

# 罐采样-预浓缩/气相色谱-质谱联用测定

## 污染源废气中 118 种挥发性有机物

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**摘要:** 该文采用预浓缩/气相色谱-质谱联用仪(配 FID 检测器), 结合 Dean Switch 中心切割和冷柱箱技术建立了一针进样同时测定污染源废气中 118 种挥发性有机物(VOCs)的分析方法。废气样品采用苏玛罐收集, 稀释后进系统分析, 其中 C<sub>2</sub>-C<sub>3</sub> 组分在 FID 上测定, 外标法定量; 其他物在质谱(MS)上测定, 内标法定量。结果显示, 118 种 VOCs 在 0.5~30 nmol/mol 浓度范围内线性良好, 相关系数( $r^2$ )为 0.995 3~0.999 9, 方法检出限为 0.01~0.38  $\mu\text{g}\cdot\text{m}^{-3}$ , 定量下限为 0.03~1.51  $\mu\text{g}\cdot\text{m}^{-3}$ ; 在低、中、高 3 个加标水平下的回收率为 83.7%~107%, 相对标准偏差(RSD)为 0.37%~5.2% ( $n=7$ ); 将其应用于移动污染源(叉车)及固定污染源(制鞋厂、家具厂、印刷厂、塑料厂、造船厂)废气样品中 VOCs 的测定, 均检出不同程度的 VOCs 污染, 其中叉车尾气中总 VOCs(TVOC)含量为 33.50~35.25  $\text{mg}\cdot\text{m}^{-3}$ , 固定污染源废气中 TVOC 为 44.54~211.71  $\text{mg}\cdot\text{m}^{-3}$ 。该方法简便快速、稳定灵敏、准确度高, 适用于移动污染源和固定污染源废气中 VOCs 的定性定量分析。

**关键词:** 挥发性有机物; 预浓缩; 气相色谱-质谱联用; 源排放; 苏玛罐

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## Determination of 118 Volatile Organic Compounds in Source Emission by Canister Sampling-Preconcentrator/Gas Chromatography-Mass Spectrometry

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**Abstract:** An analytical method was established for the determination of 118 volatile organic compounds (VOCs) in source emission by preconcentrator-gas chromatography-mass spectrometry (equipped with a FID detector) in combination with Deans Switch and cold oven technology. Samples were collected with canister, and diluted before being analyzed. C<sub>2</sub>-C<sub>3</sub>

compounds were determined by FID, and quantified by external standard method. The remaining compounds were determined by mass spectrometry (MS), and quantified by internal standard method. Results showed that the calibration curves for 118 VOCs exhibited good linearity in the concentration range of 0.5-30 nmol/mol, with the correlation coefficients ( $r^2$ ) were within 0.9953-0.9999. The limits of detection and the limits of quantification were 0.01-0.38  $\mu\text{g}\cdot\text{m}^{-3}$  and 0.03-1.51  $\mu\text{g}\cdot\text{m}^{-3}$ , respectively. The average recoveries at low, medium and high spiked levels were in the range of 83.7 %-107 % with the relative standard deviations (RSDs,  $n=7$ ) of 0.37 %-5.2 %.. The method was applied to measure the VOCs in the exhaust gases of mobile source (forklift) and stationary sources (shoe factory, furniture factory, printery, plastic factory and shipyard) were analyzed by this method, and showed varying degrees of VOCs pollution among them. The concentration of total VOCs (TVOC) in exhaust gases from the forklift and stationary sources were 33.50-35.25  $\text{mg}\cdot\text{m}^{-3}$  and 44.54-211.71  $\text{mg}\cdot\text{m}^{-3}$ , respectively. The method was simple, fast, stable, sensitive and accurate, and was suitable for the determination of VOCs in mobile and stationary source emissions.

**Key words:** volatile organic compounds; preconcentrator; gas chromatography-mass spectrometry; source emission; summa canister

挥发性有机物 (VOCs) 是大气中广泛存在的一类重要痕量有机化合物, 其成分复杂, 主要包括非甲烷碳氢化合物、卤代烃、含氧有机化合物、含氮有机化合物、含硫有机化合物等<sup>[1]</sup>。VOCs 是二次有机气溶胶及臭氧的重要前体物<sup>[2]</sup>, 对区域大气复合污染有重要影响<sup>[3]</sup>; 此外部分 VOCs 为有毒有害气体, 可刺激人体感觉器官、增加患癌风险等<sup>[4-5]</sup>。城市大气中 VOCs 主要来源于人为源排放(包括固定污染源和移动污染源<sup>[6]</sup>)。目前我国针对固定污染源废气中 VOCs 的检测, 已制定了一系列的标准方法<sup>[7-11]</sup>, 其中多种类化合物分析以 HJ734-2014<sup>[7]</sup>为主, 但该方法分析 VOCs 组分较少, 低沸点、高光化学活性的 VOCs 难以准确测定, 并且废气中酸、碱、氧化剂等对采样管吸附剂的破坏不可逆<sup>[12]</sup>; 而对于移动污染源废气中 VOCs 的检测, 目前尚未颁布相关的标准方法。为了探索移动污染源废气中 VOCs 的检测方法, 同时准确分析固定污染源废气中更多的 VOCs 种类及组分, 本研究借鉴环境空气中 VOCs 检测方法的最新研究成果<sup>[13-15]</sup>, 采用苏玛罐采样, 预浓缩-气质联用系统 (配 FID 检测器), 并结合 Dean Switch 中心切割和冷柱箱技术, 建立了适用于固定污染源和移动污染源废气样品的 VOCs 检测方法, 实现了一针进样测定 118 种 VOCs。该方法结合了预浓缩