废水中硫化物测定样品预处理方法的改进

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摘要　对废水中硫化物测定预处理方法——氮气吹气法的实验装置、预处理酸度、温度及反应瓶体积大小等条件均作了研究和改进。以多孔吹球代替单孔吹管、以 NaOH＋EDTA＋三乙醇胺代替 $ZnAc_2$—NaAc 为吸收液，并提出了逐步加压的吹气方法。通过对回收率、精密度及6种不同类型工业废水的对比测定，效果提高显著，回收率由原法的40%左右提高到95%以上，吹气时间缩短25%，装置简单，便于推广应用。

关键词　硫化物，氮气吹气法，环境监测，废水处理。

工业废水中硫化物测定样品的预处理方法——氮气吹气法，已被列为环境监测的常规分析方法，但还存在所用吹气装置及处理方法不够合理，吹气效果达不到要求等问题，回收率严重偏低，一般只达40%左右[2]，且吹气时间较长、干扰作用明显。

本法以多孔吹球代替了原法的单孔吹管，使氮气形成喷雾状均匀吹出；又以比原法吸收液吸收能力更强、吸收更稳定的 NaOH＋EDTA＋三乙醇胺混合溶液为吸收液[3]；并采取了分步加压吹气等处理方法。实验效果显著，回收率达95%以上，缩短吹气时间10～15min。

1　试验部分

1.1　仪器和试剂

1.1.1　仪器

（1）721或722型分光光度计。

（2）氮气钢瓶、水浴锅、流量计。

（3）氮气吹气装置（图1）。

1.1.2　主要试剂

（1）显色剂　按标准法[1]（对氨基二甲基苯胺光度法）配制。

（2）1∶1盐酸或磷酸。

（3）吸收液　称1g NaOH＋0.1g EDTA＋1ml三乙醇胺（TEA）于烧杯中，加水100ml溶解，贮瓶备用。

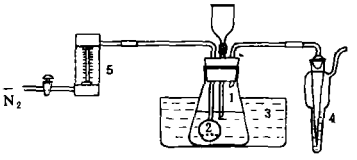

图1　氮气吹气装置

1. 三角瓶　2. 多孔吹球　3. 水浴锅

4. 吸收管　5. 流量计

1.2　试验方法

取一定量水样加入250ml三角瓶中，加水至110ml，将三角瓶放进46—50℃水浴锅。另取12ml1%NaOH混合液于吸收管，按图1连接。开启 N_2 气源，预吹气2min，关闭气源，从分液漏斗加盐酸（1∶1）20ml，迅速关闭活塞，以0.2L/min气流吹气10min，加大气流至0.35L/min续吹气15～20min，最后提高到0.55L/min再吹气5min。关闭氮气瓶，把吸收液全部转入50ml比色管，按标准法显色测定。

2　结果与讨论

2.1　条件试验

2.1.1　吸收液种类及用量试验　在吹气条件相同下，分别以不同量NaOH混合吸收液和原法 $ZnAc_2$-NaAc 吸收液试验，结果用NaOH混合

1992年10月7日收到修改稿

液效果远比 $ZnAc_2$-NaAc 显著，因为 NaOH 为强碱，与弱酸 H_2S 反应为瞬时完成的中和反应[4]，速度快，反应完全，尤在强碱中加入 TEA 后，由于有机碱 TEA 有亲核作用，在溶液中易形成溶剂化现象而增强了疏水性 H_2S 对水的亲和能力[5]，使 H_2S 反应更容易、更稳定。以 12ml 用量为宜，既可适度提高液面、延长吸收过程，又不至因加大气流而冲出损失。试验结果见表 1。

表 1　不同吸收液种类及用量所得到的回收率(%)

吸收液种类	吸收液用量					
	10ml		12ml		15ml	
NaOH 混合液	96.53	93.67	100.01	95.74	96.25	96.21
	95.47	91.83	97.34	93.52	94.44	95.31
$ZnAc_2$-NaAc	45.04	38.43			55.41	80.63
	46.60	60.40			48.49	37.81

2.1.2　吹气瓶体积试验

吹气效率和速度与吹气瓶容积有相当关系，实验表明若体积过大，导气管口小，将使气液接触面小；气体回旋余地宽、保留体积多致使吹气效率下降。本实验采用 250ml 三角瓶，加水量为 110ml。结果见表 2。

表 2　吹气瓶容积对回收率影响(%)

水样号	150ml 三角瓶 (100ml 水)	250ml 三角瓶 (110ml 水)	500ml 烧瓶 (200ml 水)
1#	100.00	94.48	89.95
2#	94.86	102.57	87.29
3#	95.78	97.31	86.90
4#	92.54	98.02	78.03
5#	91.60	92.20	79.59
均值	94.96	96.92	84.35

2.1.3　吹气方法、气流速度和吹气时间试验

如何控制氮气速度既使 H_2S 吸收完全又可缩短吹气时间，这是关系到吹气效率、回收率高低及批量分析的关键问题。试验表明，载气采用分步加大流量法效果较好，因为在 H_2S 初始浓度较大时，气流小，可以避免吸收不及而损失，中间加大流量，可缩短吹气时间，最后几分钟再提高流量，能彻底赶尽残余 H_2S，这样吹气 30—35min 已达到满意结果(表 3)。

2.1.4　加热温度试验

改变水浴温度，试验结果见表 4。由表 4 可见，温度过高，容易造成各种氧化还原反应发生[6]，尤其对成分比较复杂的废水，结果高低不稳定；而温度太低，吹气效率受影响，本实验控制在 50℃左右。

2.1.5　加酸种类及用量试验

以 1∶1 盐酸和 1∶1 磷酸不同量进行试验，结果表明加入 10ml 磷酸和 20ml 盐酸都同样得到较满意回收率(表 5)。

2.1.6　干扰作用试验

主要以 SO_3^{2-} 和 NO_2^- 进行试验，结果表明，NO_2^- 的干扰作用比 SO_3^{2-} 更明显，浓度在 0.5mg/L 已使回收率严重偏低。SO_3^{2-} 随着 S^{2-} 浓度递增干扰作用略有减弱，当 S^{2-} 浓度在 0.1—0.5mg/L 时，12mg/L SO_3^{2-} 无影响，比原法稍有提高(表 6)。

2.2　样品分析

2.2.1　回收率测定

按本实验方法进行不同浓度样品测定，回收情况良好，平均回收率达 95%以上，部分实验见表 7。

2.2.2　方法精密度

对同一样品进行多次吹气测定，结果标准偏差为 2.13%，变异系数为 7.58%(见表 8)。

表 3　吹气方法及吹气时间对回收率的影响(%)

气流速度(L/min)			20min		30min		35min		40min	
0.35(始、终)					90.21	93.02	91.41	94.44	89.23	94.37
					94.42	87.36	92.53	85.95	92.40	90.15
0.20	0.40	0.55	78.30		96.46	94.42	100.60	96.80	95.43	108.32
(前 5')(中间 20')		(后 5')	84.21	87.35	94.51	97.31	95.06	98.02	97.92	94.81

表4 温度试验

温度(℃)	回收率(%)	回收率平均值(%)
30	98.05 96.01 94.28 91.12 91.00 86.78	92.87
46—50	103.38 108.24 97.91 97.75 94.31 93.41 92.54	97.79
60	105.07 104.55 96.93 91.11 90.67 97.49	97.64
70	107.00 99.04 95.83 92.12 88.15	96.43

表5 酸的种类及用量与回收率的关系(%)

酸种类	酸用量(ml)			
	5.0	10.0	15.0	20.0
盐酸(1∶1)		93.97 89.10	91.00 92.34	99.39 96.97
		86.19 84.53	97.55 96.40	95.83 93.94
磷酸(1∶1)	43.87 41.21	99.94 96.51	97.58 92.43	
	38.54 36.77	94.25 98.21	97.33 96.27	

表6 干扰作用对回收率的影响(%)

S^{2-}浓度(μg/100ml)	SO_3^{2-}(μg/100ml)			NO_2^-(μg/100ml)	
	1500	1200	1000	50	60
8	83.33 82.49	87.88 86.73	90.15 91.37	37.68 32.12	31.03 30.48
16	82.89 83.56	94.43 102.34	101.58 94.40	32.02 35.85	35.41 37.02
40	83.65 89.75	97.74 95.38	98.55 97.55 105.89[1)]	63.14 48.59	58.32 78.91[1)] 81.00[1)]

1)加磷酸

表7 回收率测定结果

编号	1	2	3	4	5	6	7	均值
加标量(μg)	10.0	13.43	29.0	23.2	53.8	99.0	30.0	
测得值(μg)	10.10	13.00	27.11	23.40	51.60	83.20	28.70	
回收率(%)	101.00	96.80	93.48	100.86	96.11	94.14	95.47	96.84

表8 方法精密度测定结果

编号	1	2	3	4	5	6	7	8	CV
测得值(μg)	27.73	28.22	27.60	27.11	27.79	30.2	28.11	2.13	7.58%

2.2.3 方法检出限

按本法重复测定5批全程序空白值,每批2个,得方法检出限为0.014mg/L,比原法0.02mg/L较优。

2.2.4 样品分析

用本法和原标准法进行6种不同类型工业废水对比测定,结果见表9。

3 结语

(1)本实验以多孔吹球代替了原法的单孔吹管,使氮气能在液体中形成致密致匀的喷雾状分布,接触面成几倍以致几十倍增加,并因适当缩小了反应瓶体积,使吹气效率大大提高。

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表10　SW01　MS样品的定量结果

化合物	扫描(次)	保留时间(min)	浓度(μg/L)
溴氯甲烷(内标-1)	227	7:34	50.0
1,4-二氯苯(内标-2)	532	17:44	50.0
氯苯-d_5	675	22:30	50.0
丙酮	144	4:48	19.3
1,1-二氯乙烯	209	6:58	73.1
2-丁酮	310	10:20	16.5
三氯乙烯	442	14:44	52.7
苯	455	15:10	56.7
甲苯	645	21:30	51.9
氯苯	679	22:38	47.2
甲苯-d_8	639	21:18	50.2
溴氯苯	793	26:26	49.6
1,2-二氯乙烷-d_4	310	10:20	51.1

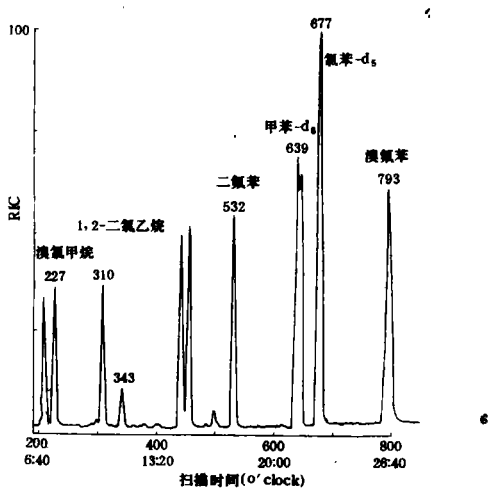

图2　SW01 MS样品的总离子流图

定性和定量了14个峰，大部分属于分析前加入的标样，一些峰是作为目标化合物鉴定的。只有一个峰，扫描号为343，经库检索，推测鉴定为2-甲基-2-甲氧基丙烷，浓度大约为10μg/L。

本方法一般用来测定环境(水和土壤)样品中的挥发性有机化合物，不同的样品基质采用不同的预处理方法，此方法用来定量大部分沸点在200℃以下，不溶于水的挥发性有机物。然而，对于很多溶解于水的化合物，定量检测限大约要高10倍，因为它们的吹扫效果很差。本方法的精确度和准确度直接与分析的样品基质和污染浓度有关，实际上对于水样的定量检测限大约是5μg/L，对土壤和底泥是5μg/kg。

本方法需进一步完善，某些质量控制参数也有待于进一步讨论。

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表9　工业废水对比测定结果(mg/L)

测定方法	糖厂废水	制革厂废水	纸厂废水	印染厂废水	化工厂废水	罐头厂废水
原标准法	1.23	6.90	0.41	3.82	1.10	0.23
本法	2.15	16.51	0.71	8.54	2.46	0.44

(2)以强碱氢氧化钠混合液为吸收液，对H_2S吸收完全、稳定，并避免了$ZnAc_2$为吸收液所形成的ZnS沉淀粘附于吸收管尖的损失。总回收率由原法40%提高到95%以上，减少吹气时间25%。

(3)由于处理温度控制较低，抑制了废水中各种类型反应发生，减少了干扰作用。

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of sludge clogging, liquid shortcuting and aggregation of scum have been solved. The exeperiment of treating aerobic excess sludge studied in 120 liter reactor at 35℃ shows that the organic pollutant removal efficiency of 51.4%—58% is reached corresponding to HRT=3.53—8.57 days. When HRT is fixed at 7.5 days, the organic loading rate, COD loading rate and average organic removal efficiency are 2.97 KgSS/(m^3. d), 3.89 kgCOD/(m^3. d) and 55.3%, respectively. The methane content of biogas is more than 66%.

Key words: two-phase digestion, anaerobic reactor, aerobic excess sludge treatment.

Production Test on Facultative Anaerobic-AB Process in Treating Slaughterhouse Wastewater and Its Microbiological Characteristics. Zheng Dandan et al. (Chengdu Institute of Biology Academia Sinica, Chengdu 610041); *Chin. J. Environ. Sci.*, **14**(4), 1993, pp. 66—70

To treat the slaughterhouse wastewater of Neijiang Comprehensive Processing Plant, facultative anaerobic-AB process was used. During the trial operation, the loading rate of facultative anaerobic regulating tank was 0.50kgCOD_{Cr}/m^3, and its removal rate of COD_{Cr} (ηCOD_{Cr}) was 31.15% the sludge loading rate (B_{TS}) in A-stage was 4.78kgBOD_5/(kgMLSS · d) and ηCOD_{Cr}=53.37%; in B-stage, B_{TS} = 0.73 kgBOD_5/(kgMLSS · d) and ηCOD_{Cr} = 54.70%. There was no problem for this process in compliance with the national standards, the effluent had COD_{Cr} 103.1mg/L (η = 88.77%), BOD_5 32.0mg/L (η=94.47%), SS 36.1mg/L (η=89.64%), Color 26 times (η=80.60%), and pH 7.72. When this process was put into formal operation, its effluent quality remain stable with γ=0.48. Results indicated that this process was stable with high efficiency and low investment needed. It is an advanced process worth spreading. There was an anaerobic digestion microorganism community in the biomembrane formed on the support material in facultative anaerobic regulating tank; besides this, there were different biosystematics existing in A and B stages' aerobic tanks, A-stage is predominant in bacteria and B-stage in protozoa. The analysis of the microbiological characteristics of this process offer theoretical basis for using it to treat other kinds wastewater.

Key words: facultative anaerobic-AB process, slaughterhouse wastewater, production test, microbiological characteristics.

A Study on the Treatment of Paint Wasterwater by a Sequencing Biological Batch Reactor. Zhou Yuexi et al. (Chinese Research Academy of Environmental Sciences, Beijing 100012); *Chin. J. Environ. Sci.*, **14**(4), 1993, pp. 71—73

In this paper, the research was made on the treatment of paint wastewater by a sequencing biological batch reactor. The experimental results demonstrate that the biological batch system can effectively remove organic matter. With the experimental time sequence (flow-in 1 h., anaerobic 6 h., aerobic 14h., setting 1 h. and flow-out 1 h.), the removal rate of COD is 84%—96% (influent COD is 1000—4000 mg/L).

Key words: sequencing biological batch reactor, paint wasterwater.

The Effects of the UV Light on the Catalase (CAT) Activity of Several Species of Aquatic Plants. Li Hongwen et al. (Suzhou Institute of Urban Construction and Environmental Protection, Suzhou 215008); *Chin. J. Environ. Sci.*, **14**(4), 1993, pp. 74—77

By testing the volume of O_2 which is released after the CAT of the plants exposed to exceeded UV decomposed H_2O_2, the CAT activity of the exposed plants is determined. The results show that the CAT activities for three plant species, Azolla imbricata, Lemna minor, Alternanthera philoxeroides, obviously rose respectively after they had been exposed to exceeded UV in defferent hours. But the maximum values of the CAT activities for three plant species is vary with defferent species. There is a maximum value of the CAT activity for Azolla imbricata which is exposed to exceeded UV in 72 hours. There is a maximum value of the CAT activity for Lemna minor which is exposed toexceeded UV in 24 hours. There is a maximum value of the CAT activity for Alternanthera philoxeroides which is exposed to the exceeded UV in 8 hours. The CAT activities for three plant species decreased respectively in some hours after the influence of the UV had been withdrawn. This shows that there obviously are stimulative affects of the exceeded UV on the CAT active for three plants. Meanwhile, the tissues and metabolism of the exposed plants are injured by the exceeded UV. It finally leads up to decrease the CAT activity of the exposed plants. The ecological effects of various plant species on the exceeded UV are defferent.

Key words: Catalase (CAT). UItraviolet (UV), Lemna minor, Azolla imbricata, Alternanthera philoxeroides.

Improvement in the Pretreatment Method of Samples for the Determination of Sulfides in Wastewater. Wu Yuzhen. (Nanning Environmental Monitoring Station, Nanning 530012); *Chin. J. Environ. Sci.*, **14**(4), 1993, pp. 78--80

The pretreatment method of samples, known as N_2-blowing method, for the determination of sulfides in wastewaer has been further studied and improved. The improvement includes the test apparatus, pretreatment procedure, acidity and temperature used in the pretreatment, and the volume of reaction bottle. Particularly, a multihole blowing ball was used to replace the sigle hole blowing pipet, and a mixture of NaOH, EDTA and TEA was used as the blowing-absorbing solution instead of $ZnAc_2$-NaAc. Then a stepwise pressure procedure has been suggested. The studies on the recovery and precision of the improved method and the comparative determination of six different kinds of industrial wastewater show that the improvement has seen an obvious effectiveness and the recovery increases from 40% for the original method to over 95% for the improved method. The blowing time is shortened by 25%. The apparatus is easy to operate.

Key words: N-blowing method, multi-hole blowing ball, sulfide.

Quality Control for the Analysis of Volatile Organic Pollutants by GC-MS. Sun sien et al. (The Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing 100085); *Chin. J. Environ. Sci.*, **14**(4), 1993, pp. 81—86

This paper described the Quality control for the analysis of volatile organic pollutants by GC-MS according to the US EPA CLP programme. The criteria of quality control in the process of analysis were presented. Five samples have been analysed in order to demonstrate the procedure. This method is used to quantify most volatile organic compounds having boiling points below 200℃ and compounds are insoluble in water. The practical quantitation limit