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※封面论文※

# 基于可调谐二极管激光吸收光谱技术的烟气氨逃逸检测研究及应用(特邀)

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**摘 要:** 烟气氨逃逸是许多大型能源转化设备脱硝系统都存在的问题, 大量的氨逃逸不仅威胁机组运行, 增加系统维护成本, 而且还会形成二次污染, 危害大气环境和人体健康, 因此, 必须对氨逃逸进行实时监测和有效控制。可调谐二极管激光吸收光谱技术是一种先进的痕量气体检测技术, 具有灵敏度高、选择性强、可实时在线测量等优点, 广泛应用于各种污染气体检测领域, 并且已经成为当前烟气氨逃逸在线检测的主流技术。本文介绍了可调谐二极管激光吸收光谱技术的基本原理, 总结了氨逃逸的常用检测方式, 综述了可调谐二极管激光吸收光谱技术在烟气氨逃逸检测方面的研究和应用进展, 并对未来的发展应用进行了展望。

**关键词:** 可调谐二极管激光吸收光谱; 氨逃逸; 浓度; 检测限; 灵敏度

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## 0 引言

$\text{NO}_x$  是一种常见的大气污染物, 大气中  $\text{NO}_x$  主要来自煤、石油、天然气等化石燃料的燃烧, 大型能源转化设备和机动车尾气是  $\text{NO}_x$  的主要排放源。为降低  $\text{NO}_x$  排放, 我国相继颁布各种法规对  $\text{NO}_x$  排放值进行限制。目前烟气脱硝是大型能源转化设备控制  $\text{NO}_x$  排放的重要手段<sup>[1]</sup>, 主要包括: 选择性非催化还原(Selective Noncatalytic Reduction, SNCR)技术、选择性催化还原(Selective Catalytic Reduction, SCR)技术以及 SNCR/SCR 混合脱硝技术。其中, SCR 技术因具有脱硝效率高(可达 80%~90%)<sup>[2]</sup>、对机组影响小、系统全自动控制、设备安装维护方便等优点, 成为目前应用最广泛、最成熟的烟气脱硝技术。氨是 SCR 技术的常用还原剂, 喷入过量的氨虽然可以提高脱硝效率, 使  $\text{NO}_x$  满足排放要求, 但是容易造成氨逃逸, 从而引起以下几个突出问题: 1) 造成  $\text{NH}_3$  资源浪费; 2)  $\text{NH}_3$  容易腐蚀催化剂, 缩短催化剂寿命; 3)  $\text{NH}_3$  还会与烟气中的  $\text{SO}_3$  反应生成  $\text{NH}_4\text{HSO}_4$ ,  $\text{NH}_4\text{HSO}_4$  具有一定粘滞性和腐蚀性, 致使尾部烟道空预器堵塞和引风机腐蚀, 影响机组运行的安全性和经济性; 4) 逃逸的  $\text{NH}_3$  进入大气、吸附在飞灰中将造成环境污染。由此可见, 一味增加喷氨量的粗放型喷氨方式存在显著弊端, 只有通过精确测量氨逃逸率并自动控制喷氨量, 才能有效降低氨逃逸。因此, 在线精确测量氨逃逸率对掌握 SCR 系统的运行效率、实现精细喷氨、提高机组运行稳定性、减少环境污染具有重要意义。

目前用于烟气氨逃逸检测的方法主要包括离线检测和在线检测两种<sup>[3-4]</sup>。离线检测方法有: 靛酚蓝-水杨酸比色法、纳氏比色法、离子色谱法、离子选择电极法等; 在线检测方法包含化学发光法<sup>[5]</sup>、光谱法等, 已经有多种光谱技术被应用于  $\text{NH}_3$  测量, 如: 腔衰荡光谱(Cavity Ring Down Spectroscopy, CRDS)技术<sup>[6]</sup>、差分吸收光谱(Differential Optical Absorption Spectroscopy, DOAS)技术<sup>[7]</sup>、光声光谱(Photo-Acoustic Spectroscopy, PAS)技术<sup>[8]</sup>、可调谐二极管激光吸收光谱(Tunable Diode Laser Absorption Spectroscopy, TDLAS)技术等。

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与其他光谱技术相比, TDLAS 技术因具有选择性强、灵敏度高、成本低等突出优点, 已经广泛应用于工业现场, 成为当前氨逃逸率在线测量的主流技术。TDLAS 是一种具有高灵敏度的激光光谱检测技术, 通过调谐二极管激光器的温度或电流改变激光波长, 扫描目标分子的吸收线, 获得与吸收强度有关的吸收光谱信号, 从而计算介质浓度、温度、压强等参数。TDLAS 技术可以测量气体、液体等不同介质<sup>[9]</sup>, 其中气体检测方面的研究和应用较多。TDLAS 技术的缺点是影响因素复杂, 存在背景干扰, 且二极管激光器的调谐范围较小, 限制了多组分同步测量。随着可调谐二极管激光器生产技术的成熟化和商业化, TDLAS 检测技术得到了充分发展和应用。

本文主要介绍了 TDLAS 技术的原理, 概括了 NH<sub>3</sub> 检测常用的谱线范围和四种氨逃逸检测方式, 对近年来 TDLAS 技术在烟气氨逃逸检测方面的研究和应用进行了综述, 最后对 TDLAS 技术在氨逃逸检测方面的发展进行了展望。

## 1 TDLAS 技术

### 1.1 TDLAS 原理

根据 Beer-Lambert 定律<sup>[10]</sup>, 当一束频率为  $\nu$ 、初始光强为  $I_0$  的激光穿过某气体介质时, 由于气体分子的吸收, 出射光强  $I(\nu)$  可以表示

$$I(\nu) = I_0 \exp[-S(T)\Phi(\nu)PXL] \quad (1)$$

式中,  $S(T)$  表示气体特征谱线的强度, 单位为  $\text{cm}^{-2}\text{atm}^{-1}$ ;  $\Phi(\nu)$  表示吸收谱线的线型函数, 单位为  $\text{cm}$ ;  $P$  表示气体的总压强, 单位为  $(1 \text{ atm} = 101\,325 \text{ Pa})$ ;  $X$  表示待测气体的体积浓度;  $L$  表示激光在气体介质中的传输距离, 单位为  $\text{cm}$ 。在其他物理量已知的情况下, 根据光强的变化即可计算出浓度信息。TDLAS 技术主要包括直接吸收光谱 (Direct Absorption Spectroscopy, DAS) 技术和调制光谱技术, 其中调制光谱技术又包含波长调制光谱 (Wavelength Modulation Spectroscopy, WMS) 技术和频率调制光谱 (Frequency Modulation Spectroscopy, FMS) 技术。

DAS 技术是指对激光器的电流加载一个频率较低的扫描信号, 周期性调谐激光波长, 获得气体吸收随波长变化的吸收光谱<sup>[11]</sup>。DAS 技术的优点是装置简单、操作方便, 缺点在于容易受低频噪声干扰, 探测灵敏度有限。DAS 技术经常用于气体浓度、温度、压强等参数测量中。通过对探测的光强信号进行线型函数拟合, 根据积分吸光度可以直接计算气体浓度, 由于光强信号容易受  $1/f$  噪声的干扰, 导致出现基线偏移和拟合残差等问题, 从而造成气体浓度计算误差较大。为了降低  $1/f$  噪声的干扰, 有科研人员提出将调制技术与可调谐激光器结合, 发展了调制光谱技术。WMS 技术的调制频率远小于吸收谱线线宽, 通常在几 kHz 到几十 kHz 之间。对光强信号进行高频调制的同时, 吸收信号也会受到调制, 而  $1/f$  噪声未经过调制, 在高频下进行解调便可以去除  $1/f$  噪声的干扰<sup>[12-13]</sup>。比 WMS 技术调制频率更高的是 FMS 技术, 调制频率可以达到上百 MHz 或 GHz, 由于激光调制频率较高, 噪声可降到散粒噪声极限, 极大提高了吸收光谱的测量灵敏度, 逐渐被应用于激光稳频、瞬态分子弱吸收探测等领域<sup>[14]</sup>。

### 1.2 谱线选择

NH<sub>3</sub> 的吸收谱线分布较广, 从近红外到中红外都有分布, 图 1 表示  $0.5 \sim 10 \mu\text{m}$  之间 NH<sub>3</sub> 以及大型能源转

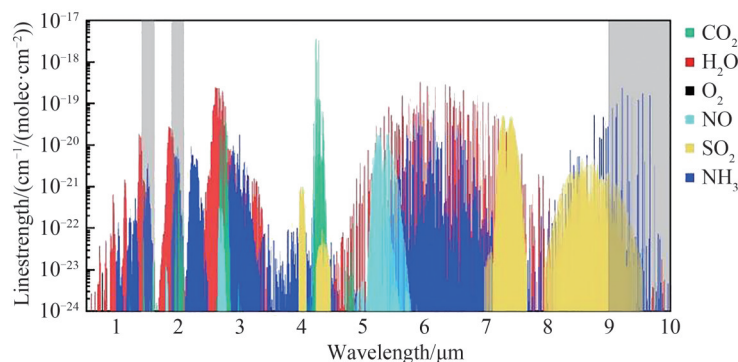


图 1 NH<sub>3</sub> 和烟气主要成分的吸收谱线分布 (来源于 HITRAN 数据库)

Fig. 1 Absorption spectrum distribution of NH<sub>3</sub> and main components of flue gas (from HITRAN database)

化设备烟气主要成分的吸收谱线分布情况。目前国内外基于TDLAS技术检测NH<sub>3</sub>的常用波段主要集中在1.5 μm、2 μm以及9~10 μm附近,如图1中阴影部分所示,在此波段范围内,干扰组分较少,且NH<sub>3</sub>谱线强度明显高于其他组分。尤其是9~10 μm波段,由于基频吸收带的吸收线强度大于泛频带,9~10 μm附近的吸收线强度比泛频带高1~2个数量级,因此,利用9~10 μm波长的光源进行测量可以获得更高的探测灵敏度。在实际测量中,需进一步筛选无重叠干扰的NH<sub>3</sub>谱线。

### 1.3 检测方式

NH<sub>3</sub>的物理化学性质独特,同时烟道内环境复杂,为在线测量氨逃逸率增加了难度,氨逃逸检测的难点具体表现为:1)NH<sub>3</sub>易溶于水,在常温下具有较强的吸附性,且烟道中水汽含量较高,大量的溶解和吸附将导致NH<sub>3</sub>浓度严重偏离真实值,因此氨逃逸检测不宜在常温下进行;2)当温度低于230℃时,烟气中的NH<sub>3</sub>和SO<sub>3</sub>容易反应生成NH<sub>4</sub>HSO<sub>4</sub>,同样造成氨损失;3)烟气中夹杂粉尘颗粒物,特别是燃煤电站,国内燃煤电站锅炉的含尘量可达数十克每立方米,对氨逃逸在线检测产生严重干扰;4)SCR脱硝出口的氨逃逸分布不均匀,单点测量无法准确反映烟道内氨逃逸分布情况;5)《火电厂烟气脱硝技术导则》规定,SCR脱硝设备的氨逃逸率应小于2.3 mg/m<sup>3</sup>(3 ppm, 1 ppm=1×10<sup>-6</sup>)<sup>[15]</sup>。综上,复杂的测量环境和严格的排放限值对氨逃逸在线检测设备的抗干扰能力、稳定性、检测限和灵敏度都提出了较高的要求。根据应用需求,科研工作者开发了不同的氨逃逸检测方式,目前主要包括四种:原位对穿式、传统取样式、渗透管式和原位取样式。

#### 1.3.1 原位对穿式

原位对穿式是指激光发射单元和接收单元分别安装在烟道两侧(或对角),如图2所示。激光直接穿过烟道进行探测。原位对穿式系统简单,无需烟气取样、传输系统,并且直接在烟道内测量,烟气组分未发生变化,测量结果可以反映实际NH<sub>3</sub>浓度。然而,该方法具有比较大的局限性:1)烟道内部粉尘含量较高,使激光强度衰减严重;2)启停机时烟道变形会使光路发生偏移,且机组运行时产生较大振动也会影响光路稳定性;3)烟道内环境恶劣,光谱信号的信噪比和测量精度较低;4)在线标定困难。

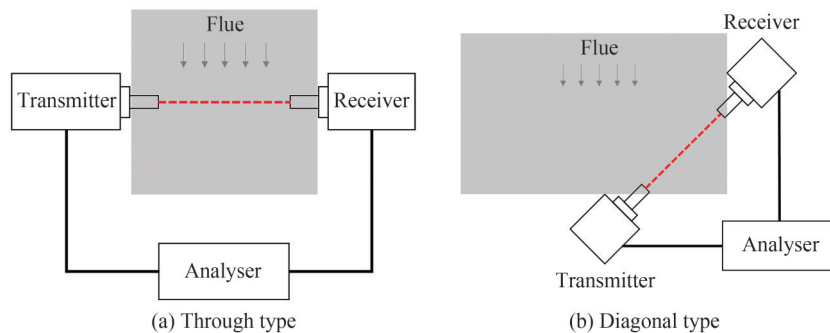


图2 原位对穿式示意图

Fig. 2 Schematic diagram of in-situ measurement type

#### 1.3.2 传统取样式

与烟气连续排放监测系统(Continuous Emission Monitoring System, CEMS)的测量方式相同,氨逃逸测量也可采用传统取样式,即利用取样装置将烟气抽取到外部分析单元进行测量,整套系统由取样枪、预处理单元、高温伴热管线、分析单元等几部分组成,如图3所示。与原位对穿式相比,取样测量在气体进入分析单元前,可以通过过滤等预处理手段降低颗粒物对NH<sub>3</sub>测量的影响。而且分析单元位于烟道外部,测量环境稳定,可以获得高信噪比的光谱信号,易实现在线标定。对于氨逃逸测量而言,传统取样式的缺点在于:1)取样、预处理、伴热等工序增加了系统的复杂性;2)NH<sub>3</sub>具有吸附性,容易附着到气路管线和吸收池内壁上,造成测量值偏小;3)虽然高温伴热可以降低NH<sub>3</sub>吸附,但是伴热管线的温度通常只有200℃左右,低于烟道温度(350℃),易在管线内部反应生成NH<sub>4</sub>HSO<sub>4</sub>,引起氨损失;4)烟气经过长距离传输会产生一定测量延时。综上,多重因素导致传统取样式测量的氨逃逸结果不具代表性,难以实时反映烟道真实值。

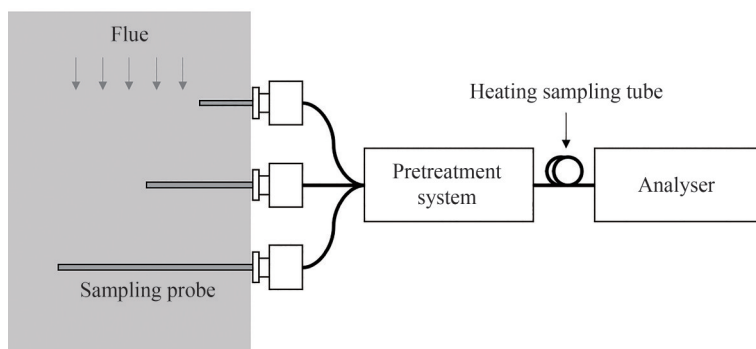


图3 传统取样式示意图

Fig. 3 Schematic diagram of traditional sampling type

吸收池作为取样测量方式的关键部件,直接影响氨逃逸率的测量精度。根据 Beer-Lambert 定律可知,当目标气体的浓度、温度、压强等参数一定时,光程越长,吸光度越大,因此,增加吸收光程可以有效提升探测灵敏度。为了在有限的分析单元中增加光程,人们利用多次反射原理设计了各种长光程多通吸收池,如 White 型<sup>[16]</sup>、Herriott 型<sup>[17]</sup>、Chernin 型<sup>[18]</sup>及环型<sup>[19]</sup>吸收池等,四种吸收池的结构如图 4 所示,四种吸收池优缺点如表 1 所示。

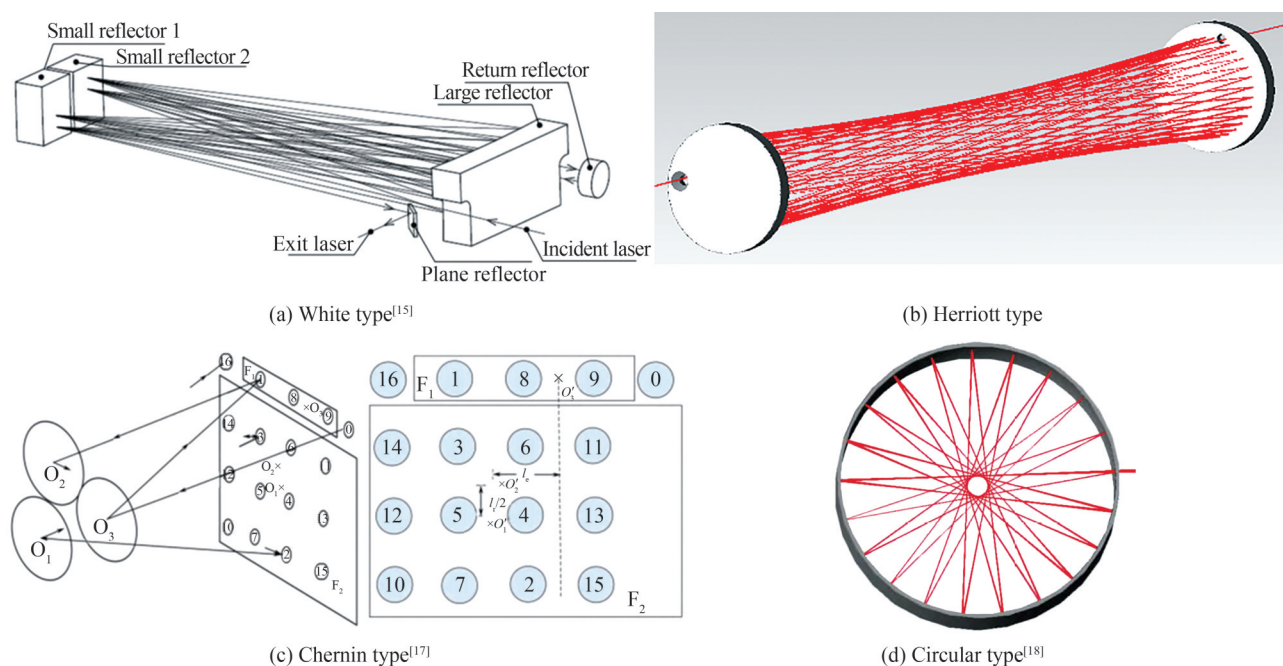


图4 四种吸收池的结构示意图

Fig. 4 Schematic diagram of the structure of the four absorption cells

光学多通池一直是吸收光谱领域研究的重点,近年来,随着激光光谱传感器逐步趋于小型化、便携化,小体积、长光程、高稳定性的多通池成为当前吸收池的研究热点。KRZEMPEK K 等<sup>[20]</sup>设计了一种紧凑的球形多通池,激光在相距 12.5 cm 的两反射镜之间反射 459 次,有效光程达到 57.6 m。CUI R 等<sup>[21]</sup>在传统 Herriott 基础上,提出一种由两个相同球面镜组成的密集光斑多通池计算模型,用高填充系数获得的奇异光斑提高了镜面的利用率,以较低的镜面成本实现了较长的光程。LIU K 等<sup>[22]</sup>基于两块镀银凹面镜开发了一种经济、稳定的紧凑密集型多通池,有效光程为 26.4 m,体积仅 280 mL。吴飞龙等<sup>[19]</sup>根据环型吸收池提出一种由多个圆环形凹面反射镜螺旋封闭构成的紧凑型多通池,入射光在多通池内部呈有规律放射性分布,反射次数可调节。许棕等<sup>[23]</sup>提出一种新型平面镜光学多通池设计方案,由两个平面镜和两个透镜组成,与传统的 White 池与 Herriott 池相比,该多通池有效光程数与体积比更大,空间利用率更高。

表 1 四种吸收池优缺点对比

Table 1 Comparison of the advantages and disadvantages of four types of absorption cells

Absorption cell type	Advantages	Disadvantages
White type	1) Large aperture angle, suitable for general and laser light sources; 2) Adjustable light path	1) More reflectors used (3 pieces); 2) Insufficient use of mirrors
Herriott type	1) Simple structure; 2) Easy adjustment of light path	1) light path fixation; 2) Insufficient use of mirrors; 3) Smaller aperture angle, suitable for laser light sources only
Chernin type	1) Large aperture angle, suitable for general and laser light sources; 2) Adjustable light path; 3) Fuller use of mirrors	1) More reflectors used (5 pieces); 2) Structural complexity; 3) Larger volume
Circular type	1) Smaller size and compactness; 2) Adjustable light path; 3) Easy adjustment of light path	1) More difficult to process

### 1.3.3 渗透管式

为了克服烟道内部的恶劣环境,在原位对穿式的基础上,科研人员提出了渗透管式测量方法<sup>[24]</sup>,即在光路外侧增加陶瓷渗透管,烟气在压差作用下进入渗透管,在渗透管内部与激光相互作用,如图5所示。渗透管通常选择微孔陶瓷材料,该材料具有良好的透气性、耐腐蚀性,可有效流通气体和过滤粉尘,避免了粉尘的消光作用,提高测量精度。同时,激光发射和接收单元固定于渗透管两侧或同侧,克服了原位对穿式光路稳定性差的弊端。渗透管测量也具有一定缺点:1)微孔陶瓷对NH<sub>3</sub>有吸附作用,且吸附和解析量与温度有关,导致测量值不能反映烟道真实值;2)微孔陶瓷表面容易被粉尘堵塞,工作一段时间后,烟气更新速度会变慢甚至完全无法进入管渗透内,需频繁维护。

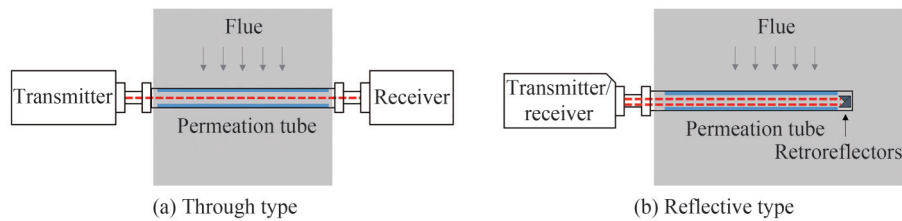


图 5 渗透管式示意图

Fig. 5 Schematic diagram of permeation tube type

### 1.3.4 原位取样式

为了进一步提高烟气氨逃逸测量的准确性,在前三种测量方式的基础上,科研人员提出一种结合原位和取样测量优点的检测方式:原位取样式,如图6所示。原位取样式是指吸收池位于取样探头内部,激光与烟气的相互作用在烟道内部进行,吸收池内部温度与烟道基本一致,无需伴热,减少了吸附和化学反应造成的氨损失。烟气通过气泵抽取进入吸收池,然后回注烟道,气体更新速度快,响应时间短。烟气入口安装有过滤器,可以有效过滤粉尘。同时吸收池可根据需求设计成不同的光程来满足探测精度。这种测量方式的难点在于:烟道内部长期高温、高粉尘,对取样探头、光学吸收池的材料选择和结构设计具有较高的要求。

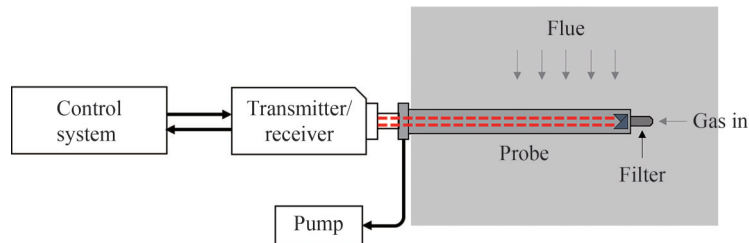


图 6 取样测量式示意图

Fig. 6 Schematic diagram of sampling measurement type

## 2 烟气氨逃逸检测研究进展

### 2.1 烟气氨逃逸检测研究现状

根据应用需求,科研人员对不同检测方式的氨逃逸分别进行了研究,下文对不同检测方式的研究现状做了详细介绍。

原位测量方式系统简单,无需考虑 $\text{NH}_3$ 的吸附性,目前大型火电机组脱硝氨逃逸在线监测大多采用原位测量式<sup>[25]</sup>,但是其受烟道工况影响较大,测量精度有限,且不适用于含尘量高的环境。为提高原位测量的准确性,科研人员进行了深入研究。何莹等<sup>[26]</sup>选择 $\text{NH}_3$ 位于 $1.53\ \mu\text{m}$ 处的吸收线为目标谱线,采用TDLAS结合波长快速扫描技术,基于反射式开放光路测量系统,对高温烟气氨逃逸进行了原位测量,并设计了烟道氨浓度免标定反演算法,系统最大相对误差为1.5%。YU L等<sup>[27]</sup>选择 $2.25\ \mu\text{m}$ 的DFB激光器作光源,通过校正烟气温度进而修正 $\text{NH}_3$ 浓度,在 $200^\circ\text{C}$ 时, $\text{NH}_3$ 浓度相对误差从67.53%下降到3.33%,有效提高测量准确度;对嘉兴新嘉爱斯电厂某动力装置SCR氨逃逸进行了原位在线测量,可以反映该动力装置氨逃逸率的实时情况。唐忠华等<sup>[28]</sup>利用原位氨逃逸分析仪测量了中国石油某石化公司热电厂的烟气氨逃逸率,结果表明,氨逃逸浓度与 $\text{NO}_x$ 浓度具有明显相关性。

国内燃煤电站烟道含尘量较高,对于原位对穿式而言,严重影响其激光传输和氨逃逸率测量精度。相比之下,传统取样式具有稳定的测量环境,可获得高信噪比的光谱信号,不少科研人员对传统取样式进行了相关的研究。GUO X Q等<sup>[29]</sup>开发了一种近红外便携式 $\text{NH}_3$ 传感器,如图7(a)所示,使用中心波长 $1.515\ \mu\text{m}$

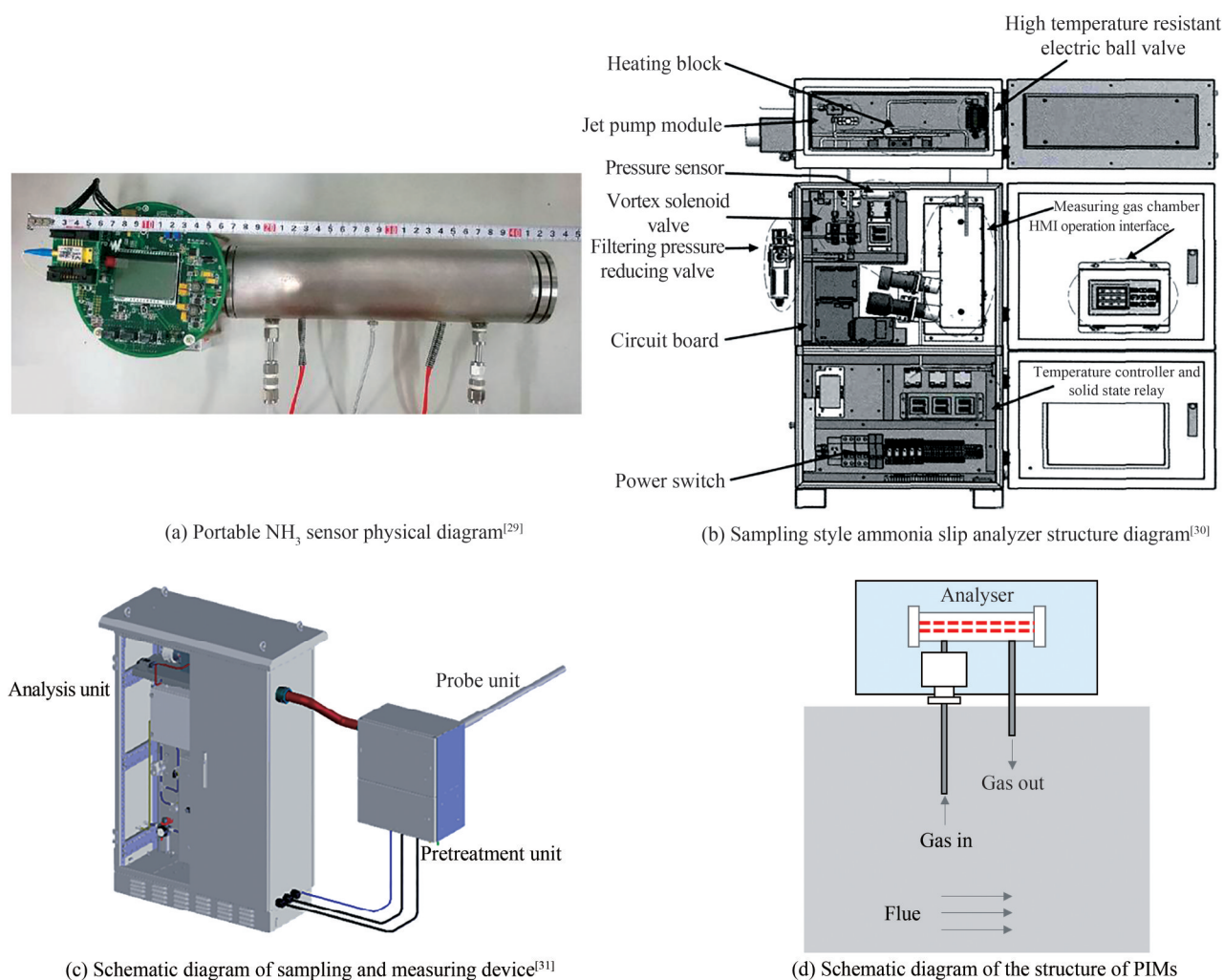


图7 取样测量装置示意图  
Fig. 7 Schematic diagram of sampling and measuring device

的DFB激光器作光源,结合有效光程15 m且带温控的Herriott型多通池进行测量,该传感器的物理尺寸为43 cm×18 cm×16 cm;在温度为415 K、积分时间184 s内,NH<sub>3</sub>的最低检测限可达0.16 ppm,系统动态响应上升和下降时间分别为4.5 s和3.7 s,利用该传感器对西山煤电集团煤气化焦炉烟气进行实时测量,经SCR脱硝处理后的烟气中NH<sub>3</sub>浓度为约10 ppm,1小时内的波动范围在3 ppm以内。张涵等<sup>[30]</sup>研制了一套抽取式氨逃逸分析仪,装置示意图如图7(b)所示,选择NH<sub>3</sub>位于1 512.2 nm处的吸收谱线,采用WMS技术结合多次反射吸收池(高温加热)进行测量;实验室测量该仪器性能指标如下:线性度≤±1% F.S,重复性指标≤1%,检测限为0.38 ppm,对某水泥厂SCR出口的氨逃逸浓度进行连续监测,可以准确反映氨逃逸浓度的变化。JIAN W等<sup>[31]</sup>利用离轴集成腔输出光谱(Integrated Cavity Output Spectroscopy, ICOS)和TDLAS技术,测量了低至0.1 ppm的NH<sub>3</sub>浓度;通过管道伴热,解决了测量过程中微量NH<sub>3</sub>采样丢失的问题,如图7(c)所示。苗丰等<sup>[32]</sup>研制了一套便携式氨逃逸分析仪,分别进行了实验室和现场测试,全程高温伴热取样,保证烟气取样的真实性,系统的响应速度小于70 s,测量准确度优于2%,与标准方法的最大偏差小于5%。郑利武<sup>[33]</sup>、张进伟<sup>[34]</sup>、李阳山等<sup>[35]</sup>介绍了聚光科技LGA-4500氨逃逸在线分析系统,采用精细过滤采样和大流量引流技术进行不失真取样,系统量程为 $3.5\times 10^{-5}$ ,探测下限为0.019 6 ppm,系统可靠性高,维护方便,目前已经在国电兰州热电有限公司、锦州热电有限公司等单位进行了现场应用,证明了该系统的稳定性和可靠性。

为解决单一取样不具有代表性的问题,在取样测量的基础上,逐渐发展出一种多点取样的测量方式。多点位数据可以反映烟道截面不同区域的氨逃逸率,有利于全面分析脱硝运行状态,对脱硝优化运行更具指导意义。孟林辉等<sup>[36]</sup>设计了多点抽取式氨逃逸在线分析模型,在实验室和现场都进行了测试,结果表明,该系统可以实现不同区域0~10 ppm的氨逃逸精确测量。杨剑等<sup>[37]</sup>开发了一套近红外氨逃逸多点在线监测系统,系统准确度在±0.2 ppm之间,量程漂移小于2.0% F.S/24 h,可以实现烟气氨逃逸的快速、准确和多点测量。吴世民<sup>[38]</sup>、吴晔等<sup>[39]</sup>介绍了一种伪原位监测(Pseudo In-Situ Measurement system, PIMs)的多点氨逃逸在线监测方案,装置图示意如图7(d)所示。PIMs集成高温采样、光学组件于一体,直接安装于烟道上,省略了传统的采样管线,烟气被直接抽取到高温吸收池并回注烟道,形式和功能上近似于原位检测;且PIMs系统可以进行多点测量,通过对大唐王滩电厂600 MW机组SCR脱硝系统进行在线检测优化,SCR出口氨逃逸均值从9.41 ppm下降到2.72 ppm。

取样测量分析仪内部吸收池的光学稳定性直接影响系统的整体性能,单次吸收池虽然稳定性好,但是吸收光程短,难以对痕量NH<sub>3</sub>进行高灵敏检测。与单次吸收池相比,多次反射的吸收池可以有效拓展光程,提高测量精度,缺点是其稳定性较差,微小的角度、位置移动都会对光路结构造成较大影响;而且对窗片的污染较敏感,反射镜微小的污染会导致光强迅速衰减。因此,开发适用于脱硝现场的吸收池对氨逃逸准确检测具有重要意义。为避免多次反射吸收池的缺点,阎杰等<sup>[40]</sup>设计了长度1.2 m的加长单次吸收池用于氨逃逸测量,可以达到亚ppm量级的灵敏度,经过现场连续运行,设备零点漂移在±0.4 ppm以内,长期稳定性较好。张增福等<sup>[41, 42]</sup>对比测试了White型和Herriott型两种吸收池对NH<sub>3</sub>测量的优缺点,实验中两种吸收池的最低检测限分别为1.21 ppm和1.61 ppm,虽然Herriott吸收池的噪声更大,但是其镜片少,易于安装,更适用于工业现场测量。同时,为克服烟道取样高温、高粉尘及测量滞后等问题,张增福设计了新型的Herriott吸收池,如图8(a)所示,采用中空光路、气路带加热等结构设计,吸收池容积减小近2倍,有效改善了系统响应时间,通过实验测试,该系统的最低检测限为0.22 ppm,可以满足烟气氨逃逸的测量要求。PANELLA B等<sup>[43]</sup>设计了一种适用于现场氨逃逸测量的Herriott吸收池,如图8(b)所示,为了降低NH<sub>3</sub>的吸附效应,吸收池在

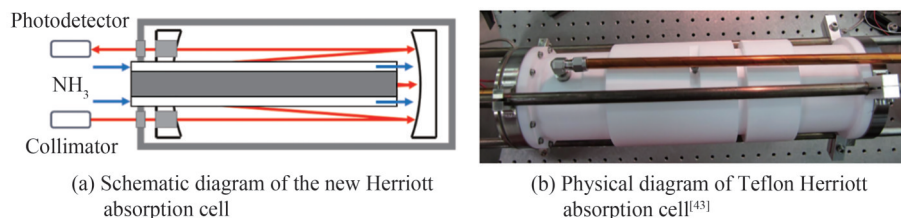


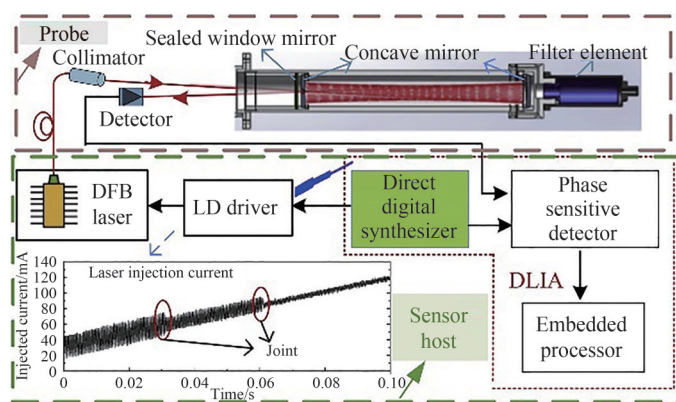
图8 吸收池示意图和实物图

Fig. 8 Schematic and physical diagram of the absorption cell

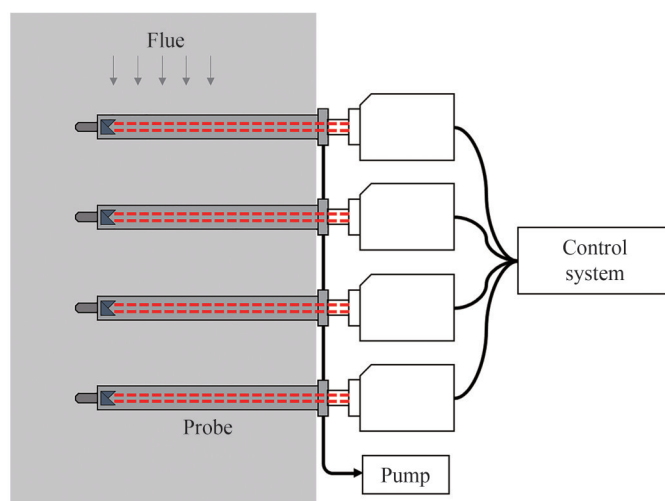
180℃下均匀加热,并且吸收池采用低吸附系数的特氟龙材料,通过CFD模拟和实际测量对比,表明该吸收池的防吸附效果良好;并且特氟龙壳体具有柔性结构,加热过程仍然可以保持良好的气密性。

通过调研发现,渗透管式的氨逃逸分析仪极少<sup>[25]</sup>,说明此方式应用范围比较有限。周佩丽等<sup>[24]</sup>为改善渗透管式的实用性,利用CFD数值模拟进行了烟气流场模拟,并在此基础上研制了原位渗透式预处理装置,通过现场与便携式分析仪进行对比,测量结果一致,误差小于2%,证明了装置的可靠性。

为进一步提高烟气氨逃逸测量的准确度,降低系统复杂性,有科研人员综合考虑TDLAS的技术特点和氨逃逸特性,将原位取样式应用于氨逃逸测量,经过实验室和现场测试,证明了这种方法的可行性。LI等<sup>[44]</sup>设计了一种多功能便携式氨逃逸检测仪,装置原理图如图9(a)所示,可以同时测量氨逃逸率、水蒸汽浓度和烟气温度的,采用的光源为中心波长1.512 μm的DFB激光器,在测量NH<sub>3</sub>浓度的同时,利用两条H<sub>2</sub>O的吸收线(6 612.02和6 609.85 cm<sup>-1</sup>)获得烟气温度和H<sub>2</sub>O浓度;通过实验室验证,该传感器对NH<sub>3</sub>浓度、H<sub>2</sub>O浓度和烟气温度的测量精度分别为5.1%、4.8%和2.9%,在5s的积分时间内对NH<sub>3</sub>和H<sub>2</sub>O浓度的测量灵敏度分别为0.1 ppm和300 ppm,最后在某燃煤电厂进行了现场测试,SCR反应器前后NH<sub>3</sub>浓度分别约为71 ppm和3 ppm。JI Y等<sup>[45]</sup>同样开发了一种可同时测量氨逃逸率、水蒸汽浓度和烟气温度的中红外激光吸收传感器,该传感器使用QCL激光器以1 103.45 cm<sup>-1</sup>的NH<sub>3</sub>吸收线为目标,并利用4 029.52 cm<sup>-1</sup>和4 029.78 cm<sup>-1</sup>的谱线对测量H<sub>2</sub>O的浓度和温度;采用时分复用(TDM)方案实现了DAS技术对水和温度的测量、免校准波长调制光谱(CF-WMS)技术对NH<sub>3</sub>浓度的测量,经过实验验证,在100 s的积分时间内,NH<sub>3</sub>检测限可达7 ppb。郝志国等<sup>[46]</sup>研发出单端插入原位取样式的SCR氨逃逸分析系统(AEMS10),灵敏度达到0.1 ppm,通过现场连续运行证明了系统可靠性。杨松等<sup>[47]</sup>针对原位取样探头中角锥反射镜易引起光束干涉、易受机械振动等



(a) Portable ammonia slip detector device principle diagram<sup>[44]</sup>



(b) Distributed measurement solution schematic

图9 原位取样测量装置图

Fig. 9 In-situ sampling and measuring device diagram



问题,重新对角锥反射镜进行了设计加工,通过改变反射镜的角度,达到消除干涉的目的,同时具有耐烟气冲刷腐蚀、反射率高等特点,现场运行证明了整套系统具有较高的稳定性和准确性。史玉伟等<sup>[48]</sup>对北京新能源科技有限公司NLAM1512原位取样式氨逃逸率在线监测仪在通辽电厂的应用情况进行了分析,系统灵敏度达到0.1~0.2 ppm,并且系统运行稳定,准确度高。与传统取样测量类似,单点原位取样同样面临测量不具代表性的问题。刘瑞锋等<sup>[49]</sup>在原位取样的基础上设计了分布式在线监测方案,并进行了现场应用,装置示意图如图9(b)所示,结果表明同一烟道不同位置氨逃逸不均匀,该分布式监测系统可准确反映SCR脱硝出口各区的氨逃逸率,为指导精准喷氨提供参考。张爱军等<sup>[50]</sup>同样利用原位取样式氨逃逸分析仪进行了多点测量,根据不同位置分区的氨需求量进行精准喷氨,氨逃逸率明显降低。

为了提高现场烟气氨逃逸测量的准确性,科研人员还从仿真模拟、颗粒物干扰修正、噪声处理以及其他方面入手,对基于TDLAS技术的NH<sub>3</sub>检测进行了深入研究。禹迎春等<sup>[51]</sup>利用Simulink软件分别仿真了QCL激光器和DFB激光器测量NH<sub>3</sub>的直接吸收光谱,模拟了SCR脱硝出口的NH<sub>3</sub>测量灵敏度、检测限和分辨率,结果表明,QCL系统比DFB系统灵敏度高50倍,检测限与分辨率可达ppb量级。王飞等<sup>[52]</sup>为了解决颗粒物对NH<sub>3</sub>测量产生干扰的问题,提出同步测量激光强度信号并进行线性拟合,对2f信号进行校准,校准后的2f峰值变化在5%以内,证明了该方法的有效性。邹得宝等<sup>[53]</sup>为改善基于TDLAS技术的氨逃逸测量光谱信号,采用不同的数字滤波方法进行了处理比较,结果表明,与其他方法相比,算术平均-小波变换滤波效果更好,提高了系统信噪比和信号平滑度,使系统浓度检测限由原来的10 ppm降低到1.25 ppm,信噪比提高了约14倍,为低浓度氨逃逸检测提供了一种有效的数据预处理方法。张立芳等<sup>[54]</sup>基于新型Herriott池及高温管式炉,结合DAS技术和WMS技术,选取2.25 μm附近的吸收线作为目标谱线,在实验室实现了对不同温度下NH<sub>3</sub>的高灵敏检测;常温下DAS和WMS技术的探测极限分别为0.225 ppm和0.022 5 ppm,温度为650 K时,WMS技术的探测极限1.8 ppm,证明了该技术在脱硝氨逃逸现场测量的适用性。QIU X B等<sup>[55]</sup>基于1 514 nm的DFB激光器设计了一种用于SCR/SNCR过程中NH<sub>3</sub>温度测量的传感器,通过实验证明该传感器在453~653 K范围内的最大温度测量误差小于2%,平均误差小于1.8%,具有较高的精度和线性度,可用于现场脱硝温度测量。RAZA M等<sup>[56]</sup>研制了一种基于SCAN-WMS技术的高温CO/NH<sub>3</sub>双组分检测传感器,利用2.3 μm DFB激光器对CO和NH<sub>3</sub>谱线进行了探测,在700 K条件下,NH<sub>3</sub>的噪声等效吸收系数为4.9×10<sup>-7</sup> cm<sup>-1</sup>,所研制的双组分传感器有潜力应用于烟气氨逃逸检测领域。

## 2.2 产品应用

鉴于烟气氨逃逸在线检测的强大市场需求,目前国内外已有许多成熟的、不同检测方式的氨逃逸分析仪,具有代表性的产品如表2所示。

可以看出,国内外各种类型的烟气氨逃逸在线分析仪的检测限(或灵敏度)基本小于0.5 ppm,满足现场需求。国际上主流烟气氨逃逸分析仪以原位测量方式为主,适用于含尘量较小的环境;国内自主研发的氨逃逸分析仪则以取样测量和原位取样的方式居多,更加适用于我国的含尘量高的大型燃煤电站锅炉。然

表2 烟气氨逃逸分析仪性能指标  
Table 2 Performance indicators of flue gas ammonia slip analyzer

Manufacturer	Country	Model	Measuring way	Detection limit or sensitivity/ppm	Reference
SIEMENS	Germany	LDS 6	In-situ	0.1	[57]
ABB	Germany	AO2000-LS25	In-situ	0.3	[58]
NEO	Norway	LaserGas™ II SP	In-situ	0.15	[59]
SERVOMEX	Britain	Laser 3 Plus	In-situ	0.1	[60]
SICK	Germany	GM700	Permeation tube	0.3	[61]
UNISEARCH	Canada	LasIR R	PIMs	0.1	[62]
JUGUANG	China	LGA-5500	Sampling	0.1	[63]
XUEDILONG	China	SCS-900LS	Sampling	0.25	[64]
DAFANG	China	DLGA-3000	Sampling	0.1	[65]
ZETIAN	China	GA-5000DN	Sampling	0.38	[66]
GUANGLI	China	AEMS10	In-situ sampling	0.1	[67]
XINYE	China	NLAM1512	In-situ sampling	0.1	[68]

而,根据实际调研反映,目前市场上的多数氨逃逸在线分析仪存在长期运行稳定性较差的共性问题,需要频繁维护甚至更换设备,因此,目前的产品在运行稳定性方面还具有一定提升空间。

### 3 总结与展望

本文综述了基于TDLAS技术的烟气氨逃逸检测研究进展和应用现状。在现有光谱技术中,TDLAS以其灵敏度高、选择性强、可实时在线测量、造价低廉等突出优点成为氨逃逸在线检测的主流技术,随着理论研究的深入和技术装备的成熟,TDLAS技术将在烟气氨逃逸检测和控制工作中进一步发挥重要作用。1)常用于检测NH<sub>3</sub>的波段有1.5 μm、2 μm以及9~10 μm,与近红外相比,9~10 μm波段的吸收线强度高1~2个数量级,探测灵敏度更高,适用于痕量NH<sub>3</sub>检测。通过采取适当的检测方式,不同波长的分析仪基本都可以满足烟气氨逃逸现场的测量要求。虽然中红外激光源可以提供较高的探测灵敏度,但是成本较高,限制了其大范围应用,目前的商业产品仍然以1.5 μm光源为主。2)不同的氨逃逸检测方式具有不同的优缺点和适用性,目前原位测量的设备占有的比重最高,同时其余三种方式的研究和应用也在不断深入,根据不同的现场环境选择合适的检测方式才能保证氨逃逸测量的准确性和系统运行的稳定性。由传统取样方式发展而来的原位取样式克服了取样系统复杂、实时监测能力差等缺点,更加适合国内含尘量高的燃煤电站锅炉氨逃逸检测,结合免校准波长调制、分布式多点测量等技术方案可以有效提高氨逃逸检测的准确性、实时性和代表性。因此,原位取样式氨逃逸分析仪将得到进一步发展应用。

基于TDLAS技术的烟气氨逃逸检测产品研发速度逐渐加快,尤其是国内,随着科研投入力度增加,我国自主研发能力逐步提升,自行设计的氨逃逸分析仪具有更好的适用性和可编程性,将逐步满足我国的应用需求。

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## Research and Application of Flue Gas Ammonia Slip Detection Based on Tunable Diode Laser Absorption Spectroscopy (Invited)

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**Abstract:** Nitrogen oxides ( $\text{NO}_x$ ) are important precursors of air pollution.  $\text{NO}_x$  in the atmosphere mainly comes from the combustion of fuels such as coal, oil, and natural gas. Large energy conversion equipment and motor vehicle exhaust are the main sources of  $\text{NO}_x$  emissions. In order to reduce  $\text{NO}_x$  emissions, China has promulgated various regulations to limit  $\text{NO}_x$  emission values. At present, flue gas denitrification is an important means to control  $\text{NO}_x$  emissions from large energy conversion equipment, including SNCR technology and SCR technology, etc. Among them, SCR technology has the advantages of high denitrification efficiency, low impact on the unit, fully automatic control of the system, easy installation and maintenance of equipment, etc., which has become the most widely used and mature flue gas denitrification technology. Ammonia ( $\text{NH}_3$ ) is a common reductant for SCR technology. Although spraying excessive ammonia can improve denitrification efficiency, it is easy to cause ammonia slip. Ammonia slip from flue gas is a problem in many large energy conversion equipment SCR systems. A large amount of

ammonia slip not only threatens unit operation and increases system maintenance costs, but also forms secondary pollution, which endangers the air environment and human health, so ammonia slip must be monitored and controlled effectively in real-time.

Tunable Diode Laser Absorption Spectroscopy (TDLAS) technology is an advanced trace gas detection technology with the advantages of high sensitivity, selectivity, and real-time online measurement, which is widely used in various pollutant gas detection fields and has become the mainstream technology for flue gas ammonia slip online detection. The modulation spectroscopy technique includes Wavelength Modulation Spectroscopy (WMS) and Frequency Modulation Spectroscopy (FMS). Compared with NIR, the intensity of absorption lines in the 9~10  $\mu\text{m}$  band is 1~2 orders of magnitude higher, making it more sensitive for trace  $\text{NH}_3$  detection. By adopting appropriate detection methods, analyzers of different wavelengths can basically meet the measurement requirements of flue gas ammonia slip sites. Although the mid-infrared laser source can provide high detection sensitivity, the high cost limits its wide range of applications, and the current commercial products are still mainly 1.5  $\mu\text{m}$  laser sources.

The unique physicochemical properties of  $\text{NH}_3$  with strong adsorption and the complex environment in the flue make online detection of ammonia slips difficult. The complex measurement environment and strict emission limits place high demands on the anti-interference capability, stability, detection limits, and sensitivity of ammonia slip detection equipment. According to the application requirements of SCR denitrification sites, researchers have developed different ammonia slip detection methods, which currently include four main types: in-situ pair penetration, traditional sampling style, permeation tube style, and in-situ sampling style. The in-situ measurement method is simple and does not need to consider the adsorption of ammonia. Currently, most of the large thermal power unit denitrification ammonia slip online monitoring adopts the in-situ measurement style. However, influenced by the flue working conditions, the measurement accuracy is limited, and not suitable for the environment with high dust content. In contrast, the traditional sampling style has a stable measurement environment and can obtain a high signal-to-noise ratio spectral signal. However, the sampling process may lead to changes in flue gas components and has a certain lag, making it difficult to reflect the true value of the flue in real-time. The penetration tube style can avoid the extinction effect of dust and improve measurement accuracy, but requires frequent maintenance. The in-situ sampling style combines the advantages of in-situ and sampling measurement. The measured value is representative, the influence of dust particles can be avoided and the measurement accuracy is high, making it suitable for domestic coal-fired power station boilers with high dust content. Different ammonia slip detection methods have different advantages, disadvantages, and applicability. Currently, in-situ measurement equipment occupies the highest proportion, while the research and application of the remaining three methods are also in progress. Choosing the appropriate detection method according to different site environments is the only way to ensure the accuracy of ammonia slip measurement and the stability of system operation.

By analyzing various types of flue gas ammonia slip online analyzers at home and abroad, it is found that their detection limits (or sensitivity) are basically less than 0.5 ppm to meet the site requirements, and the long-term stability of instrument operation depends on the actual situation. In recent years, the development of flue gas ammonia slip detection products based on TDLAS technology has accelerated, especially in China. With the increase of scientific research investment, China's independent research and development capability have gradually improved, and self-designed ammonia slip analyzers with better applicability and programmability will further meet the application needs of China. In my opinion, the in-situ sampling method developed from the traditional sampling method overcomes the shortcomings of the complex sampling system and poor real-time monitoring capability, which is more suitable for ammonia slip detection in domestic coal-fired power station boilers with high dust content, and the combination of calibration-free wavelength modulation, distributed multi-point measurement and other technical solutions can effectively improve the accuracy, real-time and representativeness of ammonia slip detection. Therefore, in situ sampling style ammonia slip analyzer will be further developed and applied.

**Key words:** Tunable diode laser absorption spectroscopy; Ammonia slip; Concentration; Detection limit; Sensitivity

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