

紫外诱导荧光的土壤石油烃类污染物原位检测技术

杨金强^{1,2,3}, 杨瑞芳^{2,3*}, 赵南京^{2,3**}, 殷高方^{2,3}, 马明俊^{2,3}, 方丽^{2,3}, 石高勇^{1,2,3}, 刘梁晨^{1,2,3}, 孟德硕⁴, 刘文清^{2,3}

¹中国科学技术大学, 安徽 合肥 230026;

²中国科学院合肥物质科学研究院安徽光学精密机械研究所中国科学院环境光学与技术重点实验室, 安徽 合肥 230031;

³安徽省环境光学监测技术重点实验室, 安徽 合肥 230031;

⁴淮南师范学院, 安徽 淮南 232000

摘要 石油烃类污染物进入土壤后会随着时间逐步迁移到土壤深层。传统的土壤石油烃检测方法因自身的局限性, 无法及时快速地检测深层土壤中的石油烃质量分数。为快速检测深层土壤中的石油烃类污染物, 提出了一种基于紫外诱导荧光的石油烃原位检测技术, 利用 280 nm 的深紫外发光二极管(LED)作为激发光源、光电倍增管(PMT)作为信号探测器完成对土壤中石油烃质量分数的探测。实验结果表明, 该检测技术能够实现对不同土壤类型(红壤、黄壤、黑土和湖底淤泥土)中各类机油(汽油机油、柴油机油和空压机油)的定量检测, 检测结果的平均相对误差(RE)小于 10.00%, 平均相对标准偏差(RSD)小于 4.00%, 土壤中各类石油烃的检出限均小于 136 mg/kg, 完成单个样本测量仅需 2.0 s。

关键词 测量; 土壤; 石油烃; 紫外诱导荧光; 光电倍增管; 原位检测

中图分类号 X53

文献标志码 A

DOI: 10.3788/AOS221531

1 引言

我国土壤石油污染问题日益严重^[1], 每年因石油开采进入环境的石油类污染物高达 4×10^7 t 左右^[2], 进入土壤的石油类污染物对土壤具有极大的危害^[3], 不仅会破坏土壤的表层结构, 还会经水土循环进入生物链, 破坏生态环境, 并威胁人类健康^[4]。为了有效防治土壤石油烃污染, 需对土壤石油烃污染状况进行现场快速检测。传统的土壤石油烃类检测方法(红外分光光度法、高效液相色谱法、气相色谱法、气相色谱-质谱法和索氏提取法等)^[5-6]均需对土壤样品进行萃取处理, 复杂耗时, 使用环境苛刻, 无法用于场地土壤石油烃类污染物的现场测量, 且石油烃类污染的土壤样品在采集、运输和预处理过程中容易造成二次污染^[7]。此外, 某些石油烃类污染物(氯氟烃、二氯甲烷等)具有较强的挥发性, 这会导致土壤中石油烃类污染物的质量分数检测结果出现偏差, 对土壤中石油烃类污染物进行实时原位检测是提高检测速度与准确性的重要前提, 也能够显著提高土壤修复、土壤普查的效率, 故目前急需发展土壤石油烃类污染物的快速原位检测方法。

当前, 越来越多的光学方法被应用于土壤石油烃类的现场检测中。在紫外光照射下, 石油烃中含有的大量不饱和烃及其衍生物会产生荧光, 基于石油烃的荧光特性^[8], 国内外学者采用激光诱导荧光光谱(LIF)技术对土壤中的石油烃进行检测^[9]。LIF 技术具有速度快、灵敏度高和选择性好等特点, 成为了当前土壤石油烃检测的研究热点。Schultze 等^[10]利用 LIF 技术研究了对未知多环芳烃污染的土壤样品进行定量分析的方法, 并制定了在野外条件下安全应用校准程序的策略。Löhmannsröben 等^[11-12]采用 LIF 技术对浅层土壤中石油烃类有机污染物进行了定性和定量测量。左兆路^[13]将 LIF 技术与三维荧光光谱技术相结合, 完成了土壤石油烃的分类和定量测量, 提高了检测精度和准确度。然而, 利用 LIF 技术来现场检测土壤石油烃类污染物也有一定的局限性, 如激光要求高、检测系统复杂、维护成本高和土壤样品的片剂处理时间长。系统的小型化和现场检测是难以实现的。高能脉冲激光器会引起样品中石油烃类的光解, 对同一样品的检测重复性较差。为提高土壤石油烃类原位检测的效率和准确性, 本文采用深紫外发光二极管(LED)作为激发光源, 基于紫外诱导荧光技术对土壤石油污染物进行研

收稿日期: 2022-07-26; 修回日期: 2022-08-18; 录用日期: 2022-08-25; 网络首发日期: 2022-09-04

基金项目: 国家重点研发计划子课题(2020YFC1807204-1)、中国科学院科技服务网络计划(STS计划)区域重点项目(KFJ-STQ-QYZD-2021-04-001-4)、安徽省重点研究和开发计划(201904a07020089)

通信作者: *rfyang@aiofm.ac.cn; **njzhao@aiofm.ac.cn

究,相较于激光光源,深紫外LED具有稳定性高、重复性好、体积小、成本低和系统维护简单等优点,为土壤石油烃类原位检测提供了一种新技术。

2 实验和方法

2.1 实验材料

实验选用红壤(GBW07407)、黄壤(GBW07455)、黑壤(NST-1)和湖底淤泥作为土壤基底。机油是典型土壤石油烃类污染物,实验选用3种相对密度分别为0.85、0.88、0.91 g/cm³的中质机油(汽油发动机机油、柴油机机油和空压机机油作为实验用油)和标准原油(JB-4002)作为测试油类。所有油类样品先溶解在乙醇溶剂中,完全溶解后与不同类型的土壤混合,经自然干燥,研磨制成含高质量分数机油的土壤样品。然后,将样品与空白土壤均匀混合,配制土壤机油质量分数范围为0~1%(0~10000 mg/kg)的样品,将制备好的样品密封备用。

2.2 实验系统的搭建

合理的激发波长和探测波长对检测系统的检测效率至关重要。采用三维荧光光谱仪(日立高新技术公司,F-7000)对标准原油(JB-4002)样品进行分析,获得原油的标准三维荧光光谱。

如图1所示,原油荧光峰的激发波长在250~300 nm之间,发射波长在300~450 nm之间,主荧光峰

的激发波长为280 nm。因此,采用280 nm作为实验系统的激发波长。为了选择合适的发射波长,先采用280 nm-LED对不同类型的土壤空白样本进行照射,利用光谱仪对激发出的荧光信号进行探测。光谱仪采用海洋光学公司生产的maya 2000-Pro光谱仪,分辨率为1.1 nm,探测范围为200~1100 nm,获得对应的发射光谱后采用S-G平滑滤波,结果如图2所示。

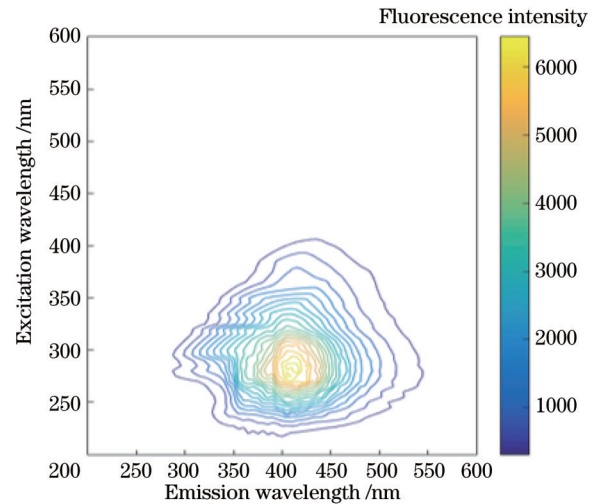


图1 原油的三维荧光光谱

Fig. 1 Three-dimensional fluorescence spectra of diesel engine oil

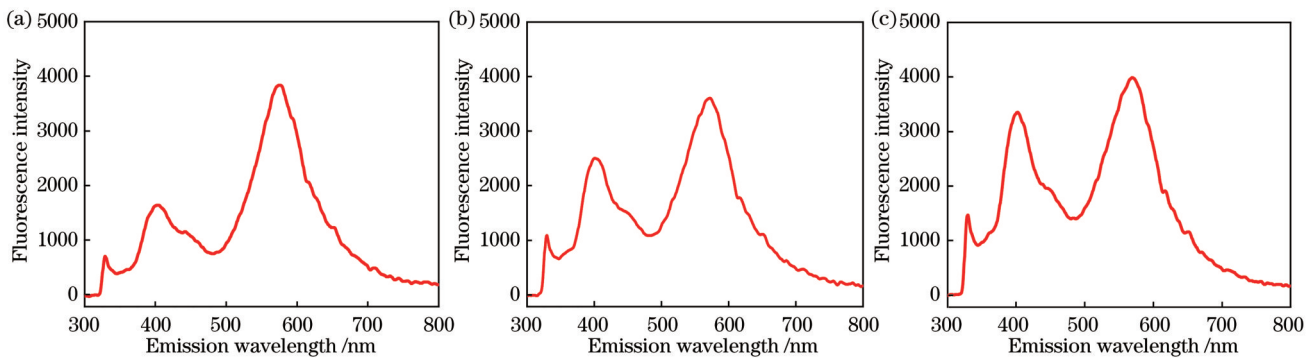


图2 280 nm-LED照射下不同土壤空白样本的发射光谱。(a)红壤;(b)黄壤;(c)黑壤

Fig. 2 Emission spectra of different soil blank samples under 280 nm-LED irradiation. (a) Red soil; (b) yellow soil; (c) black soil

在280 nm-LED照射下,土壤本身会发射大量的荧光,其发射光谱在400 nm和580 nm处具有两个特征荧光峰,配制含10%原油的3种不同土壤基底样品,通过减去相应的土壤空白背景,获得其发射光谱,如图3所示。

如图3所示,在280 nm-LED照射下,不同土壤中原油的发射光谱具有明显的荧光峰,荧光峰位置基本不变,最大荧光峰对应的发射波长在390 nm左右。为了降低土壤背景干扰,选择380 nm作为检测系统的检测波长。

确定好激发波长和探测波长后,将光源与探测器集成进自研的探测装置中,探测装置为长度为

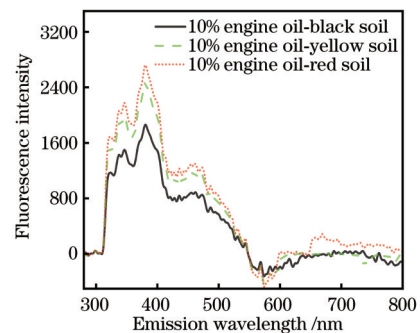


图3 280 nm-LED照射不同土壤类型下含10%原油样本的发射光谱

Fig. 3 Emission spectra of samples containing 10% engine oil under different soil types irradiated by 280 nm-LED

280 mm、直径为 80 mm 的圆柱形装置,如图 4 所示。装置外侧有一个边长为 10 mm 的正方形石英光学窗口,可以透过中心波长为 280 nm 的紫外 LED(额定光功率为 8 mW)发出的光,并在窗口的中心外侧形成面积为 1 cm²的光斑,光斑的光功率为光源初始光功率的 45% 左右,利用紫外辐照度计测得其光斑的激发光功

率为 3.78 mW/cm²。样品在窗口经光源照射后,产生的荧光通过 380 nm 带通滤光片进入探针内部,由光电倍增管对荧光进行接收。光电倍增管(PMT)采用滨松光子学株式会社生产的 H10721-01 光电倍增管,检测灵敏度为 200 μA/lm, PMT 电压为 0.55 V,默认积分时间为 1000 μs,单个样品测量时间为 2 s。

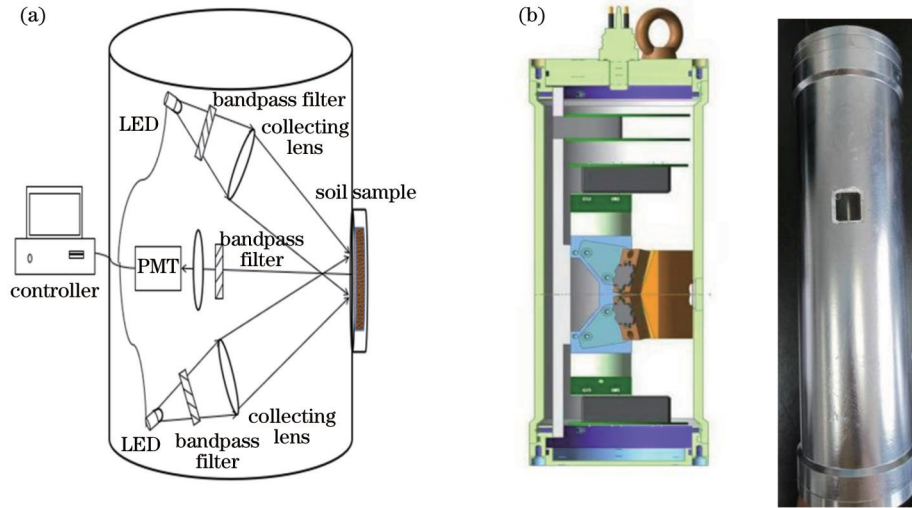


图 4 实验系统原理图和实物图。(a)原理图;(b)实物图

Fig. 4 Schematic diagram and physical picture of experimental system. (a) Schematic diagram;(b) physical picture

3 方法原理

土壤中的石油烃类污染物在紫外光照射下会发出荧光,荧光强度的表达式为

$$F = \varphi I_0 (1 - 10^{-\epsilon lc}), \quad (1)$$

式中: F 为荧光强度; φ 为荧光量子产率; I_0 为激发光强度; ϵ 为摩尔吸光系数; l 为液面厚度; c 为土壤中机油的质量分数。对式(1)两边同时进行求对数运算,可得

$$\ln[\varphi I_0 (1 - 10^{-\epsilon lc})] = \ln F, \quad (2)$$

含油土壤的样本可以视为低质量分数的稀溶液样本,当测定的荧光物质为稀溶液时,可以将式(2)^[14]简化为

$$F = 2.3k\varphi I_0 \epsilon lc, \quad (3)$$

式中: k 为测试系统的相关常数。通过 PMT 将得到的荧光信号 F 转化为荧光信号 Q ,即

$$Q = F\alpha TS_{\text{PMT}}, \quad (4)$$

式中: α 为荧光收集效率; T 为光学系统透过率; S_{PMT} 为 PMT 转换效率。 α 、 T 和 S_{PMT} 与实验装置的光学设计和 PMT 的性质有关,检测系统设计完成后不再变化,故在保证激发光源稳定的状态下,荧光信号与土壤中污染物的质量分数成正比。

对于光学分析方法,可测量的最小信号 X_L 的计算公式为

$$X_L = X_b + \frac{K_d S_d}{m}, \quad (5)$$

式中: X_b 为多次测量的空白样品的光谱平均信号; S_d 为多次测量的空白样品信号的标准偏差; m 为测量方法

的灵敏度(定标曲线斜率); K_d 为常数,国际纯粹与应用化学联合会建议值为 $K_d=3$ 。检测限 V_{LOD} 的计算公式为

$$V_{\text{LOD}} = X_L - X_b = \frac{K_d S_d}{m}. \quad (6)$$

4 结果与讨论

4.1 检测系统的稳定性和灵敏度

为验证系统检测信号的稳定性,制备了含 0.05% 柴油机机油的黄壤样品,测量 PMT 积分时间为 0.4、0.6、0.8、1.0、1.4、1.6、2.0、2.2、2.4、2.6、3.0 s 时的荧光信号数据,计算各积分时间下信号的相对标准偏差(RSD),相应的表达式为

$$V_{\text{RSD}} = \frac{1}{\bar{C}} \sqrt{\frac{\sum_{i=1}^n (C_i - \bar{C})^2}{n-1}} \times 100\%, \quad (7)$$

式中: \bar{C} 为样本测量信号均值; C_i 为样本测量信号; n 为样本测量次数。

如表 1 所示,增加 PMT 的积分时间可以有效降低系统检测信号的 RSD,但当集成时间达到 2.0 s 时,检测系统的 RSD 将很难进一步降低,在保证信号稳定性的前提下,为提高所提方法的检测速度和检测效率,选择单次采样时间为 2.0 s。

为了更好地展现检测方法的灵敏度,将实验系统与 LIF 系统的检测结果进行对比。LIF 系统采用 Quantel 公司的 Q-smart 850 激光器产生波长为 266 nm

表 1 不同积分时间下实验系统的信号的 RSD

Table 1 RSD of signal of experimental system under different integration times

Integration time / s	RSD / %
0.4	6.77
0.6	5.56
0.8	4.72
1.0	4.57
1.4	4.41
1.6	4.23
2.0	3.61
2.2	3.67
2.4	3.65
2.6	3.61
3.0	3.52

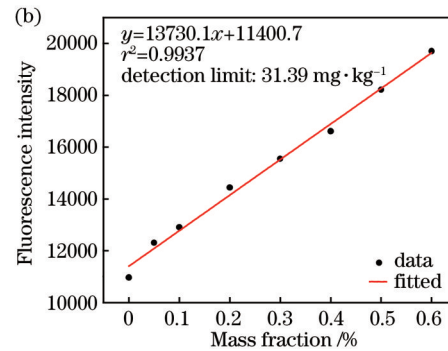
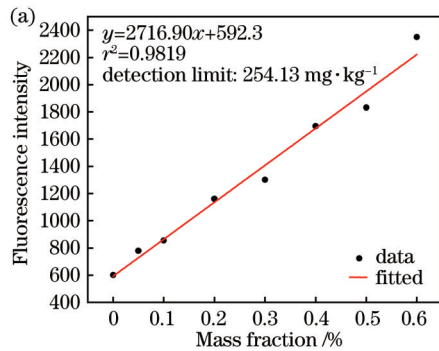


图 5 土壤中油的质量分数与荧光电信号的相关性。(a) LIF 系统;(b)实验系统

Fig. 5 Correlation between mass fraction of oil in soil and fluorescent electrical signal. (a) LIF system; (b) experimental system

4.2 检测系统的适用性

土壤基底中有机质成分与含量的差异会对检测结果造成较大的影响。为了验证不同土质下检测系统的适用性,选用 3 种国标土壤作为基底对土壤石油烃进行定量研究,其中红壤有机质含量低于 0.2%,黄壤有机质含量范围在 0.5%~1.0%之间,黑壤有机质含量高于 3.0%。

的激发光作用在土壤样品表面,其激发功率为 440 mW/cm²,样品产生的荧光经透镜耦合到光纤中,利用光谱仪进行采集。LIF 系统整合于长度为 90 cm、宽度为 50 cm、高度为 80 cm 的长方体检测平台中,利用荧光分析法对 380 nm 的荧光信号进行分析。

采用实验系统和 LIF 系统对配制好的含有柴油发动机油不同质量分数梯度(0、0.05%、0.10%、0.20%、0.30%、0.40%、0.50%、0.60%)的土壤样品进行检测。

如图 5 所示,在含不同质量分数的机油土壤中,实验系统和 LIF 系统的检测信号与机油质量分数均有良好的相关性。与 LIF 系统相比,实验系统的体积和能耗都具有 LIF 系统无法比拟的优势,在采用极低的激发光强度下,实验系统的检测结果具有更高的相关性和更低的检出限。其中, R^2 为相关系数。

表 2 不同土壤类型的土壤石油烃定量分析

Table 2 Quantitative analysis of soil petroleum hydrocarbons for different soil types

Soil type	Petroleum hydrocarbon	Regression equation	Correlation coefficient R^2	Detection limit / ($\text{mg}\cdot\text{kg}^{-1}$)
Red soil	Gasoline engine oil	$y=7121.3x+8803.12$	0.9734	60.38
	Diesel engine oil	$y=14374.4x+8791.96$	0.9941	29.91
	Air compressor engine oil	$y=49681.01x+8827.11$	0.9953	8.66
Yellow soil	Gasoline engine oil	$y=6915.7x+10724.4$	0.9625	62.37
	Diesel engine oil	$y=13730.1x+11400.7$	0.9937	31.39
	Air compressor engine oil	$y=48622.8x+11641.1$	0.9964	8.87
Black soil	Gasoline engine oil	$y=6001.63x+18761.29$	0.9572	104.97
	Diesel engine oil	$y=12113.57x+18912.43$	0.9901	52.01
	Air compressor engine oil	$y=37619.13x+18317.61$	0.9926	16.75

的质量分数与荧光信号均具有良好的线性相关性,相关系数均大于 95%。随着土壤中有机质含量的增加,各类型土壤机油的检测限均降低,这是因为有机质丰富的土壤基底对机油具有吸收包裹作用,被吸收包裹的机油会降低样品测试表面机油的质量分数,从而引起测量的灵敏度降低和检出限升高。实验系统的荧光信号变化规律与土壤中机油的化学和物理性质一致,在不同土壤类型和不同机油类型下,系统获得的信号与机油质量分数均具有良好的相关性,检测系统可以很好地对不同类型

土壤中不同类型的机油进行检测。

4.3 所提方法的准确性

为验证紫外诱导荧光技术定量检测土壤机油的准确性,分析了不同土壤类型下含汽油机油、柴油机油和空压机机油土壤样品测量时的相对误差(RE)和 RSD,如表 3~5 所示。RE 的计算公式为

$$V_{RE} = \frac{|X - \mu|}{\mu}, \quad (8)$$

式中: X 为系统反演质量分数; μ 为真实质量分数。

表 3 红壤中不同类型石油烃预测结果

Table 3 Prediction results of different types of petroleum hydrocarbons in red soil

unit: %

Petroleum hydrocarbon	Standard mass fraction	Predicted mass fraction	RE	Average RE	RSD	Average RSD
Gasoline engine oil	0.150	0.143	4.67	5.62	3.70	3.53
	0.250	0.233	6.80		3.71	
	0.350	0.371	6.00		3.42	
	0.600	0.579	3.50		3.49	
	0.800	0.857	7.13		3.33	
Diesel engine oil	0.150	0.141	6.00	4.76	3.59	3.59
	0.250	0.257	2.80		3.61	
	0.350	0.341	2.57		3.44	
	0.600	0.613	2.17		4.17	
	0.800	0.882	10.25		3.12	
Air compressor engine oil	0.150	0.155	3.33	4.40	3.36	3.36
	0.250	0.261	4.40		3.28	
	0.350	0.357	2.00		3.51	
	0.600	0.631	5.17		3.55	
	0.800	0.859	7.38		3.12	

表 4 黄壤中不同类型石油烃预测结果

Table 4 Prediction results of different types of petroleum hydrocarbons in yellow soil

unit: %

Petroleum hydrocarbon	Standard mass fraction	Predicted mass fraction	RE	Average RE	RSD	Average RSD
Gasoline engine oil	0.150	0.134	10.67	7.69	3.17	3.70
	0.250	0.234	6.40		4.63	
	0.350	0.329	6.00		3.76	
	0.600	0.570	5.00		3.01	
	0.800	0.883	10.38		3.92	
Diesel engine oil	0.150	0.137	8.67	6.31	2.42	3.16
	0.250	0.261	4.40		3.31	
	0.350	0.332	5.14		3.86	
	0.600	0.567	5.50		3.01	
	0.800	0.863	7.88		3.19	
Air compressor engine oil	0.150	0.143	4.60	6.40	3.21	3.04
	0.250	0.232	7.20		2.01	
	0.350	0.326	6.86		3.45	
	0.600	0.626	4.33		3.12	
	0.800	0.728	9.00		3.43	

表 5 黑壤中不同类型石油烃预测结果

Table 5 Prediction results of different types of petroleum hydrocarbons in black soil

unit: %

Petroleum hydrocarbon	Standard mass fraction	Predicted mass fraction	RE	Average RE	RSD	Average RSD
Gasoline engine oil	0.150	0.159	6.00	8.25	3.33	3.40
	0.250	0.270	8.00		3.71	
	0.350	0.377	7.71		3.12	
	0.600	0.672	12.00		3.29	
	0.800	0.891	11.38		3.61	
Diesel engine oil	0.150	0.162	8.00	6.72	3.52	3.51
	0.250	0.263	5.20		3.90	
	0.350	0.359	2.57		3.37	
	0.600	0.663	10.50		3.21	
	0.800	0.862	7.75		3.53	
Air compressor engine oil	0.150	0.138	7.33	7.24	3.53	3.01
	0.250	0.268	7.20		3.52	
	0.350	0.369	5.43		3.23	
	0.600	0.654	9.00		3.09	
	0.800	0.853	6.62		2.19	

对各土壤中汽油机油(oil 1)、柴油机油(oil 2)和空压机机油(oil 3)的 RSD 和 RE 进行分析,结果如图 6 所示。

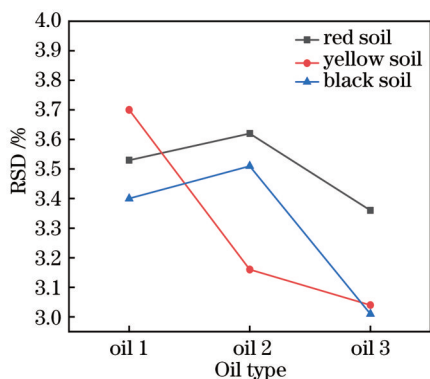


图 6 不同土壤类型下所提系统测量的平均 RSD

Fig. 6 Average RSD measured by proposed system under different soil types

由图 6 可知:在红壤基底上,汽油机油、柴油机油和空压机机油测得信号的 RSD 分别为 3.53%、3.62% 和 3.36%;在黄壤基底上,3 种机油的 RSD 分别为 3.70%、3.16% 和 3.04%;在黑壤基底上,3 种机油的 RSD 分别为 3.40%、3.51% 和 3.01%。对于含不同机油的不同类型的土壤,实验系统检测的 RSD 均小于 4.00%,且稳定在 3.50%,表明土壤和机油类型对所提方法的稳定性影响较小。

由图 7 可知:在红壤基底上,汽油机油、柴油机油、空压机机油的平均 RE 分别为 5.62%、4.76% 和 4.46%;在黄壤基底上,3 种机油的平均 RE 分别为 7.69%、6.31% 和 6.40%;在黑壤基底上,3 种机油的

平均 RE 分别为 8.25%、6.72% 和 7.24%。图 7 表明:不同土壤基质的测量 RE 不同,即土壤有机质含量越高,测量的 RE 越大,测量精度越低。总体而言,不同类型的机油在每种土壤基质中测量的平均 RE 小于 10.00%。

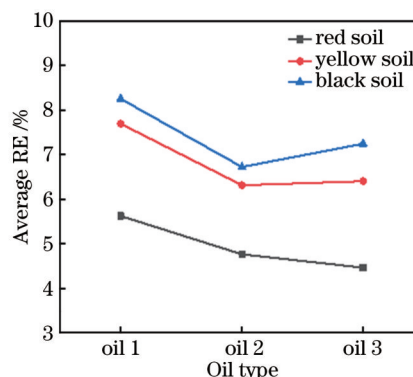


图 7 不同土壤类型下所提系统测得的平均 RE 值

Fig. 7 Average RE measured by proposed system under different soil types

4.4 实际土壤检测

为了验证所提方法对实际土壤的检测效果,将从合肥市董铺水库采集的湖底淤泥作为土壤基底与 3 种机油进行混合,制备出不同质量分数的含油土壤。使用检测系统进行测试,结果如表 6 所示。

当将湖底淤泥作为土壤基底时,不同种类机油的相关系数为 0.9515、0.9793、0.9901,检测限为 135.65、59.37、19.62 mg/kg。相较于国家标准土壤,其相关系数降低,检测限上升。对于复杂土壤背景的湖底淤泥,实验系统仍具有良好的线性相关性和较低

的检出限,能够满足实际测量的需要。为了测试实验系统在复杂土壤背景下的检测能力,对其检测准确性

进行了分析,结果如表 7 所示。

表 6 湖底淤泥中土壤石油烃定量分析

Table 6 Quantitative analysis of soil petroleum hydrocarbons in lake bottom mud

Petroleum hydrocarbon	Regression equation	Correlation coefficient R^2	Detection limit / ($\text{mg}\cdot\text{kg}^{-1}$)
Gasoline engine oil	$y=4718.51x+46940.9$	0.9515	135.65
Diesel engine oil	$y=10781.53x+47113.3$	0.9793	59.37
Air compressor engine oil	$y=32629.52x+47467.6$	0.9901	19.62

表 7 湖底淤泥中不同类型石油烃预测结果

Table 7 Prediction results of different types of petroleum hydrocarbons in lake bottom mud

unit: %

Petroleum hydrocarbon	Standard mass fraction	Predicted mass fraction	RE	Average RE
Gasoline engine oil	0.150	0.178	18.67	8.25
	0.250	0.275	10.00	
	0.350	0.326	6.86	
	0.600	0.565	5.83	
	0.800	0.846	5.75	
Diesel engine oil	0.150	0.128	14.67	6.72
	0.250	0.236	5.60	
	0.350	0.323	7.71	
	0.600	0.571	4.83	
	0.800	0.764	4.50	
Air compressor engine oil	0.150	0.163	8.69	7.24
	0.250	0.234	6.40	
	0.350	0.329	6.00	
	0.600	0.563	6.17	
	0.800	0.773	8.63	

如表 7 所示,当将河底淤泥作为土壤基底时,汽油发动机机油、柴油机机油和空压机机油的平均 RE 分别为 8.25%、6.72% 和 7.24%,均低于 10.00%,满足实际测量要求。

5 结 论

基于紫外诱导荧光技术,采用深紫外 LED 作为光源、PMT 作为检测器实现了对土壤中石油烃类污染物的定量检测研究。通过对不同土壤类型中不同油类污染物进行定量检测,发现土壤石油烃质量分数与检测信号间具有良好的线性关系,研究了不同土壤基底土壤机油检测技术的可行性,并验证了检测技术在不同土壤基底下的适用性。实验结果表明,紫外诱导荧光的土壤石油烃类污染物原位检测技术可以很好地应用于土壤石油烃类污染物的检测中,为土壤深层石油烃原位快速检测提供了一种可行的方法。

参 考 文 献

[1] Wu B, Guo S H, Wang J N. Spatial ecological risk assessment for contaminated soil in oiled fields[J]. Journal of Hazardous Materials, 2021, 403: 123984.

[2] Zhang J, Dai J L, Du X M, et al. Distribution and sources of petroleum-hydrocarbon in soil profiles of the Hunpu wastewater-irrigated area, China's northeast[J]. Geoderma, 2012, 173/174: 215-223.

[3] Tang J C, Wang M, Wang F, et al. Eco-toxicity of petroleum hydrocarbon contaminated soil[J]. Journal of Environmental Sciences, 2011, 23(5): 845-851.

[4] Patowary R, Patowary K, Devi A, et al. Uptake of total petroleum hydrocarbon (TPH) and polycyclic aromatic hydrocarbons (PAHs) by *Oryza sativa* L. grown in soil contaminated with crude oil [J]. Bulletin of Environmental Contamination and Toxicology, 2017, 98(1): 120-126.

[5] Matz G, Schroeder W, Kuebler J. Field method for the detection of total petroleum hydrocarbon in water and soil samples[EB/OL]. (1997-12-31)[2022-02-04]. <https://www.osti.gov/biblio/613770>.

[6] 樊鑫, 赵新达, 杨大佐, 等. 优化超声萃取滩涂底质中石油烃总量的研究[J]. 应用化工, 2015, 44(7): 1206-1209.
Fan X, Zhao X D, Yang D Z, et al. Determination of total petroleum hydrocarbons content in beach sediment by optimizing ultrasonic extraction[J]. Applied Chemical Industry, 2015, 44(7): 1206-1209.

[7] Hoang S A, Sarkar B, Seshadri B, et al. Mitigation of petroleum-hydrocarbon-contaminated hazardous soils using organic amendments: a review[J]. Journal of Hazardous Materials, 2021, 416: 125702.

[8] Okparanma R N, Mouazen A M. Determination of total petroleum hydrocarbon (TPH) and polycyclic aromatic

- hydrocarbon (PAH) in soils: a review of spectroscopic and nonspectroscopic techniques[J]. Applied Spectroscopy Reviews, 2013, 48(6): 458-486.
- [9] Knowles D S, Lieberman S H. Field results from the SCAPS laser-induced fluorescence (LIF) sensor for *in-situ* subsurface detection of petroleum hydrocarbons[J]. Proceedings of SPIE, 1995(2504): 297-307.
- [10] Schultze R H, Lewitzka F. On-site and *in situ* analysis of contaminated soils using laser induced fluorescence spectroscopy [J]. Proceedings of SPIE, 2005, 5983: 59830V.
- [11] Löhmannsröben H G, Schober L. Combination of laser-induced fluorescence and diffuse-reflectance spectroscopy for the *in situ* analysis of diesel-fuel-contaminated soils[J]. Applied Optics, 1999, 38(9): 1404-1410.
- [12] Löhmannsröben H G, Roch T. *In situ* laser-induced fluorescence (LIF) analysis of petroleum product-contaminated soil samples [J]. Journal of Environmental Monitoring, 2000, 2(1): 17-22.
- [13] 左兆陆. 土壤石油烃类污染物荧光测量技术及应用研究[D]. 合肥: 中国科学技术大学, 2020.
- Zuo Z L. Application study on fluorescence measurement technology of petroleum hydrocarbon pollutants in soil[D]. Hefei: University of Science and Technology of China, 2020.
- [14] 孙石天. 基于荧光 CPTU 测试技术的有机污染物检测理论及应用研究[D]. 南京: 东南大学, 2019.
- Sun S T. Research on theory and application of organic pollutant detection based on LIF-CPTU technology[D]. Nanjing: Southeast University, 2019.
- [15] Zhang Y R, Liu P, Li Y P, et al. Study on fluorescence spectroscopy of PAHs with different molecular structures using laser-induced fluorescence (LIF) measurement and TD-DFT calculation[J]. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2020, 224: 117450.

In-situ Detection of Petroleum Hydrocarbon Pollutants in Soil by Ultraviolet-Induced Fluorescence

Yang Jinqiang^{1,2,3}, Yang Ruifang^{2,3*}, Zhao Nanjing^{2,3**}, Yin Gaofang^{2,3}, Ma Mingjun^{2,3},
Fang Li^{2,3}, Shi Gaoyong^{1,2,3}, Liu Liangchen^{1,2,3}, Meng Desuo⁴, Liu Wenqing^{2,3}

¹University of Science and Technology of China, Hefei 230026, Anhui, China;

²Key Laboratory of Environmental Optics and Technology, Anhui Institute of Optics and Fine Mechanics, Hefei Institutes of Physical Science, China Academy of Sciences, Hefei 230031, Anhui, China;

³Key Laboratory of Optical Monitoring Technology for Environment of Anhui Province, Hefei 230031, Anhui, China;

⁴Huainan Normal University, Huainan 232000, Anhui, China

Abstract

Objective Soil petroleum hydrocarbon pollution is increasingly serious. Petroleum pollutants released into the environment due to oil extraction are as high as 4×10^7 t per year. Petroleum pollutants are extremely harmful to the soil, destroying the surface structure of the soil. Worse still, the pollutants enter the food chain through soil and water cycles, destroying the ecological environment and threatening human health. To effectively prevent and control petroleum hydrocarbon pollution in soil, it is necessary to conduct on-site rapid detection of petroleum hydrocarbon pollution in soil. However, some traditional detection methods of petroleum hydrocarbon in soil, including infrared spectrophotometry, high-performance liquid chromatography, gas chromatography, gas chromatography-mass spectrometry, Soxhlet extraction, and gravimetric method, have to extract soil samples first, which is complicated to operate. Therefore, these traditional technologies cannot be used as on-site detection of petroleum hydrocarbon pollution in soil. Moreover, it is easy to cause secondary pollution during the collection, transportation, and pretreatment of soil samples contaminated by petroleum hydrocarbons. Some components of pollutants are very easy to volatilize, which leads to deviations in the detection results of petroleum hydrocarbon content. Therefore, a real-time *in-situ* detection of petroleum hydrocarbon pollutants in the soil is an important prerequisite for improving the detection speed and accuracy, and it is urgent to develop a rapid *in-situ* detection method of petroleum hydrocarbon pollutants in soil. To further improve the efficiency and accuracy of the rapid *in-situ* detection of petroleum hydrocarbons in soil, this paper applies deep ultraviolet (UV) light emitting diode (LED) as the excitation light source to detect petroleum pollutants in soil based on UV-induced fluorescence technology, which provides a new method for the rapid *in-situ* detection of petroleum hydrocarbons in soil.

Methods Three types of soil substrates mixed with three types of oil are selected as test samples, and the samples are detected by constructing a UV-induced fluorescence system. The sensitivity, stability, applicability, and accuracy of the detection system are verified. The detection system adopts a deep UV LED driven by a parallel constant current circuit (central emission wavelength of 280 nm, half-wave width of 10 nm, and rated optical power of 8 mW). A dual-lamp-bead combined symmetrical illumination system is constructed. After the sample passes through a 280 nm bandpass filter, an

excitation spot with an area of 1 cm^2 is formed on the surface of the soil sample. The excitation light power measured by the UV irradiance meter is 3.78 mW/cm^2 . The fluorescence detector uses the Hamamatsu H10721-01 photomultiplier tube (PMT) with the detection sensitivity of $200\text{ }\mu\text{A/lm}$ and the PMT voltage of 0.55 V . The sample is loaded into a special circular sample cell, and a flat surface is formed by pressing. The detection system structure is shown in Fig. 4.

Results and Discussions Since it is difficult to detect petroleum hydrocarbons in the soil *in situ*, the deep UV LED-induced fluorescence system is built to detect different types of oil in the soil in this study. The detection system has high sensitivity and stability, and its detection effect is significantly better than that of the laser induced fluorescence spectroscopy (LIF) system. The detection system is utilized to detect different types of engine oils (gasoline engine oil, diesel engine oil, air compressor engine oil) on different soil substrates, and the detection results are as follows. The detection limits of three kinds of engine oils on the soil substrate of red soil are 60.38 mg/kg , 29.91 mg/kg , 8.66 mg/kg , respectively. The detection limits of three kinds of engine oils on the soil substrate of yellow soil are 62.37 mg/kg , 31.39 mg/kg , 8.87 mg/kg , respectively. The detection limits of three kinds of engine oils on the soil substrate of black soil are 104.97 mg/kg , 52.01 mg/kg , 16.75 mg/kg , respectively. The relative standard deviation of oil in different types of soil is less than 4.00% , and the average error of measurement is less than 10.00% . The experimental system constructed in this study completes the accurate quantification of different soil types and different oils, and verifies the feasibility of the UV-induced fluorescence *in-situ* detection technology of petroleum hydrocarbon pollutants in soil. Using deep-UV LED as the light source and PMT as the detector, the detection system is miniaturized, which provides a new method for the *in-situ* detection of petroleum hydrocarbon pollutants in soil and provides an important technical reference for the detection of petroleum hydrocarbon pollutants in deep soil in the future.

Conclusions This study uses UV-induced fluorescence technology to achieve quantitative detection of engine oil in soil. The use of deep-UV LED as the light source and PMT as the detector realizes the miniaturization of the detection system and significantly improves the detection sensitivity of the system. Through quantitative detection of different types of engine oil pollution in the soil, it is verified that there is a good linear relationship between the engine oil fluorescence intensity and its mass fraction. The feasibility of UV-induced fluorescence detection of engine oil under different soil substrates is studied, and the applicability of the method under different soil substrates is verified. The experimental results show that the detection method of engine oil based on UV induction technology can be well applied to the detection of engine oil in the soil, which provides a feasible method for the rapid *in-situ* detection of petroleum hydrocarbons in soil in the future.

Key words measurement; soil; petroleum hydrocarbon; ultraviolet-induced fluorescence; photomultiplier; *in-situ* detection