

聚乙烯吡咯烷酮修饰碳糊电极溶出 伏安法测定水中硝基酚

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摘要 提出用聚乙烯吡咯烷酮(PVPr)修饰碳糊电极同时测定水中对硝基酚和2,4-二硝基酚的方法。在0.1 mol/L KCl的酚试液中开路富集,然后在磷酸盐缓冲液介质中溶出,以微分脉冲伏安法测定,检测限分别为0.50 $\mu\text{g/L}$ 和1.80 $\mu\text{g/L}$ 。讨论了测定的影响因素以及2种硝基酚在该修饰电极上的反应机理。测定了地面水中对硝基酚和2,4-二硝基酚的含量,回收率分别为 $90\pm6\%$ 和 $86\pm5\%$ 。

关键词 聚乙烯吡咯烷酮, 修饰碳糊电极, 硝基酚。

气相色谱法测定硝基酚一般需经衍生化处理^[1]。有人提出用离子选择性电极法测定对硝基酚^[2]。本文提出了聚乙烯吡咯烷酮修饰碳糊电极溶出伏安法同时测定水中对硝基酚和2,4-二硝基酚,具有灵敏度高、测定速度快、设备简单,操作方便和可免除样品的前处理等优点。

1 实验部分

1.1 仪器及试剂

仪器: F-78型微分脉冲极谱仪;磁力搅拌器;挤压式聚乙烯吡咯烷酮修饰碳糊电极(自制);铂丝对电极;Ag-AgCl参比电极。

试剂: 聚乙烯吡咯烷酮(Polyvinylpyrrolidone)(HEIDE/BERG, New York);对硝基酚(C. P.), 2,4-二硝基酚(C. P.)(上海试剂三厂);液体石蜡(上海大均化工厂);石墨粉(光谱纯);NaOH-KH₂PO₄缓冲液;KCl(A. R.)等。

1.2 实验方法

电极的制备:称0.5 g光谱纯石墨粉和0.05 g PVPr充分混匀,用滴管滴入8—9滴液体石蜡调成糊状,装于内径为4 mm的玻璃管中,填装高度约1 cm,用一根直径约为2 mm的铜棒引出导线,压紧,在光滑的纸上抛光。

测定步骤:将上述所制的电极作为工作电极,置于0.1 mol/L KCl的酚试液电解池中(内含10 ml试液),在磁力搅拌下富集一定时间,然后在pH缓冲液介质中,进行伏安扫描,用微分脉冲法记录电流电位(I_p - E)曲线。电极用后在相应的磷酸盐缓冲液(pH 7.0)中浸渍1 h(或将碳糊挤出少许,在滤纸上擦去,再进行抛光),即可用于下一次实验。

2 结果与讨论

2.1 溶出液最佳pH值的选择

在其它条件不变的情况下,改变溶出液(磷酸盐缓冲液)的pH值,测定对硝基酚和2,4-二硝基酚的峰电流的大小,得到图1(a)和(b)。可见,这2种酚的 I_p -pH图相似,pH值6—8内峰电流大且稳定,这可能和这2种酚与PVPr的结合力以及这2种酚在碱性中的不稳定性有关。故本试验选择溶出液的pH为7.0。在测定过程中还发现,一般随着溶出液pH值的增大,峰电位会向负移。

2.2 2种酚在PVPr修饰碳糊电极上特性

将PVPr修饰碳糊电极直接置于pH 7.0的

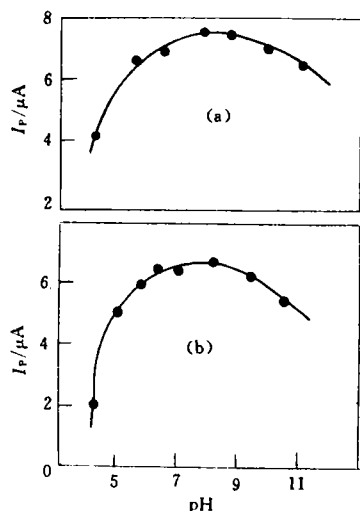


图1 溶出液的 pH 值对硝基酚的峰电流的影响曲线

(a) 对硝基酚 (b) 2, 4-二硝基酚

硝基酚浓度分别为 5.60 mg/L (对硝基酚) 和 14.50 mg/L (2, 4-二硝基酚); 富集时间为 6 min; 脉冲振幅为 50 mV; 脉冲间隔为 0.5 s; 扫描速度为 10 mV/s

磷酸盐缓冲溶出液中, 从 0~+1.25 V 进行循环伏安扫描, 即空白扫描 (见图 2)。说明在该电势范围内无氧化还原峰出现。

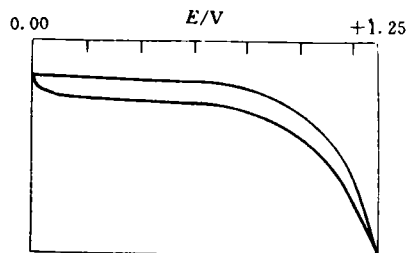


图2 PVPPr 修饰电极的循环伏安图

对硝基酚和 2, 4-二硝基酚的循环伏安曲线, 由图 3(a)(b) 所示。曲线显示 2 种酚的溶出电位分别为 +0.88 V 和 +1.12 V (VS Ag-AgCl pH7.0)。扫描时未出现对称还原峰, 说明 2 种酚在此修饰电极上的反应过程是不可逆的。

2.3 电极中修饰剂含量及富集时间的影响

随着电极中修饰剂量的增加和富集时间的延长, 其测定的灵敏度增高, 但考虑到 PVPPr 的水胀性和一般污水中酚类的含量, 选择 PVPPr 修饰剂量为 10%, 富集时间为 6 min。

对硝基酚浓度 6.50 mg/L, 2, 4-二硝基酚浓度 23.00 mg/L; 溶出液的 pH 为 7.0; 其他测

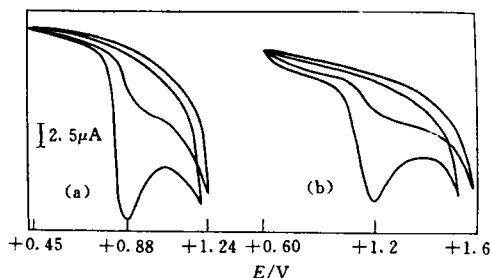


图3 硝基酚的循环伏安图

(a) 对硝基酚 (b) 2, 4-二硝基酚

定条件和图 1 相同。

2.4 富集介质的选择

将 PVPPr 修饰电极分别置于 0.1 mol/L KNO_3 , 0.1 mol/L KH_2PO_4 和 0.1 mol/L KCl 的含酚试液中富集, 发现在 0.1 mol/L KCl 溶液中富集所测得的峰形最稳且最窄。故选择了 0.1 mol/L KCl 作为富集酚的介质。

2.5 对照试验

由图 4 可见, 在所选定的条件下, 对硝基酚

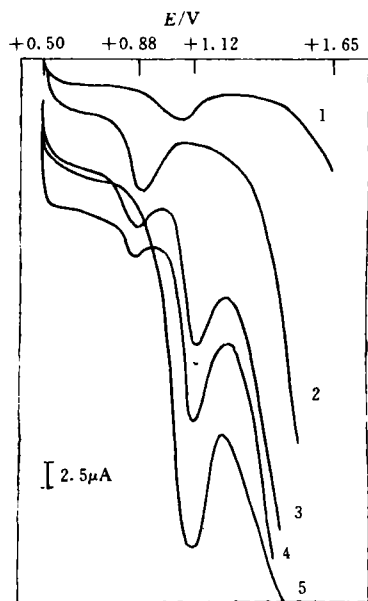


图4 对硝基酚和 2, 4-二硝基酚的伏安曲线

曲线 1 由纯碳糊电极测得。对硝基酚浓度: 5.10 mg/L; 2, 4-二硝基酚浓度: 25.20 mg/L。曲线 2 至 5 由 PVPPr 修饰电极测得, 曲线 2 是对硝基酚的伏安曲线。对硝基酚浓度: 5.10 mg/L。曲线 3 和曲线 4 是 2 种硝基酚混合液的伏安曲线。前者, 对硝基酚浓度: 2.55 mg/L, 2, 4-二硝基酚浓度: 12.60 mg/L。后者, 对硝基酚浓度: 2.00 mg/L; 2, 4-二硝基酚浓度: 19.20 mg/L。曲线 5 是 2, 4-二硝基酚的伏安曲线。2, 4-二硝基酚的浓度: 25.20 mg/L。其它测定条件和图 1 相同。

和 2, 4-二硝基酚的电位峰可完全分离, 因而能同时测定这 2 种酚。同时可看出, 用 PVP_r 修饰电极测定这 2 种酚的灵敏度和选择性均比碳糊电极好。

2.6 工作曲线的绘制和检测限的确定

用蒸馏水配制 0—0.55 mg/L 的对硝基酚和 0—0.65 mg/L 的 2, 4-二硝基酚混合试液, 在本法选定的条件下测定。测得的工作曲线如图 5 所示。并将配制溶液逐级稀释, 根据文献 [4] 规定的方法, 确定对硝基酚和 2, 4-二硝基酚的检测下限分别为 0.50 $\mu\text{g/L}$ 和 1.80 $\mu\text{g/L}$ 。

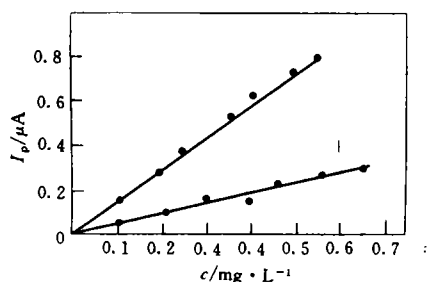


图 5 工作曲线

a. 对硝基酚 b. 2, 4-二硝基酚

2.7 干扰因素的讨论

PVP_r 修饰电极对其他有机物的响应, 如多巴胺等已有报道^[3], 笔者研究了水体中较常出现的一些有机污染物, 如阴离子表面活性剂和阳离子表面活性剂以及一些羧酸类化合物等, 发现在所测硝基酚电势范围内无氧化峰出现。同时还试验了其他酚类对所测的硝基酚的干扰情况, 发现在相同的条件下, 它们的溶出电位 (VS Ag-AgCl) 分别为: 苯酚 0.70 V, 对甲酚 0.57 V, 邻甲酚 0.60 V, 对氯酚 0.66 V, 氯酚 0.66 V, 五氯酚 0.70 V, 以及间苯酚 0.47 V, 对苯二酚 0.30 V, 以上这些酚类中最高的氧化电位为 0.70 V, 而笔者所测的对硝基酚和 2, 4-二硝基酚的氧化电位分别为 0.88 V 和 1.12 V, 故以上这些酚类对这 2 种酚的测定不会产生干扰。进一步研究了同类硝基酚对这 2 种酚的测定干扰性, 发现邻硝基酚和间硝基酚的氧化电位分别为 0.87 V 和 0.86 V, 二硝基酚中, 邻二硝基酚和间二硝基酚的溶出电位分别为 1.13 V

和 1.12 V, 而三硝基酚在所测的电势范围内无氧化峰出现。故本方法所测得的对硝基酚和 2, 4-二硝基酚的含量实为一硝基酚和二硝基酚的含量。通常在自然界中的一硝基酚以邻、对硝基酚为主, 而二硝基酚中以 2, 4-二硝基酚为主,

表 1 实际水样测定结果及其回收率 (mg/L)

酚类	水样	测得值	平均值	加入量	测得值	回收率 (%)	$\bar{X} \pm S$ (%)
对硝基酚	西溪河水	0.12	0.12	0.20	0.30	90	90 ± 6
		0.11			0.30	90	
		0.15			0.31	95	
		0.10			0.29	85	
		0.13			0.29	85	
基酚	西湖水		0.40		0.37	92	86 ± 5
					0.33	83	
					0.41	104	
					0.35	88	
					0.35	88	
2, 4-二硝基酚	西溪河水		0.21		0.17	81	86 ± 5
					0.18	86	
					0.17	81	
					0.18	86	
					0.20	95	
二硝基酚	西湖水		0.40		0.36	90	86 ± 5
					0.32	80	
					0.33	83	
					0.36	90	
					0.33	83	

这和硝基酚形成的难易程度及其用途有关^[5]。至于醛类化合物, 因其不象酚类化合物那样容易形成氢键而被电极强烈吸附, 故对用本法测定硝基酚不应有明显干扰。

2.8 实际水样的测定

用本方法测定了西溪河水 (于 1994-06-16 中午取样, 为雨水季节) 和杭州西湖水 (1994-06-30 取样) 对硝基酚和 2, 4-硝基酚含量, 结果及回收率见表 1。

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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 Sewage. 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 removal 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 restoration 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 evaluated. 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 restoration, demonstrative 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 CH₃Br was trapped by Tenax adsorbent and was determined by gas chromatography with photoionization detector. The CH₃Br concentrations in indoor and

outdoor are 24×10^{-12} (V/V) and 77.4×10^{-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 Cation 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 Cation 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 determined. The determination range of this method is 0–10 µg/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, cation, 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 µg/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 (PVP) 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 µg/L (p-nitrophenol) and 1.80 µg/L (2,4-dinitrophenol). This method had been applied to the determination of nitrophenols in pol-

luted surface water, and the recoveries of p-nitrophenol and 2,4-dinitrophenol were $90 \pm 6\%$ and $86 \pm 5\%$ respectively.

Key words: polyvinylpyrrolidone, modified carbon paste electrode, nitrophenols.

The Content and Evaluation of Lead in Soils and Plants in Both Sides of Roads in Xining Region. Suo Yourui et al. (Northwest Plateau Institute of Biology, Chinese Academy of Sciences, Xining 810001); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 74–76

The content of heavy metal lead in samples of soils and plants was determined by Atomic Absorption Spectrophotometry. The results are as follows: soils and plants are seriously polluted by lead from tail gas of automobiles. The content of lead is higher than that in clean control place: 2.7–4.1 times in soils; 3.0–4.1 times in branches and leaves of poplar; 3.0–3.7 times in wheat seedlings and 1.5–2.3 times in vegetables. Lead contents in soils, trees and crops usually decreased to local background value level in about 80–100 meters distant from both sides of roads.

Key words: both sides of roads, soil, plant, lead.

Principles of the Eco-Environmental Impact Assessment for Development Construction Projects: A Theory of Eco-Environmental Functions Conservation. Mao Wen'yong (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 77–81

All types of ecosystem on the Earth constitute the environment on which the sustainable existence and development of human beings rely, that is, the eco-environment. For a sustainable development strategy, more attention should be paid to evaluating the ecological functions of the environment in an environmental impact assessment for a development construction project. As presented in this paper, such an eco-environmental impact assessment should be based on preserving the environmental functions of ecosystems to assess the impacts on the ecological functions of the environment and to identify the measures for compensating the damaged functions. More than 12 indicators of ecological functions of the environment were identified along with the methods for their valuation suggested. It was also indicated at the same time that, in order to assess the impacts on the ecological functions of the environment, the following three concepts must be set up: ① The concept of the value of ecological resources that is different from the concept of traditional economics, land use, deforestation and water resources development were exemplified to describe the difference between both concepts and the distinguishing between the benefits from two different concepts; ② The concept of

integrating quantity with quality. Land and soil, water quantity and water quality, vegetation cover and diversity, etc., were exemplified to describe the correlation of quantity to quality; ③ The concept of the holistic harmonization of ecosystems and the priority assessment of major influencing factors.

Key words: eco-environmental impact assessment, development construction projects, environmental functions.

An Obstacle Analysis and Policy Recommendation for the Implementation of Cleaner Production in Companies. Zhang Tianzhu (Dept. of Environmental Engineering, Tsinghua University Beijing 100084); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 82–85

This paper systematically analyzes the obstacles encountered in cleaner production process. Under present conditions, the obstacles from awareness, organizational, economic, technical, and knowledge aspects are the main problems. It is a basic guarantee of promoting cleaner production in China to adjust and perfect industrial and environmental policies.

Key words: cleaner production, obstacle, policy.

Discussions on Key Problems of Plasma-Catalysis Flue Gas Desulfurization. Liu Shuhai (Institute of Electrostatics, Dalian University of technology, Dalian 116024); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 86–89

Three approaches for SO_2 removal were summarized: high energetic electron bombardment induced direct dissociation, oxidation by free radicals generated in corona, and thermo-chemical reaction with ammonia. A new way put forward by the author is discussed here of removing ammonia for SO_2 analysis. The performance of this method for flue gas is compared with that for simulated model gas. The differences resulted from gas composition were stressed. Other factors such as temperature, dose of ammonia, pulsed energization conditions were also discussed which affect the performance the most. Some incorrect conclusions in previously published papers from different authors were examined. Some existing key problems which have to be solved for the commercial application also discussed, including energy consumption, ammonia slip and production collection. Feasibility of combination with ESP was also concerned too. It was concluded that the key problem of this method is how to oxidize ammonia sulfite effectively by utilization of oxidizing environment generated by corona discharge with aims to solve simultaneously both problems of high energy consumption and ammonia slip.

Key words: flue gas desulfurization, plasma catalysis, free radicals, high energetic electron bombardment, thermo-chemical.