

串联组合离子选择电极的研究

—利用 Ag_2S 电极测定废水中 S^{2-} 离子含量

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摘要 本文依据电池串联原理将多组电极串联组合,减少了因电动势测量误差而造成的测定浓度的相对误差,明显地提高了测定的精密度和准确度。对工业废水中 S^{2-} 离子含量的测定结果令人满意。其相对偏差低于 2.5%,方法回收率为 97.5—101.7%,明显优于现有离子选择电极测定方法。与比色法进行比较,测得结果基本一致。

关键词 电极串联组合;硫离子选择电极;硫离子含量。

用硫离子选择电极测定 S^{2-} 离子含量的报道甚多^[1-3],但测定的精密度和准确度不甚理想。如何提高离子选择电极法测定的精密度和准确度仍是一项有待继续探索的课题。本文采用串联组合形式对工业废水中 S^{2-} 离子含量进行了测定,获得了满意结果。

一、实验部分

(一) 仪器和试剂

PHS-3C 酸度计(上海第二分析仪器厂)。

CSB-S-1 型硫离子选择电极(长沙半导体材料厂)。

217 型双液接饱和甘汞电极(外盐桥充 0.1mol/L KNO_3 溶液)。

S^{2-} 离子抗氧化缓冲剂(SAOB):40g 氢氧化钠,10g 乙二胺四乙酸钠,6g 氯化钠,10g 抗坏血酸溶于 1L 容量瓶中稀释至刻度(临用时配制)。

S^{2-} 离子标准溶液(3.3×10^{-2} mol/L):称取用蒸馏水洗过的 $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ 晶体 2.0g,加 25mL SAOB 溶液和 225ml 蒸馏水,于塑料瓶中低温避光保存。临用时用碘量法标定。

所有试剂皆为分析纯,实验用水为蒸馏水。

(二) 测量装置

测量装置如图 1 所示。

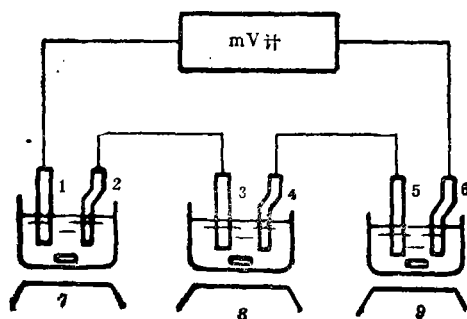


图 1 测量装置示意图

1,3,5——指示电极 2,4,6——参比电极
7,8,9——搅拌器

(三) 实验方法

取适量 S^{2-} 离子溶液于 100mL 容量瓶中,加入 25ml SAOB 溶液,用蒸馏水稀释至刻度,分盛于 3 个 100mL 干烧杯中,插入饱和甘汞电极和 S^{2-} 离子选择电极,按前述装置,由稀至浓测量其电位值,作工作曲线。

取适量废水试液,用同法测电位值,由工作曲线求 S^{2-} 离子的含量。

二、结果与讨论

(一) 单组电极与串联电极组的比较

电动势测量误差 ΔE 将影响测定的准确度。一般说来,对于二价 S^{2-} 离子,电极电位值测定误差 ΔE ,每 $\pm 1\text{mV}$ 将产生约 $\pm 8\%$ 的浓度相对误差 $(\frac{\Delta c}{c} \times 100 \approx 8\Delta E)^{[4]}$,若将 n 组电极分插于同浓度的不同溶液中,再将电极依次串联,其相对误差将降至原误差的 $\frac{1}{n}$ 。即

$$E_{总} = E_1 + E_2 + \dots + E_n$$

$$= K - n \times \frac{0.059}{2} \lg c$$

当 $n = 3$ 时,

$$\text{相对误差}(\%) = \frac{\Delta c}{c} \times 100$$

$$\approx \frac{8\Delta E}{3} \approx 2.7(\%)$$

取定量 S^{2-} 离子标准溶液,加适量 SAOB 溶液,用蒸馏水依次稀释成 1.0×10^{-2} 、 1.0×10^{-3} 、 1.0×10^{-4} 、 1.0×10^{-5} 、 $1.0 \times 10^{-6}\text{mol/L}$ 溶液,按上述实验方法测其电位值。以 PC (浓度的负对数)对 E 作图,得工作曲线(图 2)。由图 2 看出,当双组电极串联时,曲线斜率为单组电极的 2 倍,三组电极串联时,斜率为其 3 倍,继续增加电极组数,由于液接面增多,液接电位影响增大,致使测量的稳定性降低,本实验选用 3 组电极串联形式。

(二) 干扰实验

在选定实验条件下, F^- 、 NO_3^- 、 Br^- 、 Cl^- 、 I^- 、 SO_4^{2-} 、 HPO_4^{2-} 、 SO_3^{2-} 、 $S_2O_3^{2-}$ 皆不干扰测定。某些氧化性物质和 Pb^{2+} 、 Zn^{2+} 等金属离子的干扰,由于加入 SAOB 溶液而被消除。

(三) 样品分析

取工业废水水样,按上述实验步骤,不经前处理,直接以 3 组电极串联形式测定 S^{2-}

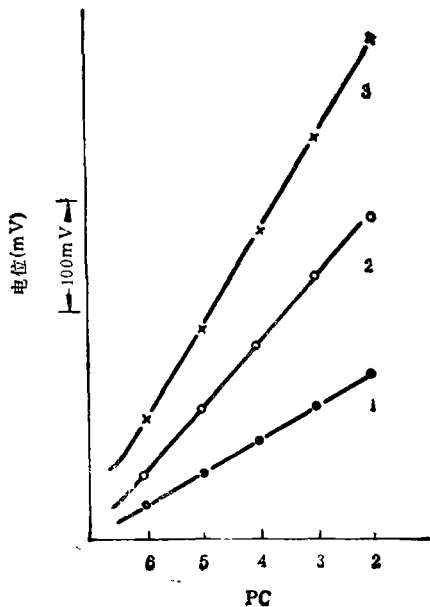


图 2 工作曲线

1——单组电极 2——双组电极 3——三组电极

离子含量,测定结果见表 1。

表 1 废水中 S^{2-} 离子含量测定结果

样 品	测定值 (mg/L)	平均值 (mg/L)	相对偏差 (%)	比色法 ^[5] 测定值 (mg/L)
湖南大学工厂水样	0.130	0.133	-2.3	0.126
	0.133		0.0	0.130
	0.136		+2.3	0.142
	0.131		-1.5	0.128
	0.134		+0.8	0.135
师大工厂水样	0.360	0.367	-1.9	0.350
	0.372		+1.3	0.360
	0.358		-2.5	0.378
	0.368		+0.3	0.380
	0.375		+2.2	0.352
造纸厂水样	3.50	3.50	0.0	3.48
	3.44		-1.7	3.42
	3.58		+2.3	3.50
	3.46		-1.1	3.52
	3.51		+0.3	3.46
制革厂水样	25.02	24.91	+0.4	24.68
	25.23		+1.3	25.20
	24.62		-1.2	25.02
	24.86		-0.2	24.91
	24.82		-0.4	24.96

表 2 回收率试验

样品	样品中硫含量 (μg)	加入硫量 (μg)	应得量 (μg)	实测量 (μg)	回收率 (%)
湖南大学 工厂水样	1.33	1.21	2.54	2.55	100.8
		2.42	3.75	3.70	98.0
		4.84	6.17	6.12	99.0
	2.66	1.21	3.87	3.85	98.3
		2.42	5.08	5.06	99.2
		4.84	7.50	7.41	98.1
师大工厂 水样	3.67	1.21	4.88	4.85	97.5
		2.42	6.09	6.09	100.0
		4.84	8.51	8.49	99.6
	7.34	1.21	8.55	8.52	97.5
		2.42	9.76	9.72	98.3
		4.84	12.18	12.20	100.4
造纸厂 水样	3.74	1.21	4.95	4.94	69.2
		2.42	6.16	6.11	97.6
		4.84	8.58	8.49	98.1
	7.48	1.21	8.69	8.67	98.3
		2.42	9.90	9.85	98.0
		4.84	12.32	12.24	98.4*
制革厂 水样	6.23	1.21	7.44	7.46	101.7
		4.84	11.07	10.98	98.1
		9.68	15.91	15.77	98.6
	12.46	1.21	13.67	13.64	97.5
		4.84	17.30	17.21	98.1
		9.68	22.14	22.08	99.4

(四) 回收率试验

将定量 S²⁻ 离子标准溶液分别加入到废水试液中,按实验方法测定回收率,结果见表 2。

三、小 结

本文采用多组电极串联形式,提高了离子选择性电极法的精密度和准确度。文中在理论上对此作了简要的阐述,并对电极组合形式进行了比较研究,从对废水中 S²⁻ 离子含量测定的实验中看出,此法简便、快速,结果准确,是提高离子选择电极法准确度的有效途径。

参 考 文 献

- [1] 邹景瑶等,化学传感器,7(3),61(1987).
- [2] 董英惠等,化工环保,7(3),159(1987).
- [3] 冯建军,离子选择电极通讯,4(2),101(1984).
- [4] 朱明华,仪器分析,第 133 页,高等教育出版社,北京,1983 年.
- [5] 中国医学科学院卫生研究所编,水质分析法,第 106 页,人民卫生出版社,北京,1974 年.

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添加不同化学形态的外源镉进行逐级回收研究,证实 Tessier 提出的颗粒态沉积物中痕量重金属逐级提取程序用于土壤中镉的化学分级基本可行。

(二) 跨级现象暗示,推荐的级分浸提剂可能对某些土壤而言,对相邻级分有一定程度的作用。不过,由于不同土壤、污泥、颗粒物的异质性,用 Tessier 程序或其它程序得到的某元素化学形态分布通常只有相对的意义。

(三) 添加 μg 级的固体状态的不同化学形态的外源镉是困难的,准确计量较难,模

拟土壤中各种天然地球化学相更难。本文采用共沉淀标准添加物获得初步成功,为解决这一难题迈出了一大步。

参 考 文 献

- [1] Tessier, A. et al., *Anal. Chem.*, 51 (7), 844 (1979).
- [2] 俞穆青等,环境科学学报,1(2),180(1981).
- [3] 陈学诚等,农业环境保护,7(4),33(1988).
- [4] 国家计量局,中华人民共和国标准物质目录(1988).
- [5] 陈学诚等,河北化工学院学报(1),76(1988).
- [6] Tessier, A. et al., *J. Geochem. Explor.*, 16, 77(1982).

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A group of silver sulfide electrode combined in series was applied to determine sulfide ion in wastewater. The experimental results show that the series combination of the electrodes greatly improved the accuracy and precision. The relative deviation is smaller than 2.5% and the recoveries are in the range of 97.5—101.7%.

Key Words: sulfide ion selective-electrode; sulfide ion.

Biochemical Mechanism of Influence of Dilution Multiple on BOD Measurement. Han Xiangkui, Zhou Chunsheng, Dong Chunlan (Jilin Architectural and Civil Engineering Institute): *Chin. J. Environ. Sci.*, 12(6), 1991, pp. 37—39

This paper discusses the biochemical mechanism of the influence of dilution multiple on the results of BOD measurement. The research show that the cause that dilution multiple influences BOD measurement results is the difference in the ratios of food to microorganism (F/M) in incubation systems. Under the same seeding condition, the greater the dilution multiple, the greater BOD and the constant of oxygen consumption rate would be, while BOD_u would basically keep constant. Further research results for the standard solution containing glucose and glutamic acid show that the peak values of active bacterial counts in both systems of different F/M values appeared in two days and the peak values of the system of higher F/M ratio appeared later than the other system. The oxygen consumption rate of bacterial population before endogenous phase is greater than that measured during the endogenous phase.

Key Words: dilution multiple; BOD; food microorganism ratio.

Linear Regression Method for the Determination of both Longitudinal Dispersion Coefficient and Transverse Mixing Coefficient of River by Instantaneous Dumping Tracer Test. Zhang Jiangshan (Institute of Environmental Science of Fujian Normal University): *Chin. J. Environ. Sci.* 12(6), 1991, pp. 40—43

Starting from the equation for two-dimensional concentration distribution of instantaneous dumping, a linear equation $Y = AT + B$ was mathematically deduced, in which variables Y and T can be expressed with t, c, and C_t, while coefficients A and B are composed of parameters of D_x and D_y to be determined, longitudinal and transverse flow velocities of the river u and v as well as the coordinates of the observation point X and Y. Through

linear regression, A and B can be determined from C_i and T_i, the observed experimental data. Then D_x and D_y can be calculated by solving the equation.

Key Words: river water quality model; longitudinal dispersion coefficient; transverse mixing coefficient.

Recovery of Organic Vapors with Composite Hollow Fiber Membrane. Wang Dongliang, Yin Guilin, Ma Miaojiang, Zhang Guihua, Xu Renxian, Jiang Guoliang (Dalian Institute of Chemical Physics, Chinese Academy of Sciences): *Chin. J. Environ. Sci.*, 12(6), 1991, pp. 44—47

Polydimethylsiloxane-polysulfone composite hollow fiber membrane was prepared by the novel phase inversion process and coating process. A hollow fiber module with 10 mm in diameter and 500 mm in length was built, with which hexane vapor was removed from nitrogen stream. The effects of pressure, feed concentration and nonpermeable flux on the concentration of hexane in the permeable and nonpermeable streams, the hexane permeability flux and the separation factor for hexane and nitrogen were investigated. The results indicate that the composite hollow fiber membrane may efficiently recover organic vapors from air.

Key Words: composite hollow fiber membrane; organic vapors.

Study on the Chemical Treatment of Straw Pulp Effluent-Black Liquor Zhou Zhiliang, Yang Jinqun, Zhao Xiangyi (Department of Environmental Protection, Changsha Research Institute of Mining and Metallurgy, Changsha): *Chin. J. Environ. Sci.*, 12(6), 1991, pp. 48—51

Silicon in the black liquor was firstly removed by coagulation and centrifugation and lignin was separated from the black liquor with acidification-precipitation. The study also focused on the removal of COD of the lignin free black liquor by coagulation and catalytic oxidation. Experimental results indicate that the technique mentioned above can effectively treat straw pulp effluent-black liquor. COD Value of the treated water can be less than 300mg/L and lignin can be recovered as by-product.

Key Words: straw pulp effluent-black liquor; acidification-precipitation; coagulation; catalytic oxidation;

Calculation and Determination of Biomass