

毛细管 GC/FID 法测定空气中甲硫醇实验研究

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摘要 研究了空气中甲硫醇(CH_3SH)的采样、液氮冷冻浓缩、热解吸和毛细管柱 GC/FID 的色谱分离分析方法. 在选定条件下, 线性范围为0.2–200 μg , 检测下限约0.2 μg , 回收率为92.6%, 重复实验变异系数3.2%, 可以满足空气中 CH_3SH 的测定. 应用于某城市污水厂及污水沟周围空气中甲硫醇的测定, 并以 CH_3SH 为代表计算了空气的恶臭度, 其分布规律可以得到合理的解释, 取得了较为满意的结果.

关键词 甲硫醇, GC/FID 分析, 采样, 恶臭.

恶臭(Malodor)作为重要的环境公害已为当今世界所公认. 在国外首批拟定的8种重点监控物质中硫类化合物占4种: H_2S 、甲硫醇、甲硫醚和二甲二硫醚(DMDS)^[1]. 有机硫恶臭特别是沸点低(7 $^\circ\text{C}$)的甲硫醇具有嗅觉阈值低(0.1 $\mu\text{g}/\text{L}$)、化学稳定性差的特点, 因此其采样分析方法的建立是国际公认的技术难题和研究重点之一, 为此众多的学者进行了大量的实验研究^[2–8].

目前有机硫的测定大都采用填充柱 GC/FPD 法, 然而随着分析仪器和毛细管色谱柱制备技术的发展, 充分利用仪器的高精密度、灵敏度和 FID 检测器的宽线性响应的特点, 把 GC/FID 应用于恶臭气体中甲硫醇的分析是可行的. 本研究在国内外工作的基础之上, 采用 Tenax 吸附剂低温浓缩-热解吸-毛细管色谱柱-GC/FID 法测定空气中的 CH_3SH , 计算并分析了空气的恶臭强度.

1 实验部分

1.1 实验仪器和试剂

HP5890Series II Puls 型 GC/FID, HP3365 化学工作站, HP-1 毛细管色谱柱(30m \times 0.53mm \times 0.88 μm , Crosslinked Methyl Sili-cone Gum), 8701 A 型热解吸仪(改装).

1L 采气瓶若干, 带流量计、真空度计量的大气采样器, 真空泵, U 形玻璃浓缩管(i. d. 4mm, 内充200mg Tenax GC, 两端用少许玻璃棉固定. 采样前应通以30–50ml/min 流量的 N_2 , 加热到250 $^\circ\text{C}$, 老化10min. 然后进行空白实验, 至无干扰成分流出为止).

甲硫醇储备液的配制: 按文献[1]抽取约50 μl 甲硫醇标准试液, 以重蒸苯定容至50ml 得到. 标定方法: 准确吸取5.0ml 标准储备液于三角烧瓶中, 再加入15ml 左右乙醇, 15.0ml 0.025mol/L 硝酸银水溶液, 摇匀5min, 若浑浊, 需再加入适量乙醇. 加入3–5ml 0.025mol/L 铁明矾作为指示剂, 用 5ml 0.025mol/L 的硫氰酸铵滴定至淡桃红色; 然后以 5ml 0.025mol/L 的硝酸银滴定至桃红色消失; 再以 5ml 0.025mol/L 的硫氰酸铵滴定至桃红色终点, 求得甲硫醇标准储备液的浓度为0.24(15.0 – a + b – c)mg/ml. 甲硫醇的标准使用液由标准储备液稀释得到, 其它化学试剂均为分析纯.

1.2 实验方法

(1) 空气样品采集与浓缩 采气瓶内表面以0.02mol/L 磷酸丙酮溶液浸泡涂渍后, 烘干,

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采样前用真空泵抽真空至压力低于 $1.0 \times 10^3 \text{ Pa}$ 备用. 现场采集代表性空气样运回实验室, 如图1以约 0.5 L/min 流速低温浓缩至采样瓶内压力低于 $1.0 \times 10^3 \text{ Pa}$.

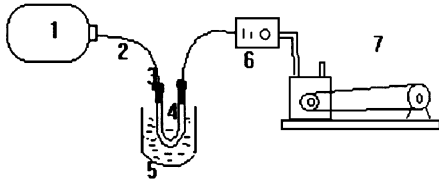


图1 空气样品的浓缩

1. 采样瓶 2. 硬塑管(i. d. 4mm) 3. 硅橡胶塞 4. U型浓缩管 5. 液氮杯 6. 大气采样器 7. 真空泵

(2) 热解吸进样 如图2方式连接浓缩管分析系统, 用加热碗加热浓缩管一定时间后, 转动气路转换阀进样, 同时启动化学工作站记录色谱图.

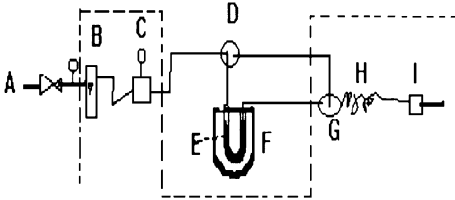


图2 热解吸进样分析系统

- A. N_2 载气源 B. 流量计 C. 流量调节器 D. 气路转向阀 E. 浓缩管 F. 加热碗 G. GC 气化室 H. 色谱柱 I. GC 内气路

(3) GC/FID 分析条件 气化室温度: 150°C ; 柱温: 35°C , 载气流量: 高纯 N_2 2.72 mL/min , 20 cm/s ; FID: 温度 200°C , 尾吹 N_2 30 mL/min , H_2 30 mL/min , 空气 300 mL/min .

2 结果和讨论

2.1 热解吸条件实验和结果

取 10 ng 甲硫醇的标准溶液注入浓缩管内, 做热解吸条件实验. 热解吸温度和解吸时间对吸附/解吸的回收率影响如图3、4所示.

由于甲硫醇沸点低, 化学稳定性差, 在一定条件下可发生分解、聚合反应, 生成例如二甲二硫醚(DMDS)等化学物. 随热解温度的增大和热解时间的延长, 回收率反而略有下降, 而且杂

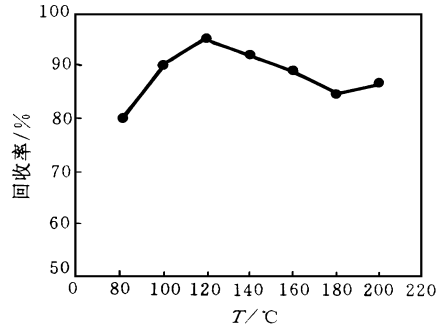


图3 回收率与热解吸温度 T 的关系

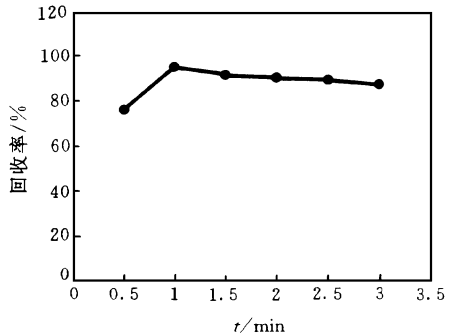


图4 回收率与热解吸时间 t 的关系

质色谱峰增多. 本实验选取热解温度为 $100-150^\circ\text{C}$, 热解时间 1 min .

2.2 热解进样与直接进样方式的比较

考察2种进样方式对 10 ng 甲硫醇的色谱响应的影响. 结果表明, 由于热解进样的死体积较大, 保留时间从直接进样的 2.18 min 增大到 2.68 min . 热解进样时分子在载气流动的过程中的扩散效应增大, 因而峰宽增大, $W_{1/2}$ 从 0.017 min 增大到 0.096 min , 色谱峰的分辨率有所下降. 实际工作中应尽量减少死体积.

2.3 线性范围和检测限

分别取不同量的甲硫醇标准溶液注入浓缩管, 按热解吸分析程序操作, 以色谱峰面积积分值计算回归, 标准曲线的线性范围为 $0.2-200 \text{ ng}$. 以基线噪声的2倍计算, 检测下限约为 0.2 ng , 采样 1 L 计, 相当于空气中甲硫醇的浓度为 $0.2 \times 10^{-3} \text{ mg/m}^3$.

2.4 回收率和精密度

在真空瓶中用微量注射器注入 10 ng 甲硫醇, 高纯 N_2 稀释配制成 10 ng/L 的样品气. 比较

冰水冷冻和液氮冷冻浓缩2种方式,前者回收率仅30%,采用液氮可达90%以上(表1).

表1 真空瓶采样液氮冷冻低温浓缩热解吸进样色谱分析回收率和精密度

试样浓度 /ng·L ⁻¹	重复测定值			平均值	变异系数 / %
10	9.04	9.42	9.70	9.26	+ 3.2
	9.21	8.96			

2.5 应用实例

为验证和确认本研究提出和开发的采样、分析检测方法的可靠性和适用性,把本方法应用于某城市污水厂和污水沟周围空气中甲硫醇的测定.本文采用6级恶臭强度表示法和臭气强度(Y)与甲硫醇浓度(X)的函数关系式: $Y = 1.25 \lg X + 1.827$ (X 浓度单位为 ng/L) 计算恶

污水厂的处理设施和污水沟是产生恶臭的污染源,污水厂域容易感觉到臭气味,在污泥排放处有较强感觉.在邻近污水沟和北面的污水厂的测点易感到臭味,居中间的办公楼测点稍稍可感觉到甲硫醇的味道.

3 小结

采用 Tenax GC 低温吸附浓缩和自行改装的国产上分厂8701A 型热解吸进样仪热解进样大口径毛细管色谱柱,研究了空气中甲硫醇的采样-液氮冷冻浓缩-热解析进样-毛细管 GC/FID 分析方法.在所选条件下,检测下限约 0.2ng,回收率和精密度能够达到空气中甲硫醇监测的国家标准要求.

本方法利用甲硫醇低沸点的特性,选取了较低的柱温(35),可使甲硫醇组分先于空气中其它许多挥发性物质分离出峰.若应用于多组分的分析,则可以35 为起点做程序梯度升温色谱分析.

致谢 上分厂郭文奎高工为改装8701A 型热解析进样仪提供了帮助,谨致谢意.

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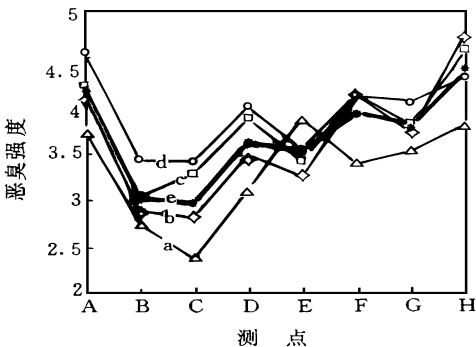


图5 一天中不同时间空气中甲硫醇恶臭强度测定分析实例
A. B. 沟边 C. 办公楼 D. 研究所 E. 格栅 F. 曝气池 G. 浓缩池 H. 排泄处
a. 07:30 b. 11:00 c. 14:00 d. 17:00 e. 平均值
(6级臭气强度分级法: 0—1: 无臭, 1—2: 勉强可感觉, 2—3: 稍可感觉, 3—4: 易感觉, 4— 5: 较强感觉, 5: 强烈感觉)

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臭强度,结果如图5所示.

这种分布规律可以得到合理的解释;城市

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stability.

Study on Effects of Developing Touristry for Songshan Conservation Area. Song Xiujie and Zhao Tongrun (Beijing Municipal Research Academy of Environmental Protection, 100037): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 57_ 59

In order to evaluate effect of touristry development for Songshan Conservation Area, the investigating site and monitoring water, quality which include surface and underground water, and atmospheric quality were carried out. It was found that the natural landscape of the conservation area was destroyed lightly because of trampling, picking and throwing by tourists and touristry facilities established, but quality of surface water and underground water are fit for National Standard. Atmospheric pollutants are fit for First National Standard. Need to strenthen management of the conservation area was suggested.

Key words: Songshan Conservation Area, environmental effect, touristry development, management.

Effect of Calcium on Cell Membrane Permeability in Acid Rain Stressed *Cucumis melo* Seedling. Zhou Qing and Huang Xiaohua et al. (Dept. of Biology Suzhou Railway Teachers College, Suzhou 215009): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 60_ 61

The relationship of calcium to cell membrane permeability in acid rain stressed *Cucumis melo* seedling has been studied. Calcium obviously decreased cell membrane permeability and protected cell membrane from acid rain insult. Optimum protection effect is that *Cucumis melo* seedling is spraiend continuously two times (once every 24 hours) with concentration of 30mmol/L $\text{Ca}(\text{NO}_3)_2$ at the test conditions. The mechanism perhaps is calcium reagent stabilizing the structure of cell membrane of *Cucumis melo* and raising catalase activity.

Key words: *Cucumis melo* seedling, calcium, cell membrane permeability, acid rain stress.

Spectrophotometric Determination of Manganese with Diantipyryl-(P-Bromo)-Phenylmethane. Yin Jiayuan and Yang Guangyu et al. (Department of Chemistry, Yunnan University, Kunming 650091): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 62_ 63

Diantipyryl-(p-bromo)-phenylmethane (DAPBM) was synthesized and indentified. A highly sensitive spectrophotometric method has been developed for the determination of manganese with DAPBM. In the presence of Mn^{2+} , Mn^{3+} can reacts with DAPBM to form an orange and yellow product in phosphoric acid medium. The molar absorptivity is $1.28 \times 10^6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 480nm. Beer's law

is in keeping in the range of 0.1 – 0.9 $\mu\text{g}/25\text{ml}$. This method has been applied to the determination of manganese in food and water, the results are satisfacted.

Key words: diantipyryl-(p-bromo)-phenylmethane, spectrophotometric, manganese.

Determination of CH_3SH in Air Using Capillary GC/FID. Wang Lizhong, Lu Yongsen et al. (Key State Lab. of Pollution Control and Resources Reuse, School of Environ. Eng., Tongji University, Shanghai 200092), Wang Wenling (Department of Chemistry, Fudan University, Shanghai 200433): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 64_ 66

The analytical procedure for methylmercaptan in air was investigated which involves four phases of sampling, low temperature concentration with liquid nitrogen, thermal separation and then capillary column GC/FID analysis. Under the conditions selected, a method linear range of 0.2– 200 ng was obtained with a minimal detection limit of 0.2 ng. The recovery was about 92.6% with a relative standard deviation of 3.2%. This Procedure was applied to determine the concentration of methylmercaptan in the environmental air around a waste water plant and a polluted river successfully. The odour strength of the air at different sampling points was also calculated, and the distribution characteristic with methylmercaptan sounded reasonable.

Key words: methylmercaptan, GC/FID analysis, sampling, malodor.

Progresses of Bioremediation Studies and Applications. Lin Li and Yang Huifang (Institute of Microbiology, Chinese Academy of Sciences, Beijing 100080): *Chin. J. Environ. Sci.* **18**(3), 1997, pp. 67_ 71

A review concerns principles and techniques on degradation of xenobiotics and recalcitrants in contaminated site. The basic principle of bioremediation that for special contaminated site different treatment techniques were selected on three factors which are decrease the toxicity of pollutants and increase the bioavailability of pollutants and the bioactivity of microorganisms. The recently advances at in-situ and ex-situ bioremediation techniques are involved in the paper which include adding nutrient, inoculate species, bioventing, land-farming, composting piles, biopiles and slurry techniques. The methods of collecting the site information and of evaluating treatment were discussed also.

Key words: bioremediation, contaminated site, xenobiotics, recalcitrants, microorganisms, bioavailability, bioactivity.

Advances in the Study of Remediation Methods of Heavy Metal-Contaminated Soil. Xia