

表 5 本方法与标准法试剂费用比较

比较项目	本方法		标准法	
	用量	费用× 100 (元)	用量	费用× 100 (元)
重铬酸钾 (g)	0.12	0.42	0.12	0.42
硫酸汞 (g)	0.40	2.40	0.40	2.40
硫酸亚铁铵* (g)	0.75	0.52	0.75	0.52
硫酸 (ml)	16.50	8.42	30	15.30
磷酸 (ml)	3.50	3.93	0	0
硫酸银 (g)	0	0	0.40	49.12
硫酸锰 (g)	0.20	0.30	0	0
合 计	15.99		67.76	
回流时间 (min)	60		120	

* 按平均消耗 0.1 N 硫酸亚铁铵 18 ml 计算。

结 论

本实验结果说明, 硫酸锰对重铬酸钾氧

化还原性物质有较强的催化作用, 用硫酸锰代替硫酸银作催化剂, 在硫酸磷酸混合溶液中, 可快速测定废水 COD。测定精度和准确度较高, 回流时间由标准法的二小时缩短至一小时, 试剂费用比标准法降低 75%。

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离子交换分离偶氮氯膦 III 钡光度法 快速测定地表水中的硫酸根

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摘要 本文报告一个测定硫酸根的快速光度法, 方法基于在酸性乙醇介质中 SO_4^{2-} 与 CPAIII-Ba^{2+} 的反应。在 15 毫升显色液中, SO_4^{2-} 浓度介于 20—120 微克遵守比尔定律, 表观摩尔吸光系数 $\epsilon' = 6.3 \times 10^3 \text{ 升} \cdot \text{摩尔}^{-1} \cdot \text{厘米}^{-1}$ 。显色体系至少能稳定 24 小时, 阳离子的干扰用强酸性阳离子交换树脂分离。水样测定的相对标准偏差为 1.85—3.10%。

水质中硫酸根的测定, 常用硫酸钡比浊法和铬酸钡间接光度法^[1-3]。前法简便, 但工作曲线线性关系不良, 定量精度较差; 后法则需分离铬酸钡沉淀, 操作手续较繁, 我们曾用偶氮氯膦 III 间接光度法测定硫酸根^[4], 但也未解决沉淀分离之弊。本文提出用偶氮氯膦 III 钡作显色剂测定硫酸根, 方法简便快速, 应用于地表水中硫酸根的测定, 结果甚佳。

实 验 部 分

一、仪器和试剂配制

721 型分光光度计。

偶氮氯膦 III 钡溶液 (A) $8 \times 10^{-4} \text{ M}$ 的偶氮氯膦 III 的 95% 乙醇溶液 (B) $4 \times 10^{-4} \text{ M}$ 氯化钡溶液: 称取结晶氯化钡 ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) 97.7 毫克溶于 10 毫升 1M 盐酸中, 然后用 95% 乙醇稀释至 1 升。使用

前按需量将 (A) 液与 (B) 液等体积混合。

硫酸根标准溶液 称取无水硫酸钠 1.480 克溶于水, 定容至 1 升。此贮备液每毫升含硫酸根 1 毫克。用时用水稀释至所需浓度。

732 强酸型阳离子交换树脂。

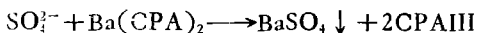
二、实验方法

取适量硫酸根(不超过 120 微克)标准溶液于 25 毫升比色管中, 加水补足至 5 毫升。然后加入偶氮氯膦 III 钡溶液 10 毫升, 充分混匀后放置 1 小时, 以试剂空白作参比, 用 1 厘米比色皿于波长 500 纳米处测定吸光度。

结果和讨论

一、反应原理

在本实验条件下, 我们用连续变化法和摩尔比法测定偶氮氯膦 III 钡络合物的组成, 均得一致结果: $\text{Ba}^{2+}:\text{CPAIII} = 1:2$ 。故试剂用此摩尔比配制。其化学式可表示为 $\text{Ba}(\text{CPAIII})_2$ 它与硫酸根的反应为:



于是测定反应定量释放的 CPAIII 便可定量硫酸根

二、吸收光谱

实验结果如图 1 所示。偶氮氯膦 III 钡络合物有两个吸收峰, 分别位于 610 和 650 纳米处, 加入硫酸根后析出的偶氮氯膦 III 仅有一个吸收峰, 位于波长 500 纳米处, 故实验选用此波长为测量波长。

三、酸度的影响

实验结果表明, 显色液中盐酸浓度在 $3.3 \times 10^{-3} - 1.3 \times 10^{-2} \text{M}$ 时, 吸光度达最大值且恒定。超过上述范围, 吸光度逐渐下降, 待盐酸超过 0.13 M 时, 络合物全部分解, 吸光度趋于零。

考虑到实际样品分析中, 水样经阳离子交换剂处理后已为酸性, 故实验中我们选用盐酸浓度为 $3.3 \times 10^{-3} \text{M}$ 。

四、乙醇浓度的影响

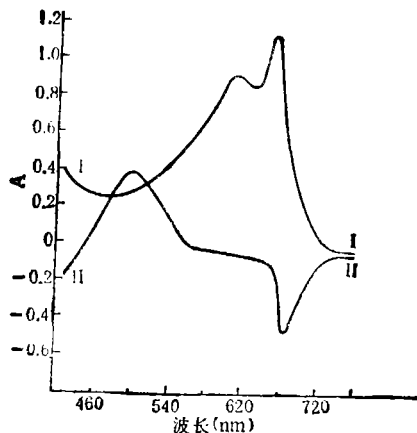


图 1 吸收曲线

曲线 I $\text{Ba}(\text{CPA})_2$ 络合物, 水参比 $[\text{Ba}(\text{CPA})_2] = 2.67 \times 10^{-3} \text{M}$ 1cm 比色皿

曲线 II $\text{Ba}(\text{CPA})_2$ 中加入 SO_4^{2-} 80 $\mu\text{g}/15 \text{ ml}$ 1cm 比色皿 用 $\text{Ba}(\text{CPA})_2$ 参比

参比浓度 $[\text{Ba}(\text{CPA})_2] = 1.33 \times 10^{-4} \text{M}$

在显色液中加入乙醇, BaSO_4 的溶解度降低, 上述反应平衡便向右移动, 随着乙醇浓度的增加, 方法的灵敏度也相应提高, 为实验上的方便, 本文选用乙醇浓度为 63%。

五、显色剂浓度的影响

从实验中我们观察到随偶氮氯膦 III 钡浓度的增加, 工作曲线的浓度范围也相应增宽, 但试剂浓度过高时, 参比液的底色强度过深, 故实验中选择 $\text{Ba}(\text{CPA-III})_2$ 浓度为 $1.33 \times 10^{-4} \text{M}$ 。

六、发色时间和显色体系的稳定性

在室温下, 反应到达平衡约需 1 小时, 此后吸光度保持稳定, 至少可达 24 小时。

七、干扰及其消除

在本实验条件下, 凡能与 CPAIII 络合的阳离子如 Ca^{2+} 和 Sr^{2+} 等均干扰, 本文用强酸型阳离子交换树脂予以分离; 在酸性介质中, 下列存量(毫克计)的阴离子无影响: $\text{PO}_4^{3-}(2)$, $\text{C}_2\text{O}_4^{2-}(1)$, $\text{CO}_3^{2-}(1)$, $\text{NO}_3^- (10)$, $\text{IO}_3^- (0.5)$, $\text{F}^- (0.5)$, $\text{WO}_4^{2-} (0.2)$, $\text{MoO}_4^{2-} (0.025)$, $\text{CrO}_4^{2-} (0.002)$ 。大量 Cl^- 也无干扰。若在显色液中加入抗坏血酸, 则 50 微克 CrO_4^{2-} 和 10 微克 MnO_4^- 无影响。

表 1 回收率实验

样品编号	SO ₄ ²⁻ 含量 (μg)			回收率 (%)
	原含量	加入量	测得量	
B ₁	35.4	40	74.1	98.2
		80	111.4	96.6
B ₂	32.2	40	70.2	97.2
		80	109.0	97.6
B ₃	38.6	40	75.8	96.4
		80	118.4	99.8
B ₄	39.0	40	76.7	97.1
		80	118.8	99.8
B ₅	31.4	40	72.5	101.6
		80	110.4	99.1

八、遵守比尔定律范围和方法灵敏度

在实验条件下, SO₄²⁻ 浓度介于 20—120 微克/15 毫升遵守比尔定律, 但校正曲线不通过原点。显色液中乙醇浓度愈高愈接近原点。表观摩尔吸光系数 $\varepsilon' = 6.3 \times 10^3$ 升·摩尔⁻¹·厘米⁻¹; 桑德尔灵敏度为 15 纳克·厘米⁻²。

九、方法的准确度和精密性

吸取通过阳离子交换柱的水样适量(含 SO₄²⁻ 120 微克以内)于 25 毫升比色管中,加

表 2 地表水中硫酸根的测定

样品编号	个别测定值 (mg/L)	平均值 (mg/L)	标准差 (mg/L)	变异系数 (%)
B ₁	5.0 5.1 5.0 5.0 5.1	5.10	0.094	1.85
	5.2 5.1 5.2 5.0 5.2			
B ₂	4.1 4.2 4.3 4.1 4.3	4.23	0.095	2.24
	4.2 4.3 4.2 4.4 4.2			
B ₃	4.9 5.0 4.9 5.2 5.1	5.04	0.11	2.13
	5.0 5.2 5.0 5.1 5.0			
B ₄	5.2 5.4 5.3 5.5 5.3	5.41	0.12	2.21
	5.4 5.5 5.4 5.6 5.5			
B ₅	5.0 4.7 5.0 4.9 5.0	4.86	0.15	3.10
	4.9 5.0 4.8 4.6 4.7			

水补足至 5 毫升,按实验方法测定吸光度,所得结果列于表 1、2。

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微生物膜 BOD 电极的研究

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摘要 本文介绍了用四种微生物膜制备的 BOD 电极及其测定废水 BOD 的试验情况。结果表明, 电极对 BOD 标准物质线性响应范围为 10—60 mg/L, 响应达到平衡时间为 4 min (对低限浓度溶液)到 7 min (对高限浓度溶液), 连续稳定地工作寿命在 20 天以上; 用该电极和 BOD₅ 标准法对照测定 7 种废水的 BOD 值, 测定结果的相关性较好。

在水质监测中, 生化需氧量 (BOD) 的测定广泛采用需时 5 天的标准检验法, 虽然也出现了差压法、库仑法等仪器测定方法, 但测定时间并未缩短, 而近年来出现的微生物

膜电极法是一种快速测定方法^[1-4], 如经过完善后用于实践, 则对监控废水处理等工作具

* 参加本试验工作的还有高云生、贺桂荣、刘良玉、单金会、刘进、冯秀娟、安文德、白君素等。

to determine the optimal numbers of stations for monitoring water quality in Xiamen region, Fujian Province. (See pp. 26—30)

Radiative Levels of Indoor Environment in Xia'n City

Qiang Yonggang et al. (Shaanxi Provincial Station of Sanitation and Epidemic Prevention, Xi'an)

This paper presents that the radiative levels of indoor environment in Xi'an City were investigated with a high sensitivity thermoluminescent dosimeter—LiF(Mg, Cu, P).

The radiative doses absorbed by local residents were also evaluated. The results show that average γ -radiation dose in air absorbed by the residents seems to be $9.10 \times 10^{-8} \text{ Gy} \cdot \text{h}^{-1}$ and the contributive component of cosmic ray to be $2.82 \times 10^{-8} \text{ Gy} \cdot \text{h}^{-1}$. The annual effective dose equivalent and collective effective dose equivalent have been determined to be $374 \mu\text{Sv}$ and $1.36 \times 10^8 \text{ Man} \cdot \text{Sv}$. (See pp. 30—34)

Study on Treatment and Utilization of Industrial Wastewater in Dexin Copper Mine

Ni Dong (Beijing Central Engineering and Research Institute for Non-ferrous Metallurgical Industry, Beijing)

Dexin Copper Mine is one of the largest mines in the world. The industrial wastewater discharged from the mine is more than $300000 \text{ M}^3/\text{day}$. The acidic water from the mine in brown colour contains a lot of heavy metal ions, such as ferric ion and copper ion etc. The pH of acidic water is 2 or 3 while the pH of the tailing slurry and sulfur-bearing basic water discharged from the concentrator is 10 to 13. As it contains comparatively high sulphur ions, this water threatens the environment around the lower reaches of the river and causes big loss of resources.

Since Fe^{3+} in mine acidic water is ten times higher than copper ion, the addition of lime can remove Fe^{3+} in the first stage and sulphur-bearing wastewater is added to form sulphide settlings and recover copper in the second stage. In the third stage, the process with addition of basic wastewater for neutralization is adopted and through multitypes of tests, the water can be discharged out or recycled for use. At the same time, copper ion in water can be effectively recovered, thus environmental and economic benefits are achieved. (See pp. 34—39)

Ambient Two-Phase UASB Process for Treatment of Brewery Wastewater

Yan Yuegen, Liu Jingsong and Hu Jicui (Department of Environmental Engineering, Tsinghua University, Beijing)

Performance of ambient (25°C) two-phase UASB process treating malting wastewater (diluted to 2000 mgCOD/L) has been investigated. It is shown that this process has a high treatability with organic loading rate of $18 \text{ kgCOD/m}^3 \cdot \text{d}$, HRT of 2.7 h and soluble COD removal of 86% on a methane phase base. A systematic research is also done on the performance of acid- and methane-phase reactors and property of granules. (See

pp. 39—43)

Rapid Method for Spectrophotometric Determination of Sulphate in Surface Water Using Ion-Exchange Separation and the Sulphate and Chlorophosphonazo III (CPA III)- Ba^{2+} Complex Reaction

Qiu Xingchu, Liu Guoping and Zhu Yingquan (Research Institute of Environmental Science of Ganzhou Prefecture Jiangxi Province)

A rapid spectrophotometric method for determination of SO_4^{2-} in surface water is reported. It is based on the reaction of CPA III- Ba^{2+} complex with SO_4^{2-} in acidic medium in the presence of ethanol. Beer's law is obeyed up to $120 \mu\text{g}$ of SO_4^{2-} in final solution. The molar absorptivity is $6.3 \times 10^3 \text{ liters} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 500 nm, and the coefficient of variation varies from 1.85 to 3.10%. The absorbance remains stable for at least 24h and the interfering ions in separated by strongly acidic cation-exchange resin. (See pp. 51—53)

Study on the Microbial Membrane Electrode for BOD Determination

Sun Yusheng and Liu Xianmei (Hebei Institute of Chemical Technology and Light Industry, Shijiazhuang)

The electrodes of four different microbial membranes have been prepared for determining BOD in wastewater. The linear response range of the electrodes is 10—60 mg/L for BOD certified reference materials. The time for reaching equilibrium is between 4 minutes (for low limit concentration) to 7 minutes (for high limit concentration). The electrodes has sustained the initial sensitivity over 20 days. Compared with the standard method for five days, the microbial electrodes prepared for determination of BOD have obtained good results. (See pp. 53—57)

Multi-Target Optimization of Environment-Economic System

Liu Youci and Ying Longgen (Department of Geography, East China Normal University, Shanghai)

Target programming as a kind of multi-target optimization technique has been found to be increasingly utilized. Taking Shanghai Taopu Chemical Industry District as a case study, the authors present three alternative schemes for reducing discharge of pollutants: (1) reduction by 5%; (2) reduction by 10%; (3) discharge in conformity with norm. Then, they set up a model of target programming for the environment-economic system of this industrial district and performed multi-target optimization simulation for the system by means of a computer. The results of optimization provide concrete approaches to rational adjustment of trade structure, which will better coordinate the two principal factors of the system, i. e. environment and economy so as to redress the existing random state of environment-economic system of the district. The system has its integral and comprehensive functions. The optimization schemes not only
(Continued on p. 83)