

二安替比林对溴苯基甲烷光度法测定锰^{*}

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摘要 合成了一个新的二安替比林试剂, 二安替比林对溴苯基甲烷(DApBM), 并研究了它和 $Mn(II)$ 的显色条件. 在磷酸介质中, $Mn(II)$ 存在下, DApBM 和 $Mn(II)$ 生成橙色产物, $\lambda_{max} = 480nm$, $\epsilon = 1.28 \times 10^6 L \cdot (mol \cdot cm)^{-1}$, 锰的含量在 $0.1 - 0.9 \mu g / 25ml$ 内符合比尔定律. 用于食品和水样中锰的测定, 结果满意.

关键词 二安替比林对溴苯基甲烷, 光度法, 锰.

锰作为一种人体必须的微量营养元素, 其摄入量对人体健康有重要影响, 因而食品和水样中痕量锰的测定具有重要意义, 目前锰的测定常用高锰酸盐光度法^[1], 但方法灵敏度太低, 不适用于痕量锰的测定. 二安替比林苯基甲烷某些衍生物由于灵敏度低, 显色条件苛刻, 多年来未得到推广应用. 自从章道昆^[2]和徐其亨^[3]等发现 $Mn(II)$ 和吐温类表面活性剂的协同增敏作用后, 该类试剂在分析中的应用得到迅速发展, 并出现了一些 ϵ 达 10^6 的超高灵敏体系^[4-6]. 本研究合成了 DApBM, 并研究过它和 $Cr(III)$ ^[7] 的显色反应, 在此基础上研究了 DApBM 和 $Mn(II)$ 的显色反应及应用, 用于食品和水样中痕量锰的测定获得满意结果.

1 实验部分

1.1 试剂的合成与鉴定

在小烧杯中称取 3.76g 安替比林和 1.85g 对溴苯甲醛, 加少量的水混匀, 加 10ml 浓盐酸, 60℃ 左右水浴加热并搅拌, 20min 后, 反应物迅速固化, 证明反应结束, 用水稀释到 200-300ml, 用氨水中和到中性, 过滤沉淀, 沉淀用蒸馏水洗净氯离子, 用乙醇重结晶 2-3 次, 得浅玫瑰色粉状固体, 产率 78% - 80%, 熔点 185-185.5℃, 由红外光谱和元素分析可证明产物为 DApBM.

1.2 主要仪器和试剂

722 光栅分光光度计; $Mn(II)$ 标准: 按常规方法配成含 $Mn(II)$ 100 $\mu g / ml$ 贮备液, 使用时稀释成 0.5 $\mu g / ml$ 的标准工作液; 2+1 磷酸; $Mn(II)$ 水溶液: 用 $MnSO_4 \cdot H_2O$ 配成含 $Mn(II)$ 6.0 mg / ml 的水溶液; 1% 过硫酸铵水溶液; 0.5 mg / ml 硝酸银水溶液; 4% (W/V) DApBM 用 95% 乙醇配制.

1.3 实验方法

吸取 0.5 μg $Mn(II)$ 标准于 25ml 比色管中, 加入 1ml 1% 过硫酸铵, 1 滴硝酸银, 氧化 $Mn(II)$ 为 $Mn(IV)$ 之后沸水浴加热 30min 赶尽过量的过硫酸铵, 冷却后依次加入 3ml 2+1 磷酸, 3ml 6 mg / ml $Mn(II)$, 0.1ml 4% DApBM, 用水稀释到近刻度, 沸水浴加热 10min, 流水冷却定容, 以试剂空白为参比, 用 1cm 比色皿, 在 480nm 处测定吸光度.

2 结果与讨论

2.1 显色反应机理初探

该反应为氧化还原反应, 无 $Mn(IV)$ 存在时, 反应速率极慢, 只有在高浓度 $Mn(II)$ 存在下才显色. 根据文献[8], $Mn(II)$ 氧化试剂生成有色化合物, 其反应速率极慢, 往往要放置数日, $Mn(II) + Mn(IV)$ 体系可生成 $Mn(IV)$,

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Mn(), Mn(), Mn()一系列的中间产物,其中 Mn()与试剂反应速率快,这是诱导显色的重要原因.产物中除加入的二价锰外,还有其它价态的锰出现,证明反应是氧化还原反应, Mn()起诱导作用.实验还发现 Ce()也有与 Mn()类似的作用.对于 DApBM 与 Mn 的显色反应,本实验未得到显色产物的分析结果,具体还有待进一步实验证明.

2.2 吸收光谱

吸取0.5μg Mn()标准于25ml 比色管中,测不同波长的吸光度,绘成吸收曲线(图1),可得 λ_{max} = 480nm,试剂空白非常小.

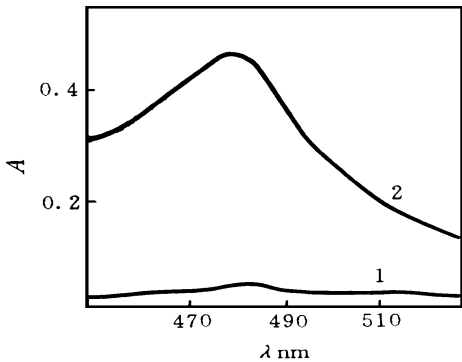


图1 吸收光谱

1. 试剂空白对蒸馏水 2. 显色体系对试剂空白

2.3 介质的选择及磷酸的用量

体系只有在酸介质中才显色,磷酸效果最佳,2+ 1磷酸用量在1.5- 5ml 内吸光度稳定,实验选用3ml.

2.4 Mn()用量的确定

无 Mn()存在时体系几乎不显色,试验表明,6mg/ ml Mn()用量在2- 5ml 内吸光度稳定且最大,实验选用3ml.

2.5 过硫酸铵用量的确定及分解时间

试验表明1% 过硫酸铵用量在1ml 即可完全氧化 Mn()为 Mn(),过量的过硫酸铵沸水浴加热迅速分解,加热30min 可分解完全.

2.6 DApBM 用量的确定

试验表明4% DApBM 用量在0.1ml 以上即可显色完全,实验选用0.1ml.

2.7 显色温度及稳定性实验

体系在常温下显色慢,加热可加快显色速度,沸水浴加热10min 可显色完全,体系在室温下可稳定0.5h,放置时间过长会有极少量沉淀生成而干扰比色.

2.8 工作曲线

在选定实验条件下, Mn()的含量在0.1—0.9μg/ 25ml 内符合比尔定律,线性回归方程为 $A = 0.004932 + 0.9254C (\mu\text{g}/25\text{ml})$, $r = 0.9984$,从回归方程可算出 $\epsilon = 1.28 \times 10^6 \text{L} \cdot (\text{mol} \cdot \text{cm})^{-1}$.

2.9 共存离子的干扰

对于1.0μg Mn(),相对误差为 ± 5%,下列离子不干扰 (mg): K^+ , Na^+ , SO_4^{2-} (20); Mg^{2+} , Ca^{2+} , NH_4^+ (10); NO_3^- (5); Al^{3+} , Pb^{2+} , Zn^{2+} (); Bi (), Cd^{2+} (0.5); Ni^{2+} , SiO_3^{2-} (0.1); Co^{2+} , In^{3+} , Mo (), Sb (), Sn (), Th () (0.05); Fe^{2+} , Zr () (0.01); Fe^{3+} , Cu^{2+} (0.005);等量的 V (), Cr (), Ce ()有正干扰; F^- ,草酸根有负干扰;卤化物因生成沉淀而干扰比色.

3 样品的分析及结果

3.1 食品中锰的测定

食品样在烘箱中烘干后磨细,准确称取样品适量,在瓷坩锅中低温碳化后放入马弗炉中灰化(600 左右),灰烬用少量硝酸溶解,滴入适量硝酸银,消除卤化物的干扰,滤去沉淀,用100ml 容量瓶定容,取适量溶液,按实验方法显色测定,结果如表1.

表1 样品分析及结果

样品	测定值 / $\text{mg} \cdot \text{g}^{-1}$	$R \cdot S \cdot D$ ($n = 5$)	标准回收率/ % (加 Mn() 0.2μg)
板栗仁	58.0×10^{-3}	3.1	94- 103
大米	9.36×10^{-3}	1.2	97- 102
昆明地下水	0.21×10^{-3}	5.3	92- 106
电池厂废水	6.32×10^{-3}	3.5	93- 102

3.2 水中锰的测定

水样用硝酸酸化后用硝酸银沉淀卤素,滤
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在现场工作中, 主要监测的生态过程包括特殊污染物降解的选择压, 导致微生物生长和最终产物生成的污染物矿化和脱毒作用, 共代谢转化反应, 营养及电子供体浓度和细菌生理状态的变化.

生物整治(Bioremediation)是近年才频频出现在生化处理专业刊物上的一个新词, 它的内容和技术方法还在不断发展中, 我国这方面可结合我国国情, 加以改进并逐步发展起来, 生物整治技术将在我国生物净化方面发挥作用.

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去沉淀, 取适当体积的滤液按实验方法显色测定, 结果见表1.

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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 strengthen 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 sprayed 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 Di-*n*-propyl-(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

Di-*n*-propyl-(p-bromo)-phenylmethane (DAPBM) was synthesized and identified. A highly sensitive spectrophotometric method has been developed for the determination of manganese with DAPBM. In the presence of Mn^{2+} , Mn^{3+} can react 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 satisfied.

Key words: di-*n*-propyl-(p-bromo)-phenylmethane, spectrophotometric, manganese.

Determination of CH_3SH in Air Using Capillary GC/FID. Wang Lizhong, Lu Yongsan 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