中国激光

相向成丝荧光增强光谱检测技术研究

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摘要 探索了一种基于两束相向传播飞秒光丝诱导荧光的光谱检测方法。实验结果表明，该方法能够延长荧光衰减时间，增强物质特征谱线强度。将该方法应用于盐水溶液中金属离子(K^+、Na^+、Mg^{2+})特征峰及含量的检测，其对Na^+含量的检测灵敏度为4.3×10^{-6}，较相同激发脉冲能量下的单丝诱导荧光检测技术提升了4倍，且具有良好的线性度。该方法有望为污染物检测提供新途径。

关键词 光谱学；光丝；荧光光谱；飞秒激光

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1 引 言

高强度飞秒激光脉冲在透明介质中传输时，由于光学克尔效应与等离子体自散焦效应呈动态平衡，会产生狭长、稳定且可操纵的等离子体通道，即光丝[1]。飞秒激光成丝伴随着超连续谱产生、荧光辐射、受激放大和脉冲自压缩等丰富的光学效应，在干预天气[2]、超快激光技术[3-4]、激光超精细加工[5-6]等方面具有广泛的应用。飞秒光丝在与物质相互作用时可诱导产生分子指纹荧光光谱[7]。基于光丝的物质检测技术具有快速、实时及多元素同时检测等特点，被应用于水污染检测[8-9]、海洋检测[10-11]等方面。

光丝诱导荧光光谱检测技术受到单丝钳制强度限制，其荧光信号强度及检测灵敏度受限。利用两束或多束光丝间的相互作用可实现光丝强度、长度和激光传输方向的调节，且该相互作用对光丝荧光寿命及荧光能量增强有一定影响[12-13]。研究表明，光丝间的相互作用可以增强荧光信号[14]，这对于提高物质检测灵敏度具有重要意义。根据光束传播方向可将光丝间的相互作用分为同向传播和相向传播两种。目前，研究者基于同向传播的光丝间的相互作用已经开展了大量理论与实验研究[15-16]。例如，利用多束飞秒脉冲在介质中形成的等离子体光栅能够有效提高荧光信号强度[17-18]。但此类方法依赖于超快光场的空间干涉效应，对激发光束空间夹角及脉冲延时等参数要求苛刻。基于相向传播光丝间相互作用的光丝诱导荧光探测方案可以避免光场干涉等问题，被用于太赫兹波的产生[19]。我们前期工作[20]研究了相向传播光丝相互作用机理及其对荧光性质的影响。但该方法在微量化合物检测应用方面的可行性仍有待验证，其检测灵敏度与线性度等亟待提高。

本文介绍了一种基于共线相向传播光丝的荧光光谱增强方法，实验研究了相向光丝激发荧光信号的衰减时间，以及特征峰强度与脉冲能量和脉冲间相对延时的关系，并将该方法应用于水溶液中盐类化合物的灵敏检测。

2 实验装置

图1为实验装置图。钛宝石激光器发射出单脉冲

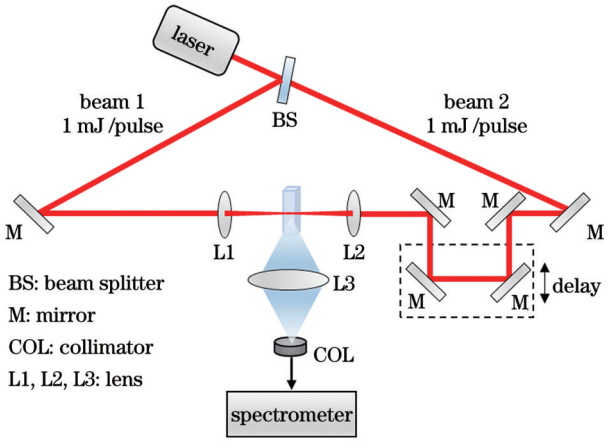

图1 共线相向传播的两束激光成丝实验装置图

Fig. 1 Experimental setup for two collinear laser beams propagating in opposite directions

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能量为 2 mJ、脉宽为 50 fs、重复频率为 1 kHz 的激发光脉冲序列。脉冲中心波长为 800 nm，光谱半峰全宽为 30 nm。激光器输出被均匀地分成两束（分别为光束 1 和光束 2），每一束激光的脉冲能量为 1 mJ。两个共线相向传播的光束分别经熔融石英聚焦透镜（L1 和 L2 焦距 f=100 mm）聚焦到同一焦点，在焦点附近形成两个空间重合的相向传播光丝。在垂直于两束光丝的路径上利用透镜（L3，焦距 f=50 mm）收集成丝诱导的荧光，并被准直镜（COL）聚焦耦合到光纤光谱仪中进行测量。通过电动平移台对两束光的相对脉冲延时进行调整。具体地，固定光束 1 的光程，在光束 2 的光路中加入由一对反射面互相垂直的反射镜和一个线性精密位移平台构成的延迟线（delay），通过改变位移台的步进实现反射镜对向前/后移动，从而达到缩短/增加光束光程的目的，实现脉冲的超前/滞后/同步。

3 分析与讨论

当两路激光脉冲之间的相对时间延迟为零时，将共线相向成丝（CPF）诱导的空气荧光光谱与单束激光成丝（SF）结果进行比对。光谱仪的积分时间设置为 100 ms，数据累积 100 次，光谱范围为 350～710 nm，分辨率为 0.3 nm。在 400～600 nm 范围内观察到了空气分子（特别是 N_2）的指纹光谱[21]，如 N III 400.85 nm、N II 500.19 nm 和 N II 653.9 nm。通过比较光谱峰值，发现在激发脉冲总能量相同的情况下，共线相向成丝激发的荧光强度较单束光丝提高了约 4 倍。这表明使用共线相向成丝的方式能获得更高的荧光辐射强度，有利于提高探测灵敏度。

同时，实验对比了两种不同成丝方式诱导的空气荧光强度与脉冲能量的关系。如图 2（b）所示，以荧光特征谱线 N II 500.19 nm 为例，研究表明，信号强度随脉冲能量的增加而不断提高，然而不同成丝方式诱导的信号涨幅有显著差异。这样的差异性主要由以下三种变化趋势构成：当激发光能量低于 0.5 mJ 时，低能量的脉冲没有达到形成光丝的最低能量阈值，因此两种成丝方式诱导的信号强度基本相等；当能量从 0.5 mJ 持续增加到 1.0 mJ 时，激发脉冲形成光丝，荧光信号随能量的增加而增加；当能量增加到 1.8 mJ 时，光丝内部的钳制强度将抑制单光丝诱导荧光信号的强度涨幅。然而，在共线相向成丝系统内，光丝间的相互作用可突破钳制强度的限制，从而提高等离子体通道中的电子密度，使荧光信号强度迅速提升。该现象也佐证了图 2（a）中共线相向成丝能够激发更强的荧光信号强度。

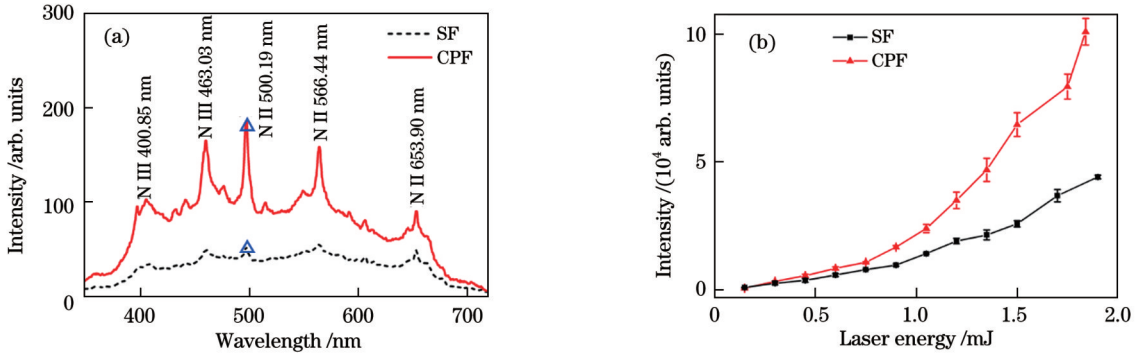

图 2 共线相向传播成丝和单束激光成丝诱导荧光信号的对比。（a）荧光光谱，三角形代表荧光线的峰值；（b）光丝诱导荧光信号强度随激光能量的变化

Fig. 2 Comparison of fluorescence signals induced by collinear counter-propagating filaments and single laser filament. (a) Fluorescence spectra in which triangle represents peak value of fluorescence line; (b) intensity of filament induced fluorescence signal versus laser energy

此外，我们还研究了光丝诱导荧光信号强度随时间的演变曲线。实验中，电荷耦合元件（CCD）传感器曝光时间设定为 0.5 s，增强电荷耦合器件（ICCD）门宽为 2 ns。为了降低激发激光的不稳定性引起的测量误差，在信号采集过程中对所有荧光谱线进行了 100 次累积。图 3 展示了 337 nm 荧光信号、427 nm 荧光信号和 481 nm 荧光信号随时间的演变及拟合曲线。结果表明，随着时间的增加，自发辐射荧光强度逐渐减小。我们将信号强度衰减到初始强度值的 1/e（约 0.368）时对应的特征时间定义为荧光衰减时间[22]。共线相向光丝激发的荧光的衰减时间（337、427、481 nm 荧光的衰减时间分别为 63、52、62 ns）比单光丝激发的荧光的衰减时间（337、427、481 nm 荧光的衰减时间分别为 42、40、47 ns）更长。需说明的是，相向成丝诱导的氮原子荧光谱线（如 N II 500.19 nm 谱线）同样表现出更长的荧光衰减时间。这意味着光丝间相互作用引起的更高峰值强度将使空气分子进一步电离，产生更多电子。等离子体通道内更多的电子将减缓电子-分子-离子的复合速率，从而延长荧光衰减时间[23]。更长的荧光衰减时间将有利于光丝诱导荧光光谱更广泛的应用。

同向传播光丝诱导荧光光谱技术（如等离子体光栅技术[17]）常受到飞秒脉冲时间重合的限制。对于相向传播的光束，两路脉冲始终满足时间重合条件。当

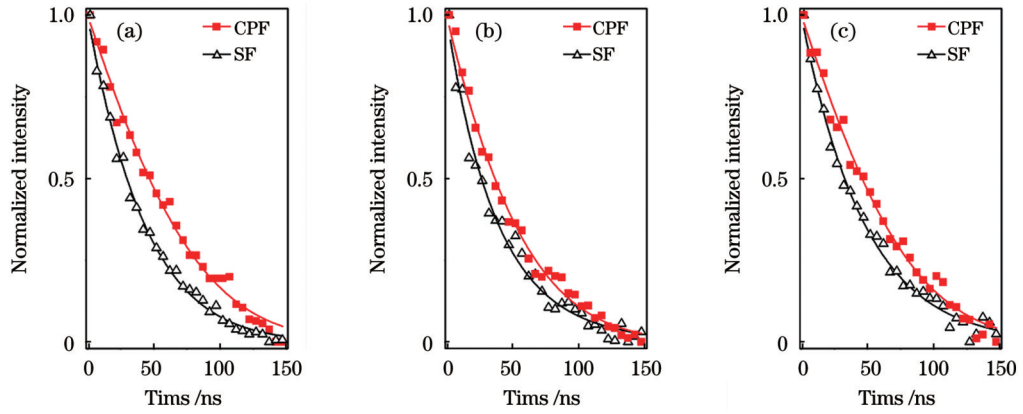

图 3　不同波长下光丝诱导荧光信号的衰减时间。(a)337 nm;(b)427 nm;(c)481 nm

Fig. 3　Attenuation time of filament induced fluorescence signals with different wavelengths. (a) 337 nm; (b) 427 nm; (c) 481 nm

然,为了实现荧光增强,需两路脉冲在各自成丝长度内相遇。图 4 展示了共线相向成丝激发的荧光信号与脉冲延时的关系。实验中,光束 1 和光束 2 间的时间延时由一维电动位移平台进行控制,电机移动步长为 0.1 mm(对应 333 fs 的时间分辨率)。正延时代表脉冲 2 在脉冲 1 前面。实验结果如图 4(a)所示,谱线强度呈高斯分布,在零延迟处达到最高。对特征峰 N III 400.85 nm 与 N II 500.19 nm 处的荧光信号强度比即 CPF 和 SF 的强度比(R)数据进行高斯拟合[图 4(b)],结果表明不同荧光特征峰信号强度比随时间延迟的变化具有一致性。当两个脉冲远离时,两个脉冲分别形成单独的光丝。当脉冲 1 和脉冲 2 在时域中相互接近时,光丝内的更多能量被转移到多光子电离或碰撞电离过程中。当两个脉冲在光丝中心处重合时,两束光丝相互作用引起的多光子电离或碰撞电离最强,因此荧光明显增强。光丝间的相互作用有利于突破光丝钳制强度的限制,进而提高等离子体密度(或电子密度)[24]和电离速度,使系统辐射更强的荧光信号。值得注意的是,图 4(b)中荧光增强区域为 −3~3 ps,该区域的时间尺度(6 ps)是激发脉冲脉宽(50 fs)的 120 倍,对应的脉冲空间传播距离为 1.8 mm,与实际观测的光丝长度一致。

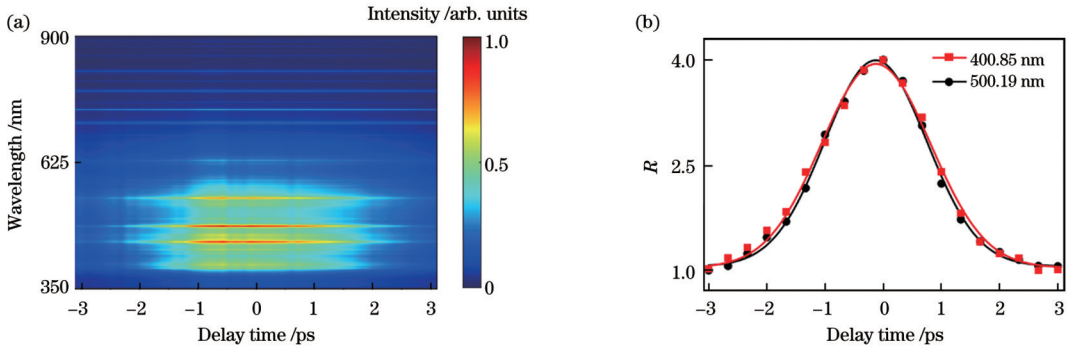

图 4　共线相向成丝激发的荧光光谱强度随时间延迟的变化。(a)350~900 nm 荧光信号强度随时间的演变;(b)特征峰 N III 400.85 nm(矩形)与 N II 500.19 nm(圆点)处的 R 随时间的演变

Fig. 4　Fluorescence signal intensity excited by CPF versus delay time. (a) Intensity of fluorescence signal versus delay time at 350–900 nm; (b) R at characteristic peaks of N III 400.85 nm (rectangle) and N II 500.19 nm (dot) versus delay time

光丝诱导荧光光谱技术在污染物检测方面具有应用价值。考虑到燃煤污染物和机动车尾气分别含有硫酸盐、硝酸盐气溶胶,因此实验利用相向光丝增强的荧光检测技术对水溶液中 KCl、Na_2SO_4、$MgSO_4$ 等盐类化合物的含量进行了测量。经过喷雾器后,样品呈雾态,利用贯穿的光丝进行检测。实验中,相向传播的两路脉冲的时间延迟为零。为减小背景连续谱线的影响,在测不同样品时采用了不同的 CCD 延时设置。KCl、Na_2SO_4 及 $MgSO_4$ 的延时分别为 50、5、5 ns。在该实验中,CCD 门宽保持不变(1 μs)。图 5(a)~(c)分别展示了 KCl、Na_2SO_4、$MgSO_4$ 质量分数为 2000×10^{-6} 时的荧光光谱,其中插图给出了 K^+,Na^+ 及 Mg^{2+} 离子的荧光特征谱线。

实验进一步验证了相向成丝诱导荧光谱线强度与物质含量的关系。实验选取特征峰 Mg II 279.6 nm,K I 769.9 nm 和 Na I 588.9 nm 处的荧光强度绘制了含量定标曲线,分别如图 6(a)、(b)、(c)所示。实验中,在同等条件下,每组实验重复测试 6 次,得到测量误差。在图 6 中,定标曲线线性拟合的决定系数(R^2)分别为 0.99(KCl)、0.98(Na_2SO_4)与 0.97($MgSO_4$),表明本文

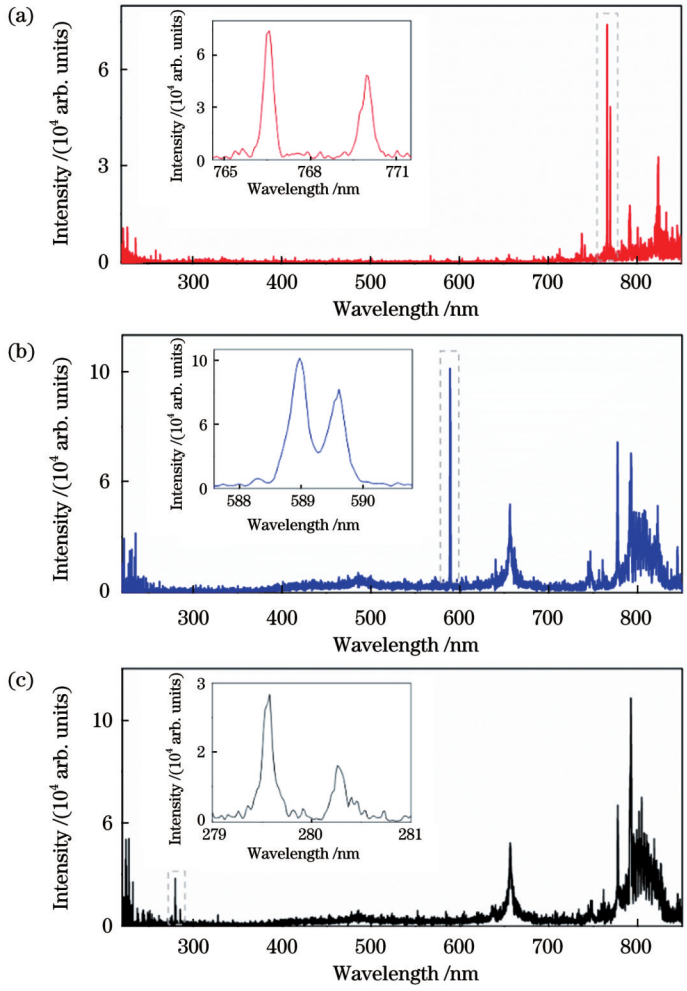

图 5　溶液质量分数为 2000×10^{-6} 时的荧光光谱。(a)KCl 溶液;(b)Na_2SO_4 溶液;(c)$MgSO_4$ 溶液

Fig. 5　Fluorescence spectra when solution mass fraction is 2000×10^{-6}. (a) KCl solution; (b) Na_2SO_4 solution; (c) $MgSO_4$ solution

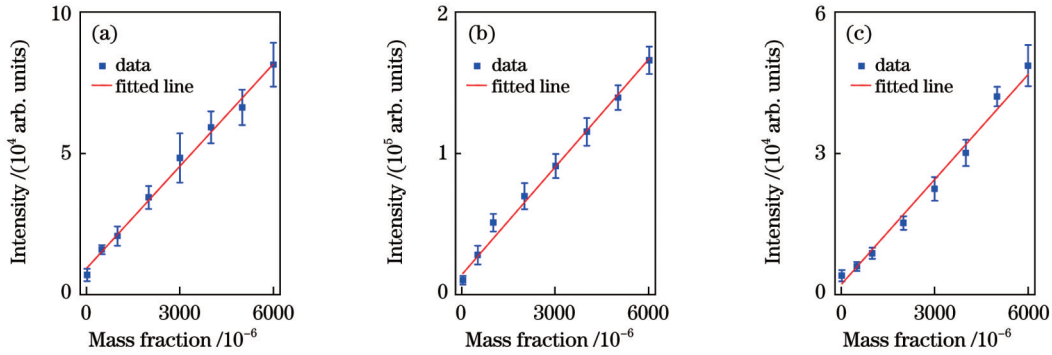

图 6　溶液质量分数与荧光强度之间的关系。(a)KCl 溶液;(b)Na_2SO_4 溶液;(c)$MgSO_4$ 溶液

Fig. 6　Relationship between solution mass fraction and fluorescence intensity. (a) KCl solution; (b) Na_2SO_4 solution; (c) $MgSO_4$ solution

方法在含量测量方面具有良好的线性度,可以在一定含量范围内对化合物样品进行定量分析。

此外,实验表明:当积分时间为 50 s 时,系统灵敏度即噪声等效质量分数为 9.3×10^{-6}(KCl)、4.3×10^{-6}(Na_2SO_4)及 16.7×10^{-6}($MgSO_4$)。该结果主要受限于激发脉冲能量。即便如此,该结果较单束光丝诱导荧光检测灵敏度(相同样品下)提高了约 4 倍,表明了相向成丝诱导荧光光谱方法在微量化合物检测中的优势。

4　结　　论

利用两束共线相向传播的光丝实现了荧光信号的增强。在相同脉冲能量下,双束光丝激发的荧光强度较单束光丝增强了 4 倍。相较于常见的同向传播光丝诱导荧光增强技术,所提方法对两路激发脉冲的延时控制要求较为宽松。更重要的是,该方法能够有效提

高化合物中金属离子的检测灵敏度,且具有良好的线性度,为微量污染物检测等提供了新的途径。

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Research on Detection Technology of Fluorescence Enhanced Spectroscopy Based on Counter-Propagating Filaments

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Abstract

Objective Laser-induced fluorescence spectroscopy (LIFS) is a novel spectroscopic technique with several advantages, such as multi-elemental simultaneous detection, rapid response, and real-time online monitoring; hence, it is a powerful tool for remote sensing. However, single-beam laser filamentation remains limited, including the limitation of fluorescence signal intensity and detection sensitivity owing to the influence of intensity clamping. Several methods have been proposed to address these problems. For

instance, the fluorescence signal can be enhanced by the interaction between two or more filaments, which is crucial in improving the sensitivity of substance detection. Previous studies about the interactions between co-propagation filaments often adopted multiple femtosecond pulses to form plasma gratings in the medium and increase the fluorescence signal intensity. However, such methods rely on the spatial interference effect of an ultrafast light field. They have high requirements for parameters such as the excitation beam's spatial angle and pulse delay. To circumvent the aforementioned problems, we study the interaction mechanism of collinear counter-propagating filaments and their influence on fluorescence properties. Experiment results demonstrate that although its enhancement effect on fluorescence can be comparable to that of the co-propagating filament, it is almost not affected by the laser polarization. Applying this technology to the spectroscopic detection of metal ions in compounds is expected to provide a novel approach to detecting trace contaminants by studying the linear relationship between characteristic spectral intensity and substance concentration.

Methods We establish a collinear counter-propagating filaments (CPF) system, which comprises two collinear beams propagating in the opposite direction and focusing on the same focus through a lens, thereby forming two spatially overlapping counter-propagating filaments near the focus. We make precise adjustments using the electronic translation platform to better control the relative pulse delay of the two light beams. The atomized sample interacts with the filaments to excite the fingerprint fluorescence and the fingerprint fluorescence is transmitted to a spectrometer using an optical fiber. In addition, we configure brine solution samples of KCl, Na_2SO_4, and $MgSO_4$ with different mass fractions to establish calibration curves and analyze the detection sensitivity of this system.

Results and Discussions First, we compare the signal intensities induced by the CPF and single filament (SF) under the same total excitation pulse energy and successfully obtain an enhancement factor of approximately 4. Furthermore, we compare the relationship between the intensity of induced fluorescence and the pulse energy of the two filamentation systems. When the laser energy increases from 0.5 mJ to 1.5 mJ, the increase in the CPF excited signal is significantly higher than the increase in the SF excited signal; this indicates that the collinear counter-propagating filaments can obtain higher fluorescence intensity. In addition, we study the evolution of fluorescence signal intensity with time and infer that the filament interaction will prolong the fluorescence decay time of excited molecules. Simultaneously, by changing the relative pulse delay of the two lasers, fluorescence enhancement can be observed in the pulse delay range of -3–3 ps, with an excitation pulse width of 50 fs. Finally, we obtain the detection sensitivity of CPF by establishing the calibration curve of metal ions (K^+, Na^+, and Mg^{2+}) in the brine solution. The experiment result demonstrates that the detection sensitivities of K^+, Na^+, and Mg^{2+} are 9.3×10^{-6}, 4.3×10^{-6}, and 16.7×10^{-6}, respectively, and their corresponding determination coefficients of the calibration curves are 0.99 (KCl), 0.98 (Na_2SO_4), and 0.97 ($MgSO_4$), respectively; this implies that the method adopted in this study exhibits optimal linearity in concentration measurement and can be utilized for the quantitative analysis of compound samples within a specific concentration range.

Conclusions This study introduces a fluorescence spectroscopy detection technique induced by collinear propagation filaments. The interaction of counter-propagating filaments prolongs the fluorescence decay time of excited state molecules and enhances fluorescence signals. The fluorescence intensity excited by counter-propagating filaments is 4 times stronger than the fluorescence intensity excited by the single filament under the same pulse energy. Compared with the co-propagation filament-induced fluorescence enhancement technology, the proposed method has loose requirements for the delay control of the two excitation pulses. More importantly, this method can effectively improve the detection sensitivity of metal ions in compounds and exhibits optimal linearity; hence, it provides a novel approach to detecting trace contaminants and other applications.

Key words spectroscopy; filament; fluorescence spectrum; femtosecond laser