三维荧光光谱法测定工业废水中的苯胺

王 伦　周运友　孙益民　杨 耿

（安徽师范大学化学系，芜湖　241000）

摘要　在计算机上运用自编程序绘出苯胺的三维荧光光谱，确定苯胺的特征荧光峰，提出了三维荧光光谱法测定苯胺的分析方法。苯胺浓度在 2.0×10^{-7}—5.0×10^{-6} mol/L 范围内与相对荧光强度呈良好的线性关系。该法相对标准偏差为 2.5%，检出限为 1.0×10^{-7} mol/L。用于工业废水中苯胺的测定，结果令人满意。

关键词　三维荧光光谱，苯胺，工业废水。

苯胺类化合物对人体具有一定毒害作用，并具有致癌性。目前，对工业废水中苯胺类化合物的监测，国际上通用萘乙二胺偶氮光度法[1]，该方法对色度深或含酚量高的工业废水样品，过程繁杂，周期长。三维荧光光谱在分析复杂物质和复杂样品等方面受到重视[2,3]。这种方法能够更加全面地展现被分析物质的荧光特性，增加分析方法的信息量，而且大大改善了分析方法的选择性。本文在计算机上，运用自编程序，测绘并研究了苯胺化合物的三维荧光光谱，在与数种结构相似的有机物的三维荧光光谱比较的基础上，确定了苯胺的特征分析峰。提出了三维荧光光谱法测定苯胺的分析方法。并应用此法测定工业废水样品中苯胺，获得较为满意的结果。

1　实验部分

1.1　仪器与试剂

RF-540 荧光分光光度计(日本岛津)，pHs-3C 型酸度计(上海第二分析仪器厂)，所用试剂均为分析纯，水为二次蒸馏水。

1.2　实验方法

于 25 ml 容量瓶中，加入待分析液，然后依次加入 Triton X-100 5% (V/V)1 ml，醋酸铵缓冲溶液 25% 2 ml(pH=7.0)。用水稀释至刻度。在不同激发波长 λ_{ex} 和不同发射波长 λ_{em} 下测定其相对荧光强度(RFI)。

1.3　数据处理

将实验得到的 $F_i(\lambda_{ex_i}, \lambda_{em_i})$ 数据输入计算机中，经 SIMS 系统处理并绘制成谱图，即三维荧光光谱。

2　结果与讨论

2.1　苯胺的荧光特征峰

苯胺的三维荧光光谱(见图 1)有 2 个峰，峰位分别为（$\lambda_{ex}/\lambda_{em}$）320/340（nm），345/460 (nm)。与数种结构相似的有机化合物的三维荧光光谱比较。发现峰 A_1(320/340)是苯环骨架荧光峰，而峰 A_2(345/460)是苯环上 $-NH_2$ 的荧光峰。前者受芳香族化合物的干扰，后者则不受干扰。根据这一性质，笔者用峰 A_2 的相对荧光强度作为分析信号。

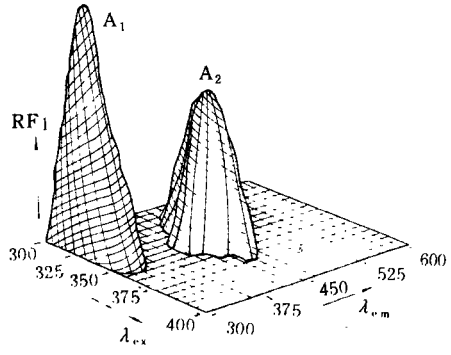

图 1　苯胺三维荧光光谱

A_1：$\lambda_{ex}/\lambda_{em}=320/340$　　A_2：$\lambda_{ex}/\lambda_{em}=345/460$

2.2　最佳实验条件

试验不同pH值及不同缓冲介质对苯胺荧

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光强度的影响。结果表明，在 25%醋酸铵缓冲介质中(pH=7.0)，苯胺的荧光发射强度最强。另外，一些表面活性剂对荧光发射有显著增敏作用。其中 Triton X-100 效果最佳，其适宜浓度范围为 0.1%—0.4%(V/V)。

2.3 工作曲线、精密度和检出限

在最佳实验条件下，苯胺的浓度在 2.0×10^{-7}—5.0×10^{-6} mol/L 范围内，与相对荧光强度呈良好的线性关系(见图 2)。对 1.0×10^{-6} mol/L 苯胺的 10 次测定，相对标准偏差为 2.5%。根据计算公式 $X=X_b+kS_b$[1]，选定置信水平为 90%，即 $k=3$。对空白值 20 次测定，经处理得到检出限为 1.0×10^{-7} mol/L。

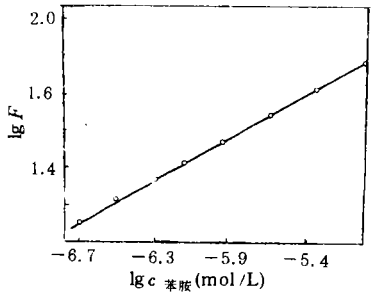

图 2 工作曲线

2.4 共存物质的影响

在最佳实验条件下，苯胺浓度为 1.0×10^{-6} mol/L，相对误差小于 5%。共存物质对苯胺化合物测定的干扰结果为(摩尔倍数)：苯(250)，甲苯(230)，乙苯(230)，硝基苯(240)，二苯胺(100)，N-甲基苯胺(75)，蒽(70)，萘(20)，芘(40)，菲(25)，酚(270)，对甲基苯酚(320)，苏(4)，苯乙烯(170)，水杨酸(150)，一氯苯(300)，三氯苯(300)，α-666(200)，β-666(250)，甲醛(500)，乙醛(500)，乙醇(100)，Na^+、K^+、NH_4^+(>10000)，Mg^{2+}、Ca^{2+}、Ba^{2+}(>5000)、Al^{3+}、Fe^{3+}、Cr^{3+}(>1000)。

2.5 样品分析及回收率试验

对 2 种工业废水(制药厂排放废水和染料厂排放废水)中苯胺含量的分析结果见表 1。该法与萘乙二胺偶氮光度法所测结果一致。在废水样品中进行加标回收试验，获得较为满意的结果(见表 1)。

表 1 样品分析结果

样 品	测定值[1)] (mg/L)	相对标准偏差 (%)	萘乙二胺偶氮光度法(mg/L)	回收率 (%)
制药厂废水	14.3	2.4	14.0	97
染料厂废水	50.3	2.6	50.9	99

1) 4 次测定的平均值

3 结束语

三维荧光光谱法测定苯胺的方法有灵敏度高、重现性好、选择性高、有一定的线性范围、取样少、节约试剂、干扰少等优点。是一种较好的监测苯胺的分析方法。

参考文献

1 国家环保局《水和废水监测分析方法》编委会. 水和废水监测分析方法. 第三版，北京：中国环境科学出版社，1989：422，49
2 李建军等. 分析化学. 1990，**18**(8)：726
3 Wolfbeis O S et al.. Anal. Chim. Acta. 1985,. **167**：203

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参考文献

1 陈国荣等. 重庆环境科学. 1993，**15**(2)：53
2 董保澍. 环境科学丛刊. 1987，**8**(9)：52
3 Multha M J. Environ. progr.. 1983，**2**(3)：193
4 陈学笑. 轻工环保. 1984，(4)：40
5 方宏庄. 重庆环境科学. 1991，**13**(3)：22
6 坂口正之. 産業う環境. 1983，**12**(5)：91
7 陈世黎等. 电力环境保护. 1991，**17**(3)：35
8 赵全福. 工业水处理. 1985，**5**(5)：10
9 余祚洁. 无锡环境保护. 1985，(4)：11

anionic surfactants in water and wastewater were determined at pH = 7.5 with azophloxine two-phase titration. The results of determination of anionic surfactants such as sulfates, sulfonates, benzesulfonates, soap and phosphates etc, with azophloxine titration and methylene blue photometry, respectively, were compared and the interference tests and actual samples analysis were performed. All results show that the azophloxine titration was superior to the methylene blue photometry. The coefficient of variation was 1.0% (n = 11); minimum detectable concentration, 0.052 mg/L (n=21); recovery of standard addition, 92.1%—110.2% on average 100.6% (n= 14). It was suggested that the concentration of anionic surfactants in water should be expressed in molar concentration or PSAA, in stead of mg/L.

Key words: azophloxine, two-phase titration, anionic surfactants, wastewater.

Determination of Aniline in Polluted Water by Tridimensional Fluorescent Spectrometry. Wang Lun et al. (Dept. of Chemistry, Anhui Normal Univ., Wuhu 241000): *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 63—64

The diagram of the tridimensional fluorescent spectrum (TDFS) of aniline was given by using an authors-developed program SIMS (serface image maker system) on a computer. The characteristic peak of aniline was defined. A new method for the determination of aniline by TDFS was suggested. When the concentration was in the range of $2.0\times10^{-7}-5.6\times10^{-6}$ mol/L, a fine linear relationship between aniline concentration and relative fluorescence intensity was shown. The R. D. S. was 2.5%. The detection limit was 1.0×10^{-7} mol/L. With the method, aniline in polluted water from industry was determined satisfactorily.

Key words: aniline, fluorescence, polluted water.

Passive Integrating Measurement of Indoor and Outdoor Radon Concentrations. Zhai Pengji (Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100080): *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 65—66

Both indoor and outdoor ^{222}Rn concentrations of an office building in Zhongguancun, Beijing, were determined by using a CR-39 detector and passive integrating radon monitor in different seasons of spring, summer, autumn and winter, with a total sampling time of 2—6 months. The results show that the radon level found in the basement was higher than that in the office rooms above the basement and the indoor radon levels were higher than the outdoor radon levels. The error sources, including the effects of CR-39 random scanning and reading ways on the results of determination, were also discussed. It was found that, except in some individual cases, the extent of influence caused by different scanning ways was within the range of statistical variation.

Key words: radon, concentration, α tracks, CR-39 detector.

Total Radioactivity in Drinking Water for the Residents Living in Cities and Towns in Liaoning Province. Ma Junjie et al. (Liaoning Provincial Institute of Labour Hygiene, Shenyang 110005): *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 67—68

The detection of total α and β radioactivities in the water samples collected from 50 waterworks companies and 40 self-supported water supply systems for factories or mines in the Liaoning Province was carried out in 1990 to 1994 and the results were reported. It was found that the total α radioactivity was in the ranges of 0.9×10^{-2}—16.3×10^{-2} and $0.3\times10^{-2}-21.6\times10^{-2}$ Bq·L^{-1}, with the averages of 0.046 and 0.065 Bq·L^{-1} which were 8% and 15% over the national standards, respectively in the above two corresponding cases. The total β radioactivity was found in the range of 0.08—1.07 Bq·L^{-1}, with less water samples which were exceeding the national standards. The results show that the natural radioactive nuclides were the major contributors to the total α radioactivity in the drinking water and the natural uranium compounds made the largest contribution by about 43% of the total α radioactivity.

Key words: uranium, α radioactivity, β radioactivity, drinking water, Liaoning Province.

Investigation on the Organic Pollutants in Suspended Solid Particles and Sediments in the Great Canal. Chen Jianlin et al. (Dept. of Environ. Sci. and Eng., Nanjing Univ., Nanjing 210093): *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 69—72

A simple and effective pretreatment procedure was developed to generally analyze the organic pollutants in suspended solid particles and sediment in the Great Canal (Changzhou part) by using a GC/MS/DS system and a method of retention time index. The results show there were relatively high concentrations of carcinogens and