交流示波极谱滴定废水中的酚

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摘要　鉴于 Br_2 在交流示波极谱曲线(dE/dt-E)上有切口，提出以盐酸和溴化钾的混合溶液作底液，用溴酸钾标准溶液直接滴定水样中酚，以 Br_2 的切口出现指示终点. 由于本法不受色度、浊度等干扰，故省去了预蒸馏等步骤，方法简便、快速. 测定范围为 11.07—2113.2 mg·L^{-1}(以苯酚计)，变异系数小于 0.9%，回收率为 95%—102%.

关键词　酚，交流示波极谱滴定，废水.

在污染源水质监测中挥发酚的测定采用溴化容量法[1]. 该法受沉淀、悬浮物、背景色等干扰，需要预蒸馏. 鉴于 Br_2 在交流示波极谱图上有切口[2]，笔者提出以盐酸及溴化钾的混合液作底液，用溴酸钾标准溶液直接滴定酚，以 Br_2 的切口出现指示终点. 以锅炉厂的煤气发生站含酚废水为样品进行分析，准确度和精密度都符合分析化学的要求.

1　实验部分

(1)　仪器　LS-1A 交流示波极谱滴定仪(山东电讯七厂)；微铂电极为工作电极，铂片(213 型)电极为参比电极；GSP-84-01 型磁力搅拌器(山东电讯七厂). 5 ml 滴定管

(2)　试剂　所有试剂的配制和废水样的稀释都用不含酚的蒸馏水. 无酚水：在全玻璃蒸馏器中加入蒸馏水，加氢氧化钠至强碱性，滴入高锰酸钾溶液至深红色，加入数粒玻璃珠，加热蒸馏. 收集无酚水于硬质玻璃瓶中.

2 mol·L^{-1} KBr 溶液，6 mol·L^{-1}HCl 溶液，0.01667 mol·L^{-1} $KBrO_3$ 标准滴定液.

(3)　试验方法　取 15 ml 6 mol·L^{-1}的 HCl 溶液于 100 ml 烧杯中，加 10 ml 2mol·L^{-1} KBr 溶液和含酚 3.76 mg 的酚溶液，用无酚水稀释至 40 ml，磁力搅拌后，插入电极，用 $KBrO_3$ 标准溶液滴定至切口出现.

2　结果与讨论

(1)　电极的选择　由文献[2]得知，Br_2 在铂电极的交流示波极谱图上有切口. 本文将双微铂电极与微铂-铂片电极进行了比较(见图 1)，并观察了微铂-钨和钨-铂片电极的示波极谱图. 实验发现，在微铂-铂片电极上 Br_2 的切口最灵敏，即同样 1 滴 $KBrO_3$ 溶液在双微铂电极上变化很小(图 1b)，而在单微铂电极上产生很明显的切口(图 1e)；在微铂-钨电极上没有切口；在钨-铂片电极上虽有切口，但图形收缩，难以观察. 故本法选用微铂电极为工作电极，铂片电极为参比电极.

(2)　底液中酸的选择　分别观察了磷酸、

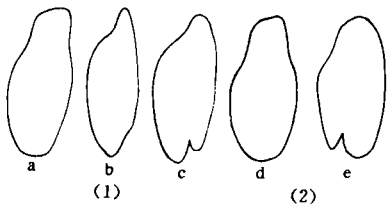

图 1　单微铂、双微铂电极上 Br_2 交流示波极谱图

(1) 双微铂电极上的示波图 (2) 单微铂电极上的示波图

a. d. HCl+KBr 的底液图；

b. e. 在底液中加 1 滴 $KBrO_3$ 时示波图

c. 在底液中加 3 滴 $KBrO_3$ 时的示波图

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硫酸和盐酸底液中 Br_2 的交流示波极谱图形. 发现在磷酸底液中切口出现很慢，有滞后现象；在硫酸和盐酸底液中切口都很灵敏(图 1e)，将两者的效果比较如表 1.

表 1 H_2SO_4、HCl 底液的比较

酸类	酸量/ml				
	5	10	15	20	25
HCl	3.78	3.76	3.76	3.76	3.78
	3.76	3.76	3.77	3.76	3.78
H_2SO_4	3.76	3.75	3.78	3.76	3.78
	3.76	3.76	3.78	3.77	3.78

由表 1 可见，2 种酸的底液效果相近，故选用硫酸或盐酸均可.

(3) KBr 和 HCl 用量的选择 实验证明，KBr 在一定浓度范围内对测定结果无影响，但随 KBr 用量的减少，切口出现时间逐渐增长，当 $V_{KBr}>10$ ml 时，切口在 2 s 内出现，$V_{KBr}<5$ 时切口在 7 s 以上出现.

HCl 用量对测定结果无明显影响，但同样影响切口灵敏度. 当 $V_{HCl}>8$ ml 时，切口在 5 s 内出现，当 $V_{HCl}<5$ ml 时在 8 s 以上出现，1 ml 以下时切口要 2 min 才出现(溶液总体积约 40 ml). 本实验选 KBr 10 ml，HCl 15 ml.

(4) 放置时间的影响 溴化法中溴化过程要放置 15 min，本法在实验中发现不受放置时间的影响，但滴定速度与反应速度要相适应，一般 0.3 ml/min.

(5) 终点的确定 到达终点后放置一段时间，切口又消失，可能是三溴苯酚继续溴化[3]及其对 Br_2 的吸附[4]所致，不利于终点的确定. 本文以标样为参照，以 Br_2 的切口出现 2 min 不消失作为终点.

(6) 酚的测定范围 酚含量在 11.07—2113.2 mg·L^{-1}(以苯酚计)范围内图形规整，切口清晰，准确度较好.

(7) 共存离子的影响 实验结果表明，1000 倍的 Cu^{2+}、1250 倍的 Zn^{2+}、125 倍的 Pb^{2+}、60 倍的 Ag^{+}不干扰；Fe^{3+}使结果偏低；甲醛、乙醛、三氯乙醛、甲酸、甲基橙和丙酮等有机物使结果偏高.

(8) 实际样品分析 移取含酚水样 2.00 ml 于 100 ml 烧杯中，加入 6 mol·L^{-1}的 HCl 溶液 15 ml，2 mol·L^{-1}的 KBr 溶液 10 ml，以无酚水稀释至 40 ml，插入电极，在电磁搅拌下滴入 $KBrO_3$ 标准溶液至终点，记录 $KBrO_3$ 的体积. 测定结果见表 2.

表 2 锅炉厂煤气洗涤废水中酚的测定

样品	测得酚/mg	相对标准偏差/%	加入标准酚/mg	回收率/%
1	4.53	0.8	1.88	102
2	4.67	1.0	1.88	95
3	4.01	0.9	1.88	101

3 结语

本法与容量法相比省去了 $Na_2S_2O_3$ 滴定 I_2 的后续步骤；操作程序省去了预蒸馏，从而使操作简便、较快速.

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ferent phenol wastewaters is better than their separate treatment result. The immobilized enzyme prepared has fair repeating usage performance.

Key words: immobilized enzyme, enzyme catalyzed oxidation, horseradish peroxidase, phenol.

Determination of Trace Copper, Lead and Cadmium in Seawater by Graphite Furnace Atomic Absorption Spectrometry with Dithizone-n-Butyl Acetate Extraction. Jin Xuegen (Zhejiang Environmental monitoring Centre Station, Hangzhou 310012): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 61—63

This paper studied the optimum conditions for the determination of trace copper, lead and cadmium in seawater by graphite furnace atomic absorption spectrometry with dithizone-n-butyl acetate extraction. The results showed that copper, lead and cadmium in the weakly alkaline medium (pH8—10) can be quantitatively extracted simultaneously. The relative standard deviation is less than 3% and the recoveries for the added standard are between 92%—102%. The detection limit (μg/L) for copper, lead and cadmium are 0.06, 0.14 and 0.002, respectively. This method is simple and rapid. The method has been successfully applied to the determination of trace copper, lead and cadmium in seawater with satisfactory results.

Key words: dithizone, extraction, graphite furnace, seawater, copper, lead, cadmium.

Determination of Lead from Automobile Exhaust Using Anodie Stripping Voltammetry at Carbon Fiber Beam Mercury Film Electrodes. Shao Mengxin et al. (Dept. of Environ. Eng., Tianjin Professional College, Tianjin 300402): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 64—66

In this paper, the preparation for carbon fiber beam mercury film microelectrodes was described. The electrode voltammetric properties were investigated. Lead content from automobile exhaust was determined using anodic stripping voltammetry. The suitable experimental conditions were assigned. This technique is simple, quick, with high sensitivity and fine reproducibility. The detection limit is about 0.1 ng • ml^{-1}, the linear range is 1.0 ng • ml^{-1}—20 ng • ml^{-1}. The relative standard deviation is 9.4%.

Key words: carbon fiber microelectrodes, anodic stripping voltammetry, automobile exhaust, lead.

Determination of Phenol in Wastewater by Alternating-current Oscilloscopic Polarography Titration. Qiu Zhiguo (Dept. of Chemistry Northeast Forestry University, Harbin 150040): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 67—68

A method to use a mixed solution of hydrochloric acid and potassium bromide as base solution to titrate phenol in water sample directly was indicated. The method is simple and rapid. The measuring range is 11.07—2113.2 mg/L, variation coefficient is bellow 0.9%, recovery rate is 95%—102%.

Key words: phenol, alternating-current oscillopolarographyic titration, wastewater determination.

Analysis on the Typical Photochemical Processes of Pollution in Autumn. Zhu Yuxiu et al. (Dept. of Environ. Eng., Shanghai Institute of Urban Construction, Shanghai 200092): *Chin. J. En-viron. Sci.*, **17**(3), 1996, pp. 69—71

Synchronous observations of O_3-NO_x concentrations and relative meteorological meterial have been lasted for one month, in order to study the characteristics of photochemical pollution and their relations with meteorology. Photochemical pollution processes in the autumn have been found. It not only includes the mechanisms of producing and accumulating of local sources as in summer and winter, but also includes the feature of high ozone pollution from outer sources as in spring. The highest and mean maximum concentrations of O_3 reaches 168.7 μg/m^3 and 114.8 μg/m^3, respectively.

Key words: autumn, processes of ozone pollution, photochemical pollution.

Study on the Indirect Determination of the Soluble Sulfide in Water by Spectrophotometry. Wang Lihong et al. (Dept. of Environ. Sci., Hangzhou University, Hangzhou 310029): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 72—74

In this paper, a new method for indirect determination of trace sulfide ion was developed. The optimum conditions of precipitate reaction of copper with sulfide and color reaction of copper with T(4-MOP) PS_4 were discussed. At about pH 8.5, CuS was formed, and at pH4.0 the surplus