

溴甲酚绿-溴化十六烷基吡啶光度法测定水中阴离子表面活性剂

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摘要 建立溴甲酚绿(BCG)-溴化十六烷基吡啶(CPB)光度法测定水中阴离子表面活性剂的方法。实验表明, 最适合的 pH 范围为 5.5—9.0, $\lambda_{\max}=614\text{ nm}$, 在 $86\text{ }\mu\text{g CPB}$ 存在下, 十二烷基苯磺酸钠(SDBS)和十二烷基硫酸钠(SDS)分别在 $0\text{—}80\text{ }\mu\text{g}/10\text{ ml}$ 和 $0\text{—}75\text{ }\mu\text{g}/10\text{ ml}$ 范围内符合比耳定律, 其表观摩尔吸光系数分别为 2.9×10^4 和 $3.1\times 10^4\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ 。用此法测定了河水和生活废水中的阴离子表面活性剂, 相对标准偏差 $<3.0\%$, 样品加标平均回收率为 99.3% 。

关键词 阴离子表面活性剂, 溴甲酚绿, 溴化十六烷基吡啶, 分光光度法。

亚甲基蓝光度法测定环境水样中阴离子表面活性剂(AS)是环境分析中普遍采用的方法^[1], 但灵敏度低, 且需有机溶剂多次萃取, 操作不便。本文研究了溴化十六烷基吡啶(CPB)分别与溴甲酚绿(BCG)和 AS 形成离子缔合物的反应。发现在 pH5.5—9.0 的缓冲溶液中, CPB 与 BCG 产生变色反应, 使 614 nm 处的吸光度下降。若依次加入 AS、CPB、BCG, 则 AS 与 CPB 缔合, CPB 浓度降低, CPB 与 BCG 形成的离子缔合物相应减少, BCG 浓度则相应增大, 且随着 AS 量的增加而增大, 溶液颜色也逐渐加深^[2]。据此建立了 BCG-CPB 光度法测定 AS 的方法。用此法测定了河水和生活废水中的 AS, 结果满意。

1 实验部分

1.1 仪器与试剂

(1) 721 型分光光度计(上海第三分析仪器厂)。

(2) pH S-2 型酸度计(上海第二分析仪器厂)。

(3) 十二烷基苯磺酸钠(SDBS)标准溶液 将工业品 SDBS 按文献^[3]方法提纯, 准确称取

0.2500 g , 用水定容至 250 ml , 即得 1 mg/ml 标准贮备液, 使用时逐级稀释成 $50\text{ }\mu\text{g/ml}$ 和 $5\text{ }\mu\text{g/ml}$ 工作溶液。

(4) 十二烷基硫酸钠(SDS)标准溶液 将化学纯 SDS 用无水乙醇重结晶一次, 准确称取 0.2500 g , 用水定容至 250 ml , 即得 1 mg/ml 标准贮备液, 使用时稀释成 $50\text{ }\mu\text{g/ml}$ 工作溶液。

(5) CPB 标准溶液 准确称取 0.1000 g CPB(分子式 $\text{C}_{21}\text{H}_{38}\text{NBr}\cdot\text{H}_2\text{O}$, 分子量 402.47), 以少量水溶解, 转入 100 ml 容量瓶, 加水至刻度, 即得 $2.49\times 10^{-3}\text{ mol/L}$ 标准贮备液, 使用时取 5.0 ml 稀释至 100 ml , 即得 $1.25\times 10^{-4}\text{ mol/L}$ 工作溶液。

(6) BCG 溶液($1.60\times 10^{-4}\text{ mol/L}$); 磷酸盐缓冲溶液(pH=6.0)。

所用试剂(除指定的外)为分析纯, 实验用水为二次蒸馏水, 其它溶液按常规配制。

1.2 实验方法

准确移取适量 SDBS 标准溶液于 10 ml 比色管中, 依次加入一定量的 CPB、 1.0 ml BCG 溶液, 0.8 ml pH 6.0 磷酸盐缓冲溶液, 稀释至

收稿日期: 1995-07-15

刻度, 摇匀, 10 min 后用 1 cm 比色皿, 以试剂空白作参比, 于 614 nm 处测量吸光度。

2 结果与讨论

2.1 吸收光谱

由图 1 可知, BCG 的 $\lambda_{\max} = 614$ nm, 加入 CPB 后吸收峰降低, 且红移 15 nm; 加入 SDBS 或 SDS 后吸收峰又增高, 证明了本文上述机理。本实验选用 614 nm 为测量波长。

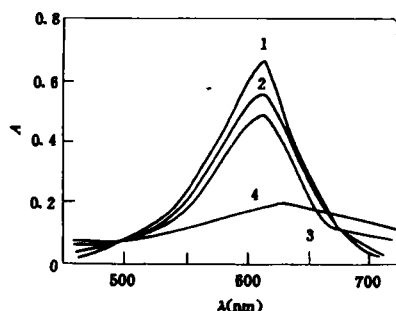


图 1 吸收光谱

1. 0.8 ml, 1.60×10^{-4} mol/L BCG
 2. 0.8 ml, 1.60×10^{-4} mol/L BCG + 80 μg SDS + 96 μg CPB
 3. 0.8 ml, 1.60×10^{-4} mol/L BCG + 80 μg SDBS + 96 μg CPB +
 4. 0.8 ml, 1.60×10^{-4} mol/L BCG + 96 μg CPB
- 1—4 均以水作参比

2.2 酸度的影响

取 0.8 ml 不同 pH 值的缓冲溶液和 30 μg SDS, 按实验方法测量吸光度。结果表明, 在 pH 5.5—9.0 范围内, 吸光度最大且稳定, 本文选用 pH 6.0 的磷酸盐缓冲溶液 0.8 ml。

2.3 温度及显色时间的影响

实验表明, 在常温下, 显色 5 min 后吸光度稳定, 本实验选定 10 min 显色时间。

2.4 BCG 浓度的影响

取 1.6 ml 1.25×10^{-4} mol/L CPB 溶液, 加入 1.60×10^{-4} mol/L 的 BCG 溶液 0.4—1.4 ml, 按实验方法测量吸光度, 结果如图 2 所示。由图 2 可见, 在 BCG 与 CPB 的摩尔比为 0.8 处, 出现一转折点, 当它们的摩尔比大于 0.8 时, 即 BCG 溶液在 1.0 ml 以上时, 吸光度随 BCG 浓度增大而线性增大, 其反应机理有待进

一步研究。考虑到实验的可操作性, 本实验选定 1.0 ml 1.60×10^{-4} mol/L BCG 溶液。

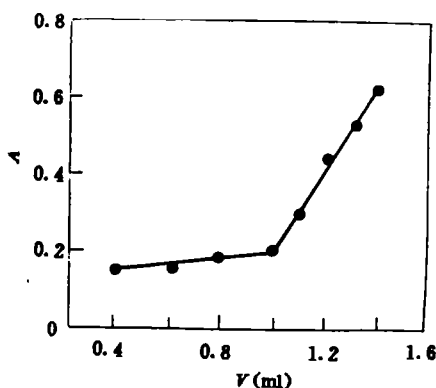


图 2 BCG 浓度的影响

$c_{\text{CPB}} = 2.00 \times 10^{-5}$ mol/L; 水作参比; $\lambda = 614$ nm

2.5 离子缔合物的组成

取 1.4 ml 1.43×10^{-4} mol/L SDBS 溶液, 加入 1.25×10^{-4} mol/L CPB 溶液 0.4—2.8 ml 和 1.60×10^{-4} mol/L BCG 溶液 1.0 ml, 按实验方法测量吸光度。由图 3 可见, $[\text{CPB}]/[\text{SDBS}]$ 的比值超过 1 时, 由于过剩的 CPB 与 BCG 产生变色反应, 吸光度下降, 出现一转折点, 表明在水溶液中 SDBS 以 1:1 和 CPB 反应, 即生成的离子缔合物的组成为 1:1。

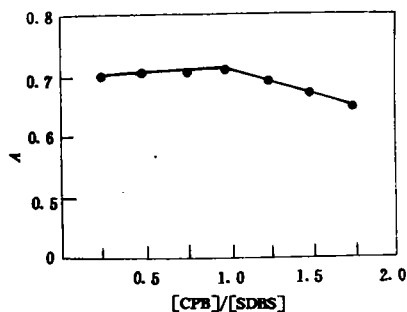


图 3 离子缔合物的组成

$c_{\text{SDBS}} = 2.00 \times 10^{-5}$ mol/L;

$c_{\text{BCG}} = 1.60 \times 10^{-5}$ mol/L; 水作参比; $\lambda = 614$ nm

2.6 线性范围

实验表明, 由于反应定量进行, 线性范围随 CPB 的量增大而增宽。SDBS 和 SDS 在 86 μg CPB 存在下, 分别在 0—80 $\mu\text{g}/10$ ml 和 0—75

$\mu\text{g}/10\text{ ml}$ 范围内符合比耳定律; 在 $191\text{ }\mu\text{g CPB}$ 存在时, 分别在 $0\text{--}160\text{ }\mu\text{g}/10\text{ ml}$ 和 $0\text{--}145\text{ }\mu\text{g}/10\text{ ml}$ 范围内符合比耳定律。其表观摩尔吸光系数分别为 2.9×10^4 和 $3.1\times 10^4\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ 。

2.7 共存离子的影响

在试验条件下, 对 $50\mu\text{g}/10\text{ ml}$ SDBS 进行分光光度测定, 相对误差不大于 $\pm 5\%$ 时, 下列离子或物质的允许量(单位 mg)分别为: K^+ 、 Na^+ 、 Cl^- 、 Br^- 、 NO_3^- 、 NH_4^+ (>20); SCN^- (>0.4); Ba^{2+} (>3.5); Cu^{2+} (0.2); Mn^{2+} (20);

BrO_3^- (6.4); 酒石酸氢钾 (9.5); $\text{C}_2\text{O}_4^{2-}$ (6.7); EDTA (3.7); Mg^{2+} (0.5); Ca^{2+} (4); SO_4^{2-} (>2); HCO_3^- (0.6)。

3 样品测定

3.1 水样测定

取经过滤的水样, 小心加热浓缩 5 倍, 取 6.0 ml , 按实验方法测定, 同时进行加标回收实验, 用工作曲线法计算水样中 AS 含量(以 SDBS 计), 所得结果与文献^[4]测定值基本吻合, 结果见表 1。

表 1 水样中 AS 含量及回收率测定

水样名称	测定值($n=6$) ($\mu\text{g}/\text{ml}$)	RSD (%)	文献 ^[4] 法 测定值($\mu\text{g}/\text{ml}$)	回收实验		
				SDBS 加入量 (μg)	SDBS 回收量 (μg)	回收率 (%)
湘江水(衡阳市区)	0.187	3.0	0.169	10.0	11.0	110
蒸水水(衡阳市区)	0.281	2.9	0.279	10.0	9.30	93.0
池塘水 ¹⁾	2.30	1.4	2.17	20.0	19.0	95.0

1) 不经浓缩直接测定

3.2 肥皂的测定

肥皂的主要成分是硬脂酸钠 $\text{C}_{17}\text{H}_{35}\text{COONa}$ (分子量 306.52), 羧酸型阴离子表面活性剂,

参照文献^[5], 分别用硬脂酸钠和碱肥皂(粉碎后 105°C 烘干 2 h)试验, 按实验方法测量吸光度, 结果见表 2。

表 2 肥皂中 AS 含量测定

样品名称	实验浓度 (mg/L)	测得浓度 ($\mu\text{mol}/\text{L}$)	相当于 SDBS 浓度 (mg/L)	含量(%)	
				本法测定值	文献 ^[5] 值
硬脂酸钠	4.00	10.8	3.77	83.0	89.2
	8.00	21.5	7.50	82.5	89.2
碱肥皂	6.00	9.93	3.46	50.7	51.6
	10.0	16.6	5.80	51.0	51.6

由表 2 可以看出, 用本法测定硬脂酸钠和碱肥皂含量, 与文献^[5]报道值基本一致, 说明本法测定的环境水样中的 AS 既包括含硫 AS, 也包括羧酸型 AS。

4 小结

本文提出用溴甲酚绿-溴化十六烷基吡啶光度法测定环境水样中阴离子表面活性剂。本法适于河水、生活污水中阴离子表面活性剂的测定, 不需有机溶剂萃取, 仪器、试剂价廉易得,

方法简便, 结果满意。

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to fluidize easily in the reactor. The treatment system can resist the loading fluctuation and possess high dehydrogenase activity.

Key words: fluidized, biofilm, treatment, phenolic wastewater, carrier.

Development of a New Type Dispelling Smoke Silencer of Diesel Engine. Zeng Defang (Turbine College, Wuhan University of Science and Technology of Traffic, Wuhan 430063); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 63—64

This paper introduces a kind of method of making a new type dispelling smoke silencer of diesel engine. The method includes adding a kind of solution which can clean the end gas of diesel engine to the bottom of the old silencer of diesel engine. The end gas of diesel engine can be both cleaned and silenced by passing through the dispelling smoke silencer. A comparison of new silencer with the old one under the same condition on the type 135 diesel engine has shown that the dispelling smoke silencer can reduce 80% of smoke and 14.1% of noise (from 99 dB to 85 dB).

Key words: diesel engine, dispelling smoke silencer, noise, end gas of diesel engine.

A Study on Treatment of Traditional Chinese Medicine Wastewater by SBR Process. Han Xiangkui et al. (Jilin Architectural and Civil Engineering Institute, Changchun 130021); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 65—67

Experimental results showed that at the concentration range of COD in influent from 1000 mg/L to 2500 mg/L, effluent COD can be reduced to less than 250 mg/L, BOD₅ and SS less than 100 mg/L. These levels conform to discharge permission standard of pharmaceutical wastewater. The variation behavior of dehydrogenase during the process of aeration is also discussed in this paper.

Key words: SBR process, wastewater treatment, traditional Chinese medicine wastewater.

Dioxins in Stack Ash from PCBs Incinerator. Ke Jiang et al. (Research Center for Eco-environmental Sciences, CAS, Beijing 100085); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 68—71

The PCDD/Fs in stack ash from a experimental incinerator for destruction of PCBs waste have been determined by ¹³C isotope HRGC/HRMS method. Seventeen 2, 3, 7, 8-substituted toxic dioxins congeners were quantitatively measured. The TEQ value of the stack ash is 47.2 ng/g.

Key words: stack ash, PCBs, dioxins.

Releasing of PAHs from Coal-ash in Seawater. Fu Yunna and Liu Yiwen (Inst. of Mar. Environ. Prot., SOA, Dalian 116023); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 72—74

Releasing of PAHs from coal-ash in seawater was determined by fluorescence spectrophotometer. The amounts of PAHs from coal-ash soaked before and after in seawater were also analysed by reversed high performance liquid chromatography with UV or fluorescence detectors. The results show that the static state releasing and adsorption

of PAHs from coal-ash in seawater are reversible, releasing of PAHs is pool, and PAHs in the fine coal-ash dumped into sea from heat and power plant have little effect to the marine environment.

Key words: coal-ash, PAHs, releasing, seawater.

Spectrophotometric Determination of Anionic Surfactants in Water with Bromocresol Green and Cetylpyridinium Bromide. Wang Yongsheng et al. (Hengyang Medical College, Hengyang 421001); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 75—77

In this paper a spectrophotometric method has been developed for the determination of anionic surfactants in water with bromocresol green (BCG) and cetylpyridinium bromide (CPB). Sodium dodecylbenzenesulfonate (SDBS) and sodium dodecylsulfate (SDS) were determined at 614 nm and pH range of 5.5—9.0. In the concentration range of 0—80 µg/10 ml for SDBS and 0—75 µg/10 ml for SDS, both of them obey Beer's law in the presence of 86 µg CPB. The apparent molar absorptivities are $2.9 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for SDBS and $3.1 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for SDS. The proposed method has been applied to the determination of anionic surfactants in river water and wastewater. The average recovery of environmental water samples was 99.3% and the relative standard deviation was less than 3.0%.

Key words: anionic surfactants, bromocresol green, cetylpyridinium bromide, spectrophotometry.

Photometric Determinations of Nickel and Copper in Wastewater by Reversed Flow Injection Analysis. Wang Peng et al. (Department of Applied Chemistry, Harbin Institute of Technology, 150006); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 78—79

The new wastewater monitoring system by use of reversed flow injection spectrophotometry has been developed with injection of different reagents to produce similar color compounds by chemical reactions. The system has been used to simultaneous determination of nickel and copper in wastewater. The detection frequency of the method is 60 samples h⁻¹, the minimum detection limits are 0.03 µg Ni ml⁻¹ and 0.04 µg Cu ml⁻¹ respectively.

Key words: environmental monitoring, flow injection analysis, nickel, copper.

Acidification Models and Their Application to the Determination of Critical Load for Acid Deposition. Xie Shadong et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 80—84

This paper briefly discusses different models developed abroad in the study of precipitation effects to predict the long-term effects of acid deposition on soil, surface water, ground water and lakes in the past ten years. The basic methods to establish these models and the principles to apply them to the determination of critical load for acid deposition are presented based on through comparisons and analyses.

Key words: acidification model, critical load, acid deposition, acid rain.

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