大气醛类化合物浓度高低与气象条件关系 密切; 晴天气温高光照强气流稳定醛浓度高, 阴 雨天醛浓度明显降低.统计处理表明, 醛与光 化学反应产物 HNO<sub>3</sub>(g)、气溶胶 SO<sup>2+</sup>、NO<sub>3</sub> 及与交通排放的一次污染物 CO、NMHC、NO<sub>5</sub> 等有较明显相关关系, 推测北京大气中醛类化 合物是一次污染与二次污染叠加的结果.

**女谢** 数据的采集是本系环境分析教研室 孙庆瑞、姚荣奎等老师和同学一起完成的,在此 表示感谢。

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# 废水中糠醛的比色测定

杨凤梧 李世伟

#### (新疆独山子炼油厂,独山子 833600)

摘要 本文采用醋酸苯胺与糠醛作用缩合成红色化合物的特性,运用正交设计合理选择实验条件. 取经水蒸汽蒸馏后的炼油废水样品,加入醋酸苯胺和稳定剂,在 20℃ 的水浴中显示 40 分钟,于波长 518nm 处比色测定糠醛含量. 测定上限 3.0mg/L,最低检出浓度为 0.3mg/L,加际回收率 90-110%,变异系数 <5%. 关键词 糠醛,炼油度水,比色测定.

糠醛又称呋喃甲醛,是一种常用的优良有 机溶剂,也是有机合成上重要的化工原料.糠 醛对人体和生物都有一定的毒性作用,目前国 内水质糠醛测定方法未见报道,本文根湿糠醛 定性实验原理,参考国外有关资料<sup>10</sup>,应用醋酸 苯胺比色法测定了炼油废水中糠醛的含量.

# 一、 实 验

1. 仪器与试剂

(1) 仪器 721 分光光度计,恒温装置(水浴),水蒸汽蒸馏器(图 1),刻度比色管(25ml).

(2) 试剂 苯胺,冰醋酸,磷酸氢二钠,糠醛(工业纯,新疆石河子糠醛厂),标定如下:

原理 在乙醇溶液中,糠醛与盐酸羟胺进 行肟化反应,生成的盐酸用氢氧化钠滴定。

$$CH=NOH + HC! + H_2O$$

Π

试剂 ①盐酸羟胺-乙醇混合液, pH3.7— 3.8. 2.5% 的盐酸羟胺 500ml 与 95% 乙醇 500ml 等体 积混 合,加入 0.4%的 溴酚 兰 1.25ml.用氢氧化钠调 pH 至 3.7—3.6. ② 溴 酚兰 0.4g 加入 12ml 0.05mol/L 的氢氧化钠 溶液,用 95% 乙醇稀至 100ml.

标定 用减量法称取 0.5g 左右糠醛试剂 于 100ml 具塞磨口锥瓶中,加入 30.0ml 盐酸

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羟胺-乙醇混合液,盖上瓶塞摇匀,静置 15min, 用 0.25 mol/L NaOH 滴定,颜色从黄色变到 兰绿色为终点。

2. 分析步骤

(1) 准确吸取 100.00ml 水样(或取适量 水样稀释至 100.00ml)。置于三口烧瓶中,按 图 1 连接好后加热。

(2)待三口烧瓶内溶液温度约为100℃时, 开始通人蒸汽,并维持温度在160±5℃。



图 1 水蒸汽蒸馏装置
1.接收瓶 (200ml) 2.冷凝管 3.250ml
三口烧瓶 4.蒸汽发生瓶 5.可调电炉
6.湿度计 7.三通

(3) 当接收瓶内馏出体积接近 200ml 时, 停止蒸馏,用去离子水补充至 200.00ml 刻度 供测定用.

(4) 于 25.0ml 具塞刻度比色管中,加入 1.0ml 新蒸馏苯胺、12.0ml 冰醋酸、2.0ml 浓 度为 20% 的氯化钠溶液,仔细摇匀后,加入 1.0ml 0.5% 的草酸溶液,0.5ml 10% 的磷酸 氢二钠溶液摇匀.

坐

(5) 将比色管于 20℃ 水浴中放置 15min,
然后加入 5.0ml 试样,加去离子水补充至 25.0ml 刻线,摇匀.

(6) 于暗处 20℃ 水浴中放置 40min, 立刻用 20mm 比色皿,以去离子水为参比,在波长 518nm 处,比色测定其吸光度.

#### 二、结果和讨论

# (一) 吸收曲线

将 3.00ng/ml 的糠醛标准液 3.00ml, 经 显色反应后,在不同波长下测定吸光度. 根据 比色波长与吸光度的关系,选择溶液有最大吸 光度时的最大吸收波长进行比色. 故确定 518 nm 为比色波长(见图 2).



图 2 糠醛溶液吸光曲线

(二) 显色条件选择

将影响显色的主要因素进行正交实验,选择最佳条件(见表1)。由于苯胺用量是重要因素,须仔细选择,所以安排了6个水平,其它因

因素水平	苯胺 A(ml)	冰醋酸 B(ml)	氯化钠 C(ml)	草酸 D(ml)	磷酸氢二钠 E(ml)	显色时间 F(min)
I	0.5	5.0	0.0	0.0	0.0	30
II	0.8	10.0	2.0	1.0	1.0	45
III	1.0	12.0	3.0	2.0	2.0	60
١V	i.2					
V	1.5					1
VI	2.0					

表 1 因素水平表

₩

素均安排 3 个水平.选用 L<sub>18</sub>(6<sup>1</sup>×3<sup>6</sup>) 正交表<sup>III</sup> 进行实验,可看出影响显色因素之大小顺序为: A>B>E>D>F>C. 经实践得到最佳 显色条件是:苯胺 1.0ml,冰醋酸 12.0ml,氯 化钠 2.0ml,草酸 1.0ml,磷酸氢二钠0.5ml, 显色时间 40min.

(三)稳定性实验

1. 糠醛对热和氧化都不稳定,在空气中2-3 天内就呈棕黑色. 氧化物为羧酸的衍生物与 醛酸. 在糠醛试剂中加入 0.02%(重量比)的对 苯二酚,至少 3 个月内氧化缓慢,保持原浅黄 色.实验如下: 取糠醛于两个滴瓶内,其中一个 加入 0.02%的对苯二酚混匀,用 20mm(5mm) 比色皿、于 495nm 波长处,分别将两滴瓶内 试剂,以去离子水为参比,进行比色测定,经过 三个多月的测定,加了抗氧化剂的糠醛吸光度 增值极小,而未加抗氧化剂的糠醛吸光度增长 很大. 使标准物质的使用与保存问题得到解决 (见图 3).



图 3 糠醛抗氧化试验

 水样经水蒸汽蒸馏后,可消除大多数干 扰物质的影响.如有机物、悬浮物等影响水样 颜色的干扰物质.

3. 游离的无机酸存在,将影响显色溶液的稳定性,若水样呈酸性,可用氢氧化钠中和水样 至中性或微碱性.

4 温度及光照都影响显色,应将显色温度 控制在20±2℃,并于暗处避光放置。 5. 比色时,不能剧烈摇动显色液,否则产生 大量微小的悬浮气泡,影响比色. 应轻而缓慢 地颠倒几次后,小心倾入比色皿中,立即比色. 其比色时间应尽量控制在 15min 内.

6. 所有试剂可按1份苯胺:12份冰醋酸: 2份氯化钠(20%):1份草酸(0.5%):0.5份磷 酸氢二钠(10%)的体积比配制成一定体积的显 色液,取16.5ml加入水样比色(总体积为25.0 ml),可减少测定时间,此显色剂有效使用期为 1d.

(四)方法特点

1.标准曲线

在 25.0ml 具塞比色管中,加入所有试剂 并放置 15min 后(20℃),分别加入 0.00、0.50、 1.00、2.00、3.00、4.00、5.00ml 的 3ng/ml 糠醛 标准溶液,用去离子水补充至 25.00ml 刻度摇 匀显色 40min(20℃). 以去离子水为参比进行 比色测定. 以糠醛含量为横座标、吸光度为纵 座标,绘制标准曲线(图 4).



### 2. 检测限

指定性检测即断定样品中确实存在有浓度 高于空白的待测物质. 其要求是做空白试验 (空白测定):用去离子水代替样品,其所加试 剂和操作步骤均与样品测定过程完全相同.以 了解本方法在实验条件下的最小浓度或最小 量.表2为6d的测定结果.由表可知,方法 检出浓度为 0.07mg/L.

3. 灵敏度(S)

它表示单位截面积光程内能检测出被测物

表 2 空白平行测定值

测定次数	1	2	3	4	5	6	备 注
空白 (mg/L) 2	0.221	0.191	0.204	0.178	0.178 0.200	0.221	$\overline{x} = 0.203$ $\Sigma x^{t} = 0.498236$
各组之和(y)	0.463	0.391	0.425	0.356	0.378	0.421	$\frac{1}{2} \Sigma y^2 = 0.497368$
批内标准差 (S <sub>wo</sub> mg/L)	$S_{pb} = \frac{\sqrt{\sum x^2 - \frac{1}{2} \sum y^2}}{m(n-1)} = 0.013$					m(n-1)=5	
检测限 (mg/L)	$DL = 2\sqrt{2} t_{(0.05,6)} S_{\mu b} = 0.07$					<b>Z</b> (€.05,6) == 1.943	

<

质的最低含量 ( $\mu g/cm^2$ )。 常用桑德尔灵敏度 表示  $S = M/\epsilon(\mu g/cm^2)$ 。 在本方法中  $S = 0.0017 \mu g/cm^2$ (摩尔吸光系数 5.65 × 10<sup>4</sup>)。

4. 精密度与准确度

于去离子水中,加入用糠醛标准溶液配制 1.00mg/L的样品,其它过程同于水样分析.将 实测值与之比较(见表 3).

编号目次	1	2		
理论值 (mg/L)	1.000	1.000		
测定值 (mg/L)	0.965	0.932		
均值(mg/L)	0.948			
变异系数(%)	2.50			
标样回收率(%)	96.5	93.2		
平均回收率(%)	94.8			

表 3 标准加入法测定结果

5. 样品分析

炼油废水中糠醛测定,是经二级设施处理 后水样的监测结果(见表 4).

## 三、 结 论

1. 在本实验条件下,糠醛比色测定上限为 3.0mg/L,最低检出浓度为0.3mg/L.

2. 最佳显色条件: 苯胺 1.0ml, 冰醋酸

表 4 糠醛水样测定值\*

	-				
「「」」 「」」 「」」 「」」 「」」 「」」 「」」 「」」 「」」 「」	测定值 (mg/L)	平均值 (mg/L)	变异系数 (%)	加标回收 率(%)	平均加标 回收率 (%)
1#	1.843	1.814	2.30	89.5 92.3	90.9
2#	4.576 4.325	4.450	4.0	85.7 87.4	86.7
3#	1.344 1.392	1.368	2.5	93.2 91.6	92.4

\* 为平行双样

12.0ml, 氯化钠 2.0ml, 草酸 1.0ml, 磷酸氢 二钠 0.5ml,显色时间 40min.

3. 糠醛试剂中加入 0.02%的对苯二酚,可 使原颜色 3 个月内基本不变,纯度不降.

4. 精密度与准确度;糠醛测定浓度为 1.0-4.5mg/L 时,变异系数为 2.3-4.0%,标准加入 平均标样回收率 94.8%,糠醛废水平均加标回 收率 90.0%。

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# Abstracts

Chinese Journal of Environmental Science

sures to the chemicals started at the blastula stage and the effect on hatching and survival were monitored for 15 days. The results showed that toxicities of phenylhydrazin to both embryos and larvae were more than those of hydrazine. The LOEC (Lowest Observed Effect Concentration) for hatching was 0.049 mg/L for hydrazine and 0.0078mg/L for phenyllydrazin, the LOEC for survival of larvae was 0.0035mg/L for hydrazine and 0.00098mg/L for phenylhydrazin, respectively. The NOEC (No Observed Effect Concentration) for hatching was 0.0245mg/L for hydrazine and 0.0039mg/L for phenylhydrazin and the NOEC for survival of larvae was 0.00175mg 'L for hydrazine and 0.00049 mg 'L for phenylhydrazin, respectively. The safe concentration was 0.00175mg/L for hydrazine and 0.00049mg/L for phevlhdrazin.

Key words : toxicity, hydrazin, phenylhydrazin, *Brachydanio rerio* 

Existing Pattern, Ionic Forms and Distribution of Aluminum in Masson Pine Seedlings. Gao Jixi, Gao Hongfa (Chinese Research Academy of Environmental Sciences, Beijing 100012): Chin. J. Environ. Sci., 13 (6), 1992, pp.69-72

Using a hydroponic system, existing pattern, ionic forms and distribution of aluminum in masson pine seedlings were studied. Results show that: (1) Most of the aluminun absorbed by the pine seedlings accumulated in the roots and only a little of the aluminun was translocated to the shoots; (2) Majority of the aluminun in the shoots were bound, but there was only little difference in the amount of free and bound aluminum in the roots; (3) The dominant ionic form of aluminum in surface free space was AL3+ which accounted for about 63-85% of the total in the shoots and 41-67% in the roots; (4) In the roots, most of the aluminum existed in the epidermis of plant tissue and a little was found in the stele, showing an increasing tendency from the inside to the outside of plant tissues.

Key words : masson pine, aluminum, existing pattern, ionic forms, distribution.

Determination of Acetaldehyde in Waste Water by Chemiluminescence Method. Lü Xiaohu, Lu Minggang (Department of Applied Chemistry, University of Science and Technology of China, Hefei 230026): Chin. J. Environ. Sci., 13(6), 1992, pp. 73-75 The chemiluminescence reaction of iso-propal alcohol with  $CLO^-H_2O_2$  is enhanced by acetaldehyde. This provides a novel chemiluminescence method for the determination of acetaldehyd<sup>a</sup>. The linear range of the method is  $5 \times 10^{-10}$ g/ml to  $1 \times$  $10^{-6}$ g/ml with a detection limit of  $8 \times 10^{-11}$ g/ml. The effect of foreign substances was also studied. The method has been satisfactorily applied to the determination of acetaldehyde in waste water.

**Key words** : Iso-propyl alcohol- chemiluminescence, determination of actualdehyde.

Concentrations and Distributions of Formaldehyde and Total Aldehyde in the Atomosphere of Beijing City in the Summer. Bai Yuhua et al. (Dept. of Technical Physics, Peking University, Beijing 100871): Chin. J. Environ. Sci., 13(6), 1992, pp. 75-80 The concentrations of formaldehyde (HCHO) and total aldehyde (TCHO) in the ambient air of Beijing city in the summer of 1986 and 1987 were determined. Formaldehyde was analyzed with Nash method and total aldehyde was determined with MBTH method. Averaldehyde concernations in the ambient air were 18.5 for 1986 and 9.9µg/m<sup>J</sup> for 1987, respectively. The average formaldehyde concentration was 4.4µg/m<sup>3</sup> for 1987, which accouted for around 50% of total aldehyde statisical analysis of the data from the two year's observation shows the effects of traffic automobile and reaction on the concentration of aldehyde. The results suggests that the appearance photochemical of aldehyde compounds in Beijing ampient air was caused by both first and second pollutions.

Key words: formaldehyde, total aldehyde, atomospheric pollution, automobile poilution, photochemical reaction.

Determination of Furfural Content in (下转封三) Analysis of Particulate and Vapor Phase Phthalate Esters in the Atmosphere ..... Tong Qing et al. (78) Determination of Trace Phenol on Waste Water by Chemiluminescence ...... Wang lun et al. (81) Determination of Sulfide in Industrial Waste Water by Oscilloscopic Polarography Titration ...... Levels of Radioactivity in the Red Mud and Red Mud Cement and Its Sendout to Local Residents Number 6 Water Pollution Detected by the Ultraweak Luminescence Measurement Technique from Zebra Fish Research on Transport and Transformation of Phenol in the Saturated Vaclose Water Zone ..... Zhu Wanpeng et al. (6) Study on the Reactivity and Temperature-Characteristic of Colcium-Based Sulfur Sorbent ..... Huang Xingyi et al. (11) Environmental Factors Causing the Low Level of Se in Human Body-A Survey on the Kaschin Beck Disease Region in Loess Plateau, Shanxi Provice..... Li Jiyun et al. (16) Study on the Fundamental Characteristics of Activated Sludge fortified with Powdered Activated A Study on Mathematical Modeling for Biological Rotating Contactor ...... Liu Changsong et al. (29) A Study on the Treatment of the Excess Activated Sludge of Gas Wastewater by Aerobic Digestion Air Oxidation of Sodium Sulphite during the Process of Recovery of Iodine ..... Feasibility Study on the Preliminary Treatment of Pharmaceutical Wastewater with Stabilization Pond ...... Wang Zhiying et al. (47) Analysis of the Cause of Filament Bulking in Activated Sludge and Controlling Mothodology ..... Impacts of the Middle-line South to North Water Shifting Project to the Ecological Environment and Studies on the Indicator of Human Exposure to Polynuclear Aromatic Hydrocarbons in Aluminum Toxicity of Hydrazine and Phenylhydrazin to Embryos and Larvae of Zebrafish (Brachysanio rerio) Existing Pattern, Ionic Forms and Distribution of Aluminum in Masson Pine Seedings ..... Determination of Acetaldehyde in Waste Water by Chemiluminescence Method ...... Lü Xigohu et al. (73) Concentrations and Distributions of Formaldehyde and Total Aldehyde in the Atomosphere of Beijing City in the Summer ...... Bai Yuhua et al. (75) **INDEX 1992** 

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Waster Water by Colorimetry. Yang Fengwu, Li Shiwei (Dushanzi Refinery, Xingjiang Dushanzi 833600):Chin.J. Environ. Sci., 1992, **13**(5), pp.80-83

The characteristics of the condensation reaction aniline acetate and furfural with the formation of a red compound was adopted to determine the content of furfural in wastewater. The conditions for the determination were optimized by using the orthogonal design. Thus, aniline acetate and stabilizing agent were added to the sample of the waste water of oil refining after preliminary treatment with steam distillation, then the sample was colourated for forty minutes in water bath at 20°C, and the content of the furfural was determined by colorimetry at wave length of 518 nm. The recovery of the method was measured to be from 90% to 110% and variation coefficient was less than 5%.

Key words: furfural, aniline acetate, colorimetry, orthogonal design.