crime scene: A comparative study of SEM/EDX and portable LIBS system [J]. *Forensic Science International*, 2018, 292: 167–175.
- [81] THOMAS L, JEFFERYS R, TALLEY I, et al. Advancing the use of LIBS mobile technology in shooting reconstructions and firearm-related investigations[J]. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2025, 232: 107274.
- [82] LAZIC V, ANDREOLI F, ALMAVIVA S, et al. A novel LIBS sensor for sample examinations on a crime scene[J]. *Sensors*, 2024, 24(5): 1469.
- [83] JADHAV R U, DIGHE P R. Liquid chromatography-mass spectrometry-a brief review[J]. *International Research Journal of Modernization in Engineering Technology and Science*, 2025, 7(4): 1327–1343.
- [84] FANG X, XIE J, CHU S, et al. Quadrupole-linear ion trap tandem mass spectrometry system for clinical biomarker analysis[J]. *Engineering*, 2022, 16: 56–64.
- [85] PEREZ J J, WATSON D A, LEVIS R J. Classification of gunshot residue using laser electrospray mass spectrometry and offline multivariate statistical analysis[J]. *Analytical chemistry*, 2016, 88(23): 11390–11398.
- [86] CASTELLANOS A, BELL S, FERNANDEZ-LIMA F. Characterization of firearm discharge residues recovered from skin swabs using sub-micrometric mass spectrometry imaging [J]. *Analytical Methods*, 2016, 8(21): 4300–4305.
- [87] WILLIAMSON R, GURA S, TARIFA A, et al. The coupling of capillary microextraction of volatiles (CMV) dynamic air sampling device with DART-MS analysis for the detection of gunshot residues[J]. *Forensic Chemistry*, 2018, 8: 49–56.
- [88] PIRRO V, JARMUSCH A K, VINCENTI M, et al. Direct drug analysis from oral fluid using medical swab touch spray mass spectrometry[J]. *Analytica Chimica Acta*, 2015, 861: 47–54.
- [89] YANG B C, WANG F, YANG X, et al. Medical swab touch spray-mass spectrometry for newborn screening of nicotine and cotinine in meconium [J]. *Journal of Mass Spectrometry*, 2016, 51(12): 1237–1242.
- [90] FEDICK P W, BAIN R M. Swab touch spray mass spectrometry for rapid analysis of organic gunshot residue from human hand and various surfaces using commercial and fieldable mass spectrometry systems [J]. *Forensic Chemistry*, 2017, 5: 53–57.
- [91] BONDZIE E H, ADEHINMOYE A, MOLNAR B T, et al. Application of a modified 3D-PCSI-MS Ion source to on-site, trace evidence processing via integrated vacuum collection[J]. *Journal of the American Society for Mass Spectrometry*, 2023, 35(1): 82–89.
- [92] HARSHEY A, SRIVASTAVA A, DAS T, et al. Trends in gunshot residue detection by electrochemical methods for forensic purpose [J]. *Journal of Analysis and Testing*, 2021, 5 (3) :

- 258–269.
- [93] OTT C E. Strategies for assessing the limit of detection in voltammetric methods: comparison and evaluation of approaches[J]. *The Analyst*, 2024, 149(16): 4295–4309.
- [94] MCKEEVER C, CALLAN S, WARREN S, et al. Magnetic nanoparticle modified electrodes for voltammetric determination of propellant stabiliser diphenylamine[J]. *Talanta*, 2022, 238: 123039.
- [95] TREJOS T, VANDER PYL C, MENKING-HOGGATT K, et al. Fast identification of inorganic and organic gunshot residues by LIBS and electrochemical methods[J]. *Forensic Chemistry*, 2018, 8: 146–156.
- [96] PROFUMO A, CAPUCCIATI A, MATTINO A, et al. A simple voltammetric method to evaluate the firing distance through determination of nitrocellulose [J]. *Talanta*, 2024, 266: 125040.
- [97] MCKEEVER C, DEMPSEY E. Electroanalysis of ethyl-centralite propellant stabiliser at magnetic nanoparticle modified glassy carbon and screen-printed electrodes with extension to forensic firearm residue analysis [J]. *Sensors and Actuators B: Chemical*, 2023, 396: 134604.
- [98] OTT C E, DALZELL K A, CALDERÓN-ARCE P J, et al. Evaluation of the simultaneous analysis of organic and inorganic gunshot residues within a large population data set using electrochemical sensors*, †[J]. *Journal of Forensic Sciences*, 2020, 65(6): 1935–1944.
- [99] GARCÍA-MIRANDA FERRARI A, ROWLEY-NEALE S J, BANKS C E. Screen-printed electrodes: Transitioning the laboratory in-to-the field [J]. *Talanta Open*, 2021, 3: 100032.
- [100] PROMSUWAN K, KANATHARANA P, THAVARUNGKUL P, et al. Nitrite amperometric sensor for gunshot residue screening [J]. *Electrochimica Acta*, 2020, 331: 135309.
- [101] AMBAYE A D, KEFENI K K, MISHRA S B, et al. Recent developments in nanotechnology-based printing electrode systems for electrochemical sensors[J]. *Talanta*, 2021, 225: 121951.
- [102] PROMSUWAN K, SAICHANAPAN J, SOLEH A, et al. New electrode material integrates silver nanoprisms with phosphorus-doped carbon nanotubes for forensic detection of nitrite[J]. *Electrochimica Acta*, 2022, 436: 141439.
- [103] WONGPAKDEE T, CRENSHAW K, WONG H M F, et al. The development of screen-printed electrodes modified with gold and copper nanostructures for analysis of gunshot residue and low explosives[J]. *Forensic Science International*, 2024, 364: 112243.
- [104] WONGPAKDEE T, BUKING S, WILAIRAT P, et al. Exploiting a gold leaf-based voltammetric sensor for the estimation of firing distance[J]. *Forensic Chemistry*, 2025, 45: 100681.
- [105] DALZELL K A, OTT C E, TREJOS T, et al. Comparison of portable and benchtop electrochemical instruments for detection of inorganic and organic gunshot residues in authentic shooter samples [J]. *Journal of Forensic Sciences*, 2022, 67 (4) : 1450–1460.
- [106] TORRARIT K, COTCHIM S, PHONCHAI A, et al. Voltammetric co-determination of lead and copper in gunshot residue based on iron oxide particle/spent coffee grounds-modified electrode[J]. *Microchimica Acta*, 2024, 191(7): 417.
- [107] COTCHIM S, THAVARUNGKUL P, KANATHARANA P, et al. A portable electrochemical immunosensor for ovarian cancer uses hierarchical microporous carbon material from waste coffee grounds[J]. *Microchimica Acta*, 2023, 190(6): 232.
- [108] DATTATRAYA SARATALE G, BHOSALE R, SHOBANA S, et al. A review on valorization of spent coffee grounds (SCG) towards biopolymers and biocatalysts production [J]. *Biore-source Technology*, 2020, 314: 123800.
- [109] MALEKI B, BAGHAYERI M, GHANEI-MOTLAGH M, et al. Polyamidoamine dendrimer functionalized iron oxide nanoparticles for simultaneous electrochemical detection of Pb²⁺ and Cd²⁺ ions in environmental waters [J]. *Measurement*, 2019, 140: 81–88.
- [110] PALAKOLLU V N, CHIWUNZE T E, LIU C, et al. Electrochemical sensitive determination of acetaminophen in pharmaceutical formulations at iron oxide/graphene composite modified electrode[J]. *Arabian Journal of Chemistry*, 2020, 13(2): 4350–4357.
- [111] CARDOSO R M, CASTRO S V F, SILVA M N T, et al. 3D-printed flexible device combining sampling and detection of explosives[J]. *Sensors and Actuators B: Chemical*, 2019, 292: 308–313.
- [112] CASTRO S V F, LIMA A P, ROCHA R G, et al. Simultaneous determination of lead and antimony in gunshot residue using a 3D-printed platform working as sampler and sensor[J]. *Analytica Chimica Acta*, 2020, 1130: 126–136.
- [113] LAPAEV D V, NIKIFOROV V G, SAFIULLIN G M, et al. Changes in luminescent properties of vitrified films of terbium (III) β-diketonate complex upon UV laser irradiation[J]. *Journal of Luminescence*, 2016, 175: 106–112.
- [114] XIONG Y J, HUANG P L, ZHANG X W, et al. Mono and heterometallic europium (III) and terbium (III) complexes: Synthesis, crystal structures and luminescent properties [J]. *Inorganic Chemistry Communications*, 2015, 56: 53–57.
- [115] MELO LUCENA M A, RODRIGUES M O, GATTO C C, et al. Synthesis of [Dy(DPA)(HDP)] and its potential as gunshot residue marker [J]. *Journal of Luminescence*, 2016, 170: 697–700.
- [116] KHULLAR S, SINGH S, DAS P, et al. Luminescent lanthanide-based probes for the detection of nitroaromatic compounds in water [J]. *ACS Omega*, 2019, 4(3) : 5283–5292.
- [117] LIAN X, YAN B. A lanthanide metal-organic framework (MOF-76) for adsorbing dyes and fluorescence detecting aromatic pollutants [J]. *RSC Advances*, 2016, 6(14) : 11570–11576.
- [118] CUI Z, ZHANG X, LIU S, et al. Anionic lanthanide metal-organic frameworks: Selective separation of cationic dyes, solvatochromic behavior, and luminescent sensing of Co (II) ion [J]. *Inorganic Chemistry*, 2018, 57(18) : 11463–11473.
- [119] LUCENA M A M, ORDOÑEZ C, WEBER I T, et al. Investigation of the use of luminescent markers as gunshot residue indicators[J]. *Forensic Science International*, 2017, 280: 95–102.
- [120] LUCENA M A M, OLIVEIRA M F L, AROUCA A M, et al. Application of the metal-organic framework [Eu(BTC)] as a luminescent marker for gunshot residues: A Synthesis, characterization, and toxicity study[J]. *Applied Materials & Interfaces*, 2017, 9(5): 4684–4691.
- [121] AROUCA A M, LUCENA M A M, ROSSITER R J, et al. Use of

- luminescent gunshot residues markers in forensic context—Part II [J]. *Forensic Science International*, 2017, 281: 161–170.
- [122] WEBER I T, MELO A J G, LUCENA M A M, et al. Use of luminescent gunshot residues markers in forensic context[J]. *Forensic Science International*, 2014, 244: 276–284.
- [123] LUCENA M A M, AROUCA A M, TALHAVINI M, et al. Ammunition encoding by means of co-doped luminescent markers [J]. *Microchemical Journal*, 2019, 145: 539–546.
- [124] CARNEIRO C R, SILVA C S, DE CARVALHO M A, et al. Identification of luminescent markers for gunshot residues: Fluorescence, Raman spectroscopy, and chemometrics[J]. *Analytical Chemistry*, 2019, 91(19): 12444–12452.
- [125] CARNEIRO C R, SILVA C S, PIMENTEL M F, et al. Application of luminescent markers to ammunition encoding in forensic routine using a Video Spectral Comparator (VSC) [J]. *Microchemical Journal*, 2020, 159: 105362.
- [126] SERWY I B, WANDERLEY K A, LUCENA M A M, et al. $[\text{Ln}_2(\text{BDC})_3(\text{H}_2\text{O})_4]$: A low cost alternative for GSR luminescent marking[J]. *Journal of Luminescence*, 2018, 200: 24–29.
- [127] GOMES E M, SILVA J P D O, COLAÇO M V, et al. Two highly photoluminescent Eu^{3+} β -diketonates complexes with ε -caprolactam as ancillary ligands: From synthesis to the first example as gunshot residue markers [J]. *Optical Materials*, 2023, 137: 113527.
- [128] GOMES E M, DE OLIVEIRA SILVA J P, DOS SANTOS OLIVEIRA G L, et al. Synthesis and characterization of two highly luminescent Eu^{3+} tris- β -diketonates with the δ -valerolactam ligand: Theoretical, experimental spectroscopy studies and viability as luminescent gunshot residues [J]. *Journal of Luminescence*, 2025, 280: 121069.
- [129] FILHO E V, DE SOUSA FILHO P C, SERRA O A, et al. New luminescent lanthanide-based coordination compounds: Synthesis, studies of optical properties and application as marker for gunshot residues [J]. *Journal of Luminescence*, 2018, 202: 89–96.
- [130] SILVA M A, DE CAMPOS N R, FERREIRA L A, et al. A new photoluminescent terbium (III) coordination network constructed from 1, 2, 4, 5-benzenetetracarboxylic acid: Synthesis, structural characterization and application as a potential marker for gunshot residues [J]. *Inorganica Chimica Acta*, 2019, 495: 118967.
- [131] LUCENA M, CÂMARA S, TALHAVINI M, et al. Yttrium orthovanadates phosphors as up-conversion luminescent markers for gunshot residue identification [J]. *Journal of Luminescence*, 2022, 250: 119020.

Research Progress on On-Site Rapid Detection Technology for Gunshot Residue

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Abstract: Gunshot residue (GSR) is a trace particle formed during the firing of a bullets. As an important research subject in forensic science, it plays a key role in the investigation of gun-related cases. Currently, conventional GSR detection mainly relies on large laboratory instruments. However, due to the complexity of sample pretreatment and the lengthy submission process, it is difficult to provide analysis results quickly, thereby affecting the decision-making efficiency of on-site investigation work. In recent years, GSR on-site rapid detection technology has received widespread attention due to its simple operation, low cost, and portability. This type of technology can be directly implemented at the crime scene without relying on large precision instruments, and can quickly output detection results. It is suitable for the preliminary screening of GSR and can also be used as the final confirmation detection method, and has become a research hotspot in this field. Therefore, a systematic review of the research progress on-site rapid detection technology for GSR is conducted, focusing on introducing five categories of methods: colorimetric methods, spectroscopic methods, mass spectrometry methods, electrochemical methods, and fluorescent labeling methods. Their advantages and limitations are thoroughly analyzed, and they are compared with the practical applications of laboratory detection technology. Finally, future research development directions are proposed, aiming to provide theoretical basis and methodological references for on-site technicians in actual detection work.

Key words: gunshot residue (GSR); on-site rapid detection; colorimetric methods; spectroscopic methods; mass spectrometry methods; electrochemical methods; fluorescence labeling methods

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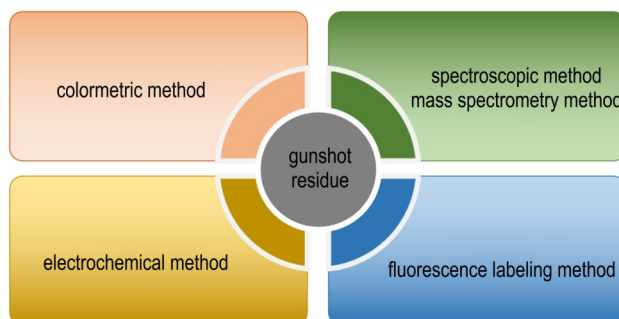
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图文摘要:



This study systematically reviews the research progress of on-site rapid detection technology for GSR (Gunshot Residue), focusing on five categories of methods: colorimetry, spectroscopy, mass spectrometry, electrochemistry, and fluorescence labeling. It thoroughly analyzes the advantages and limitations of these methods, proposes future research directions, and aims to provide field technicians with a theoretical basis and methodological references for practical detection work.