反萃取双波长光度法测定水中微量酚类和芳胺*

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摘要 研究了乙醚萃取, 10% NaOH 溶液和10% HCl 溶液反萃取, 4-氨基安替吡啉(4-AAP) 双波长光度法同时测定污水中酚类和芳胺含量的分析方法, 提高了测定灵敏度, 有效地消除多种干扰物质的干扰, 可测定0.003- 6.0mg·L^{-1}的酚类和0.0008- 0.5mg·L^{-1}的芳胺. 加标回收率, 苯酚101%- 108%, 苯胺96%- 107%. 酚类测定与国标的相对误差≤6.5%. 芳胺类测定结果与相应国标法的相对误差在±5% 左右.

关键词 酚类, 芳胺, 萃取-反萃取, 双波长光度法, 乙醚.

笔者研究了4-AAP 双波长光度法同时测定污水中酚类和芳胺的实验方法[1], 为了进一步提高测定的灵敏度及消除干扰, 本文提出用萃取-反萃取双波长光度法同时测定水中酚类和芳胺的实验方法. 时明水[2]提出用1∶1氯仿-乙醚作萃取剂, NaOH 溶液和 HCl 溶液作反萃取剂, 紫外吸收法分别测定酚类和芳胺的实验方法. 本文对有机萃取剂进行了筛选, 提出用乙醚在近中性条件下同时萃取酚类和芳胺, NaOH 及 HCl 溶液反萃取, 萃取液合并后, 4-AAP 双波长光度法[1]测定二者含量. 对含量极低浓度的含酚、胺的水样也可获得令人满意的结果.

1 实验部分

1.1 仪器及试剂

721型分光光度计, pHS-3C 型酸度计, HHS 型恒温水浴, 500ml、100ml 分液漏斗.

苯酚和苯胺标准使用液[3], HCl, NaOH (固), 乙醚, 8% $K_3[Fe(CN)_6]$, 2% $(NH_4)_2S_2O_8$ 溶液, 0.5% 4-AAP 溶液, HCl-$(CH_2)_6N_4$ 缓冲液 (pH= 5.5±0.1). 所用试剂均为分析纯.

1.2 实验方法

取污水样品250ml 于500ml 分液漏斗中, 用40ml 乙醚(注意萃取操作应在20℃以下进行) 萃取2min, 有机相收集于100ml 分液漏斗中, 分别用4, 3, 3ml 10% NaOH 及4, 3, 3ml 10% HCl 反萃取有机相, 合并无机相于50ml 容量瓶中, 按4-AAP 双波长光度法[1]进行显色测定酚类和芳胺, 酚类测定的波长对为500-554nm, 芳胺530-480nm.

2 实验结果及讨论

2.1 实验条件的选择

(1) 有机萃取剂的选择 按实验方法标加苯酚和苯胺进行了有机萃取剂的萃取试验, 结果见表1.

表1 有机萃取剂的萃取回收率1)/%

萃取剂	乙醚	氯仿	石油醚	乙酸异戊酯	氯仿-乙醚=1∶1
苯酚	81.2	37.5	67.5	88.3	76.6
苯胺	75.1		46.5	37.2	64.7

1) 表中数据为经萃取-反萃取后的测定结果, 均为3—5次平行测定结果

由表1可见, 乙醚对苯酚和苯胺的萃取效率最高, 而且分层效果好, 故本实验选用乙醚作有机萃取剂.

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(2) 反萃取剂浓度的选择　固定其它条件, 分别用 NaOH 及 HCl 溶液作为酚类和芳胺的反萃取剂, 实验了浓度对反萃取回收率的影响. 实验结果: 不同浓度的反萃取剂对水样的萃取效果几乎无影响, 本实验采用10ml 10% NaOH 和10ml 10% HCl 作为反萃取剂.

(3) 被萃取溶液的 pH 值　固定其它实验条件, 改变被萃取溶液的 pH 值, 实验了不同 pH 值的水样, 经萃取-反萃取后苯酚和苯胺的回收率见图1.

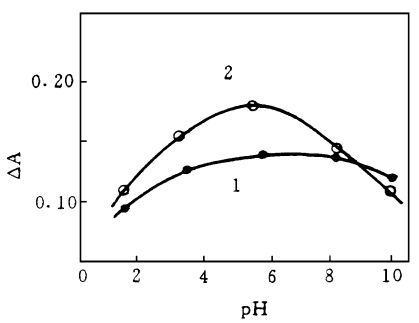

图1　不同 pH 值时苯酚和苯胺的萃取效果

1. 苯酚　2. 苯胺

由图1可以看出, 在 pH5- 7范围内, 二者的回收率均较高, 本实验将被萃取溶液的 pH 值调至6左右.

2.2　萃取法工作曲线、线性范围及检测极限

(1) 工作曲线的测绘　使标准系列中所含苯酚的浓度在0- 2.0mg·L^{-1}, 苯胺的浓度在0- 0.1mg·L^{-1}, 配成苯酚和苯胺的混合标准系列于500ml 的分液漏斗中, 先用40ml 乙醚萃取2min, 有机相收集在100ml 分液漏斗中, 用10ml 10% NaOH 溶液按4, 3, 3ml 反萃取3次有机相中的苯酚, 再用10ml 10% HCl 溶液按4, 3, 3ml 反萃取3次有机相中的苯胺, 合并2种反萃取液, 用4-AAP 双波长光度法[1]测得混合标准系列的线性回归方程分别为:

酚类:

$$\Delta A_{Ph} = 0.0215c_{Ph} + 0.00649 \qquad r = 0.9995$$

芳胺:

$$\Delta A_{Ah} = 0.0305c_{An} - 0.159 \qquad r = 0.9992$$

(2) 线性范围　按实验方法测得酚类的线性范围为0- 6.0mg·L^{-1}, 芳胺测定的线性范围为0- 0.5 ml·L^{-1}.

(3) 检测极限　用萃取后无酚水作空白, 平行实验10次, 由所得数据按下式求得萃取法测定酚类和芳胺的检测极限:

$$DL = 3\sigma \cdot c/A$$

实验结果: 酚类为0.003mg·L^{-1}, 芳胺的检测极限为0.0008mg·L^{-1}.

2.3　干扰及消除

按实验方法进行了石油类、悬浮物及金属离子的干扰实验, 结果见表2.

表2　石油类、悬浮物及金属离子的干扰实验[1)]/mg·L^{-1}

干扰物名称	干扰物浓度	苯酚		苯胺	
		测定值	E_r/%	测定值	E_r/%
石油类	36	6.74	0.8	0.760	3.8
	72	6.52	-2.5	0.766	4.6
	108	7.00	4.6	0.690	-5.7
悬浮物	80	6.60	-1.3	0.736	0.5
	100	6.64	-0.5	0.730	-0.3
	200	6.79	1.5	0.739	1.0
Ca^{2+}	200	6.82	2.0	0.740	0.8
Mg^{2+}	200	6.64	-0.7	0.722	0.4
Fe^{3+}	100	6.90	3.2	0.686	2.6
Al^{3+}	100	6.42	-4.1	0.758	-1.7

1) 苯酚浓度为6.69mg·L^{-1}, 苯胺浓度为0.732mg·L^{-1}

由表2可以看出, 100mg·L^{-1}以下石油类、悬浮物及 Ca^{2+}、Mg^{2+}、Fe^{3+}、Al^{3+} 均不干扰测定.

硫化物对酚类和芳胺测定的干扰及乙醚萃取后的测定结果见表3.

从表3可以看出, 经过萃取和反萃取操作, 10mg·L^{-1}以下的硫化物对酚类和芳胺测定的误差< ±5%.

对于含量极低的水样, 可以采用合并多份水样萃取后的有机相, 再用一份10% 的 NaOH 和10% 的 HCl 反萃取, 从而提高分析测定的灵敏度.

2.4　水样加标回收率实验

用本实验方法取水样进行了苯酚和苯胺的加标回收率实验, 结果见表4.

由表4可知, 萃取法测定水样的加标回收

率: 苯酚为101% – 108%; 苯胺为96% – 107%.

表3 硫化物对测定的干扰及消除[1)]

硫化物/ mg•L⁻¹		0.55	0.92	1.84	2.76	5.0	10.0
直接法测定值	苯酚	6.00	5.26	6.05	4.78	5.68	5.43
/ mg•L⁻¹	苯胺	0.657	0.555	0.524	0.578	0.621	0.597
相对误差	苯酚	– 10.3	– 24.8	– 9.5	– 28.6	– 14.0	– 18.9
/%	苯胺	– 10.3	– 24.2	– 28.4	– 21.1	– 15.2	– 18.5
萃取–反萃取后测定值	苯酚	6.72		6.80		6.78	6.86
/ mg•L⁻¹	苯胺	0.712		0.728		0.712	0.767
相对误差	苯酚	0.4		– 2.4		1.3	2.6
/%	苯胺	– 2.8		– 0.5		– 1.4	4.8

1) 被测物: 苯酚6.69mg/L, 苯胺0.732mg/L

表4 水样加标回收率实验[1)]

项目	标加苯酚/ mg•L⁻¹				标加苯胺/ mg•L⁻¹			
	0.12	1.03	1.36	2.27	0.037	0.090	0.150	0.192
测得总量/ mg•L⁻¹	0.18	1.61	1.90	2.80	0.036	0.092	0.160	0.184
回收率/%	108	108	103	101	97	102	107	96

1) 水样含酚量0.050mg•L⁻¹, 芳胺未检出

2.5 水样分析

用本方法对实际水样进行了分析, 酚类测定值与相应国标法[3]测定值进行对照, 芳胺测定值与国家标准的萘乙二胺偶氮(NEDA)光度法[3]对照, 结果见表5.

从表5可看出, 本法测定酚类结果与国标萃取光度法测定值的相对误差≤6.5%, 本法测定芳胺值与国标NEDA 法的相对误差在±5% 左右.

表5 水样分析结果对照

水样名称	酚类/ mg•L⁻¹			芳胺/ mg•L⁻¹		
	本方法	氯仿萃取4–AAP 法	E_r/%	本方法	NEDA[1)]	E_r/%
胜华炼厂	0.493	0.488	1.0	0.092	0.090	2.2
东营河水	0.082	0.080	2.5	0.128	0.135	– 5.2
自来水	0.033	0.031	6.5			

1) NEDA 法所用水样也经乙醚萃取, HCl 反萃取

3 结论

(1) 对于酚类和芳胺含量极低的水样可以采用萃取–反萃取法将水样中的酚类和苯胺类富集测定, 从而大大提高灵敏度.

(2) 通过萃取–反萃取处理后, 石油类、悬浮物、硫化物和金属离子不干扰测定.

(3) 由于乙醚沸点低, 易挥发, 萃取操作需在20℃以下的室温条件下进行, 且要求萃取操作在短时间内完成.

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no more than 180℃. The removal of COD by the treatment is over twenty percents more than Fenton's, while, H_2O_2 ··COD (weight ratio) less than one point two at the condition of phenol influent content more than 14000mg/L of COD. The existence of synergistic effect for COD removal in H_2SO_4+ Fenton system under the condition of added pressure and heating(0.1– 0.6MPa, 104– 165℃) was verified. It was carried out that five kinds of dye and pesticide wastewater was treated using the method.

Key words: wet oxidition, Fenton reagent, catalytic oxidation, organic wastewater, wastewater treatment.

Study on the Detoxication Effect of Chromate Sludge by Red Brick Method with Shale Rock–Clunch. Yang Guang et al. (Research Center of Resources Comprehesive Utilization Eng., Chongqing University 630044): *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 75—77

The chromate sludge brick was made using shale rock, chromate sludge and clunch as main materials. When directions for producing materials are 20% of chromate sludge and 10% of clunch. The determination of whole brick powder showed that detoxication of Cr (VI) is thorough and stable; and determination of brick surface layer powter showed that the leaching concentration of water soluble Cr (VI) is 1.16mg/L. through five years following trail of tests under the free air and sun conditions Cr (VI) concentration can still achieve the standard of GB5086–85. The detoxication effect is mainly influenced by kiln temperature, acid–alkali property of the system, coal content and auxiliary.

Key words: chromate sludge, brick manufacture, red brick method, shale rock, clunch, detoxication.

Spectrophotometric Method for the Simultaneous Determination of Phenols and Aromatic Amines in Sewage with Extraction–Reextraction. Li Meirong, Yuan Cunguang et al. (Dept. of Chem. Eng., University of Petroleum, Shandong, 257062): *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 78—80

This paper deals with a method of simultaneous determination of phenols and aromatic amines which extracted by ether, then reextracted by 10% NaOH and 10% HCl respectively. The sensitivity is improved highly, and many kinds of interferences is removed efficiently. Phenols of 0.03– 6.0 mg/L and aromatic amines of 0.008– 0.5mg/L can be determined.

Key words: phenols, aromatic amines, extraction–reextraction, double–wavelength, spectrophotometry, ether.

The Application of Artificial Neural Network in Chinese Environmental Forecast. Wang Ying and Sang Dayong (Dept. of Aeronautial Management Engineering, The Air Force Institute of Engineering, Xian 710038), Sun Linyan (School of Management , Xian Jiaotong University, Xian 710049): *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 81—83

According to suitability of models for environmet forecast, a mutiple layer perceptron environment forecast model was built using artificial neural network as a new forecast method, with which the environment indices of 2000 were forecasted based on environmental data and economic data in 12 years (1981– 1992). Future strategies were also analyzed on the basis of forecasted data.

Key words: environment forecast, artificial neural network, mutiple layer perceptron environment forecast model.

Data Acquisition for Inventory Analysis in LCA. Xi Deli, Peng Xiaoyan (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 84—87

The LCA inventory analysis is an important stage in LCA after its scope and goal are defined. According to the real situation in China, a set of methods of data acquisition for life cycle inventory analysis were developed in this paper. It also gave concrete procedures for obtaining the social data of products through pollution coefficients of industrial departments and for gathering and checking data from enterprises by using production mass scheme respectively.

Key words: life cycle assessment, inventory analysis, data acquisition.

Viewpoint on the Air Resources. Ning Datong, Yuan Jun et al. (Institute of Environ. Sci., Beijing Normal University, Beijing 100875), *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 88—90

It is proved that air resource is one of the most valuable natural resources by means of analyzing and expounding. From the standpoint of atmospheric environmental carrying capacity for pollutants, the ambient air quality is divided into two parts of "quidditative" and "heterogeous", and its method of assessment is approached. On the basis of analyzing the air resource's value, a preliminary solution in measuring its value is also given in this paper. Furthermore, the effective ways for air resources protection are studied.

Key words: air resources, value, quality assessment, atmospheric environmental carrying capacity for pollutants.