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光离子检测器测定大气中溴甲烷*

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摘要用 Tenax 作为吸附剂捕集大气中的痕量溴甲烷,用气相色谱法和光离子检测器,对其进行检测,相对偏差为 0.0521,最小检测限为 10 pg。室内外大气中的浓度分别为 24×10⁻¹²(V/V)和 77.4×10⁻¹²(V/V),污染在 10⁻¹¹(V/V)水平。

关键词 溴甲烷,气相色谱,光离子检测器。

大气中的溴代烷烃来自海洋生物的释放和 人为的排放。它不仅对人类有直接危害,也是 破坏臭氧的主要化合物。气相色谱法由于灵敏 度高被广泛用于检测溴甲烷。氢离子检测器灵 敏度低,对所有的碳氢化合物都有响应,电子 捕获检测器又操作不便,故笔者采用一种新型 的光离子检测器,用 EPA 方法,以 Tenax 作为 吸附剂捕集大气中痕量的溴甲烷,用气相色谱 法分离和光离子检测器检测,操作简单、灵敏 度高。

1 实验部分

1.1 光离子检测器原理

短波长的紫外光能使很多化合物电离,当 被测物质由色谱柱分离后进入离子室,经紫外 无极放电灯照射电离,然后测量离子电流大小, 根据计算,单位时间内产生的离子对数目为:

 $dNi/dt = 2\alpha_1 \varphi [1 - exp^{-\alpha} N(t)_L]$ 其中 Ni 为光离子对数, $a_i = \alpha_1 + \alpha_0$, $\alpha_1 =$ 光离子 化吸收系数, $\alpha_0 =$ 其他因素引起的吸收系数, φ =单位时间进入离子化池的光子数目。L=光程 长, Nt =单位体积内被测物质的分子数, 即样 品的浓度。公式说明, 载气中样品浓度与单位 时间内产生的离子对浓度成指数关系。通常情 况下, $a_i N(t) \ll 1$, 即可得 $dNi/dt = 2 \alpha_1 \varphi a_i N(t)$ L, 即样品浓度与单位时间内产生的离子对浓度 成线性关系。所以测量离子电离大小, 就可知 道物质的含量。

1.2 测试条件

仪器:110型光离子化气体分析仪,中科院 生态环境研究中心研制,120 mm 紫外无极放电 灯。

积分仪:日本岛津 RC-3B

色谱柱: Se30, 60-80 目,长2m,内径2 mm 的聚四氟乙烯管填装而成。

载气: 氮气(纯度为 99.99%)

溴甲烷:分析纯,纯度>98%,江苏激素所 生产。

1.3 样品的富集方法

由于 CH₂Br 在大气中浓度很低,一般在 10⁻¹²(V/V), 需要富集,笔者采用美国 EPA 大 气中挥发性有机物采集的方法^[1]。用 800-100 目的 Tenax 装在内径为 5 mm 的玻璃管内,长 度约为 6 cm,两端用玻璃毛堵塞制成吸附管。 用相同的玻璃管,里面填充无水氯化钙,制成 脱水管,采样时吸附管放在液氮瓶中。当一定 量的空气通过注射器进入脱水管和吸附管时, 所要分析的 CH₃Br 被吸附在 Tenax 上。

1.4 样品的分析方法

根据文献[1],吸附在 Tenax 上的 CH₃Br 需 要在 180℃时解吸,由于 110 型光离子化气体分

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析仪没有加热装置,故在进样口处装一个加热 套,维持加热套温度 180°C,分析时,将 Tenax 管从液氮瓶中取出,按图1方式连接,载气从吸 附管通入柱作为进样时间。



高纯氮 2. 气压表 3. 流量计 4.5. 截止阀
6. Tenax 吸附管 7. 加热套 8. 进样口
9. 光离子化气样分析仪

1.5 标准样品的制配

先将 1 L 的气袋抽空,用注射器注入 1000 ml 的高纯氮,然后用微量注射器注入 50 μ l 气态 CH₃Br,配成浓度为 50 \times 10⁻⁶ (V/V)的 CH₃Br 标气。再用一个气袋,抽成真空,注入 1 L 高纯氮和 500 μ l CH₃Br 标气,配成 25 \times 10⁻⁹ (V/V)的标气。

利用 RC-3B 积分仪外标的功能,选择载气 流速为 10 ml/min,进上述标气,求得校正系数 值(RF)为 2.68×10⁻¹¹(V/V)/A。

2 结果和讨论

2.1 流速对光离子检测器响应值影响

图 2 是不同流速与 CH₃Br 响应值的关系, 可以看出, CH₃Br 在光离子检测器的响应值是



随着载气流速加大而变小,在流速为 10-20 ml/min 时,其变化较小,所以选用流速为 10 ml/min。

2.2 光离子检测器的重复性实验结果

表1列出了在同一色谱条件下重复进样9 次的响应值,从这结果算出相对标准偏差为 0.0521。

表1 重复性实验结果

	峰面积		X	a n-1	相对偏差
227753	2165489	2179134			
2277143	2145232	2110081	2130955	111093	0. 0521
2073396	198322	197648			

2.3 大气中 CH₂Br 的检测

采用 Tenax 柱在液氮下吸附,180℃下解吸的方法,对大气样品进行检测,每个样品都是 富集 500 ml 的空气样。

图 3 是标准样品和空气样品色谱图,从图 3 可以看出,光离子检测器具有高的选择性,保 留时间为 2 min 左右基本上没有杂质干扰。最 小检测限为 10 pg。



测量结果表明,实验室内空气中 CH_3Br 含 量为 $24 \times 10^{-12} (V/V)$,在本单位大楼外空气中 CH_3Br 含量为 77.4×10⁻¹² (V/V)。表明 CH_2Br 污染来自农药,其污染在 $10^{-11} (V/V)$ 水平。

参考文献

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tor. Zhou Lu et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); Chin. J. Environ. Sci., 17 (2), 1996, pp. 54-56

This paper indicated a new way to speed up granulation in UASB reactor by adding GAC. The results of experiment on UASB reactor with and without GAC treating effluence from petrochemical plant showed that the time of sludge granulation in the reactors with and without GAC were 39 days and 63 days respectively. The sludge pellet in the reactor with GAC had larger diameter than one in the reactor without GAC, and maximum COD removal rate was above 86%. Organic load of reactor with GAC was 2 times larger than the reactor without GAC. The reactor with GAC became more steady in process.

Key words: UASB reactor, granular active carbon, sludge pellet, granulation.

A Study on New Purification of High Concentration Sulphur Dyeing Sewege. Sun Jianhui et al. (Research Institute of Environ. Sci., Henan Normal Univ., Xinxiang 453002); Chin. J. Environ. Sci., 17(2), 1996, pp. 57 -59

The combined technology of coagulative precipitation-iron chippings filtering-alkaline separation was used to purify the high concentration sulphur dyeing sewage. The results in the mode of production showed that the removel rates of sulphide, COD, BOD₅ and colority were 97.0%, 87.4%, 85.7% and 98.9% respectively. Every pollution index is up to the National Water Emission Standard. This technology system has the advantage in run stable, operation and management easy, engineering invest low, and treatment cost cheap.

Key words: coagulative precipitation, iron chippings filtering, alkaline separation, sulphur dyeing sewage.

Ecological Restoration of Coal Mining field in Loess Plain. Xue Ling et al. (Inner Mongolia Environmental Research Institute, Huhhot 010010); Chin. J. Environ. Sci., 17(2), 1996, pp. 60-63

This paper reports the results of an ecological restoration project in the Zhunger open cut coal mining field in Inner Mongolia. The design, technique and effectiveness of the project are described. The results showed that the key points for ecological restoraton in the Loess Plain condition include: selection of suitable plant species, proper soil treatments plus necessary construction work, adapt suitable ecological planting patterns based on site conditions. More than sixty plant species and eight ecological planting patterns were evaluted. Over 70% plant coverage and high yields of the crops (compared with the same crops in the nearby area) were obtained. A good ecological and economical return was achieved from the project.

Key words: ecological resteration, demanstrative project, Zhunger, open-cut coal mine in inner mongolia, land reclaim.

Determination of Atmospheric Methyl Bromide by Photoionization Detector. Zhong Jinxian and Liu Ye (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); Chin. J. Environ. Sci., 17(2), 1996, pp. 64-65

Atmospheric CH_3Br was trapped by Tenax adsorbent and was determined by gas chromatography with photoionization detector. The CH_3Br concentrations in indoor and outdoor are $24 \times 10^{-12} (V/V)$ and 77. $4 \times 10^{-12} (V/V)$. The standard deviation and detection limit for the method are 0. 0521, 10 pg respectively. The level of CH₃Br pollutions is $10^{-11} (V/V)$.

Key words: methyl bromide, GC, photoionization detector.

Indirect Spectrophotometric Determination of Trace Cyanide by Means of the Colour Reaction of Silver with Cadion in Presence of Triton X-100. Gong Churu et al. (Dept. of Chemistry, Hubei Normal University, Huangshi 435002); Chin. J. Environ. Sci., 17(2), 1996, pp. 66-67

Silver gives a colour reaction with Cadion in the presence of Triton X-100, and suppression of the colour competitive complex ion of the silver can be used for the indirect spectrophotometric determination of trace cyanide. Cyanide in waste water can be separated by distillation from other ions that also interfere, and then determinated. The determination range of this method is $0-10 \ \mu g/$ 25 ml. The recoveries of standard cyanide added to waste water samples are in the range of 91. 0-100%, and its relative standard deviation is less than 9%.

Key words: cyanide, cadion, indirect spectrophotometry.

The Liquid-Solid Extraction of Methomyl in Environmental Water and Gas Chromatographic Analysis. Chen Yanjun et al. (Dept. of Chemistry, Jining Medical College, 272113); Chin. J. Environ. Sci., 17(2), 1996, pp. 68-70

A solid-phase extraction procedure of methomyl from environmental water with active carbon cartridge for gas chromatographic analysis is presented. The detection limit and the minimum detectable concentration of methomyl in water were 0.2 ng and 0.2 μ g/L, respectively. The average recoveries of methomyl as added to water were in the range of 95.8–100.7%. The relative standard deviations were lower than 5%.

Key words: methomyl, solid-phase extraction, active carbon, gas chromatography.

Determination of Trace Levels of Nitrophenols in Water by Polyvinylpyrrolidone Modified Carbon Paste Electrode. Wang Kaixiong et al. (Dept. of Environ. Protection, Zhejiang Agricultural University, Hangzhou 310029); Chin. J. Environ. Sci., 17(2), 1996, pp. 71 -73

In this paper, a method to determine simultaneously p-nitrophenol and 2, 4-dinitrophenol in water by differential pulse voltammetry (DPV) with a carbon paste electrode modified with 10% (W/W) polyvinylpyrrolidone (PVPr) was described. The electrode showed a strong response to the nitrophenols, and the sensitivity and selectivity were much higher than ordinary carbon paste electrode. The nitrophenols were preconcentrated in 0.1 mg/L KCl solution during open circuit period, then the preconcentrated nitrophenols at the electrode were determined in phosphate buffer solution (pH7. 0). The oxidation peak potentials were +0.88 V and +1.23 V (VS Ag-AgCl) respectively and two current peaks were completely separated. The detection limits were 0.50 μ g/L (p-nitrophenol) and 1. 80 µg/L (2, 4-dinitrophenol). This method had been applied to the determination of nitrophenols in pol-