

黑箱理论用于甲醇废水的色谱分析*

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摘要 利用黑箱理论对色谱条件进行了优化。对于甲醇废水, 由 GC/MS 定性, 用 GDX-203+5% 聚乙二醇-20M 作固定相, FID 检测。建立了分析甲醇废水中痕量级 C_1-C_5 醇的气相色谱分析方法。检测下限: C_1-C_3 醇为 1 $\mu\text{g/ml}$, C_4 醇为 3 $\mu\text{g/ml}$, C_5 醇为 4 $\mu\text{g/ml}$ 。

关键词 甲醇废水, 黑箱理论, 气相色谱法。

甲醇废水中主要含有 C_1-C_5 醇类。对于含醇水体系, 大多采用高分子多孔微球作固定相进行色谱分析^[1, 2]。张菊珍等^[2]在分析低碳烯醇时对 GDX 系列固定相进行了考察, 发现 GDX-203 对水、环己烷及低碳醇的分离效果比较理想。水首先出峰, 这些都是常量分析, 未作痕量分析, 且 GDX 系列的缺点是使用的柱温必须很高(大大高于样品的沸点), 峰形比较宽。用 FID 检测时造成柱温越高水的干扰信号越大, 会干扰甲醇的分析, 另外用程序升温法时基线飘移严重。所以必须加以改进。

1 仪器与试剂

1.1 仪器

SP-501N 型气相色谱仪, 鲁南化工仪器厂生产; 氢火焰离子化检测器, COMC-1B 型色谱处理机, 上海计算技术研究所生产; JB-3000 型微型计算机。

1.2 试剂

所用试剂均为分析纯试剂。

2 固定相的选择与处理

在 GDX-203(60—80 目)上分别涂上 5% 的 OV-17, polyethylene glycol succinate, 乙二醇二酸聚酯和聚乙二醇-20M 进行试验, 色谱柱为长 2 m, 内径 4 mm 的不锈钢柱。结果表明这几种固定液均能不同程度地减小醇类的保留值。但是, OV-17 使水峰拖尾后移, 甲醇峰拖尾严重, 聚乙二醇-20M 最好, 不仅使保留值减小,

而且峰形很好, 其它次之。再涂上 2% 和 8% 的聚乙二醇-20M 作试验, 发现涂 2% 对保留值影响不很大, 而涂 8% 又大大改变了高分子多孔微球对水的弱保留性能, 使水峰拖尾并后移。由于分析时进样量比较大, 大量水会在 FID 上留下干扰信号, 严重干扰甲醇和乙醇的测定。为此选用 GDX-203+5% 聚乙二醇-20M 作固定相。

3 色谱条件的优化^[3]

3.1 黑箱理论

实验中要优化的指标(称为目标函数)好比是一只“黑箱”, 这个目标函数值与各因子的函数表达式无法知道。由多元泰勒定理可知, 复杂函数(其偏导存在)可以展开成多项式, 可舍去高次项, 而用二次多项式来近似表示。二次回归方程表示为:

$$y = f(x) = a_0 + \sum_{i=1}^m a_i x_i + \sum_{i < j} a_{ij} x_i x_j + \sum_{j=1}^m a_{jj} x_j^2 \quad (1)$$

式中, y , $f(x)$ 为目标函数; a_0 , a_i , a_{ij} , a_{jj} 为常数, m 为因子数, x 为向量, $x = (x_1, x_2, \dots, x_m)^T$, x_i 为因子。

用最小二乘法根据正交试验数据可以拟合出回归方程(1), 方程(1)即成为预测方程。对方程(1)在约束条件下求极值即得最佳条件。

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3.2 色谱条件优化

选正丙醇配制 51 $\mu\text{g/ml}$ 的水溶液。柱温为 126℃, 汽化室温为 140℃, 检测室温为 160℃, 按正交设计 $[L_9(3)^4]$ 安排实验。每个点做 2 次, 测定不同条件下的响应值(峰面积)。因子与水平数(流量 ml/min , 26℃)关系见表 1。

表 1 因子与水平数据

| 因 子 | 水 平 | | |
|-----|-----|-----|-----|
| | 1 | 2 | 3 |
| 氢气 | 30 | 40 | 50 |
| 氮气 | 30 | 50 | 70 |
| 空气 | 300 | 400 | 500 |

设氢气的流量为 x_1 , 氮气为 x_2 , 空气为 x_3 ,

则二次回归方程为:

$$y = f(x) = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3 + a_{11}x_1^2 + a_{22}x_2^2 + a_{33}x_3^2$$

正交试验数据用多元线性拟合方法求得回归方程为:

$$y = f(x) = 4947.894 + 174.5x_1 - 58.875x_2 - 21.031x_3 + 4.359x_1x_2 + 0.083x_1x_3 + 0.004x_2x_3 - 5.137x_1^2 - 1.003x_2^2 + 0.022x_3^2 \quad (2)$$

正交试验结果和回归方程(2)的计算结果见表 2。

表 2 正交试验结果与回归方程(2)计算结果

| 试验号 | 列 号 | | | | 峰面积($\mu\text{V} \cdot \text{s}$) | | | |
|------|------|------|------|------|-------------------------------------|----------------------|----------------------|----------------|
| | 1 氢气 | 2 氮气 | 3 空气 | 4 空列 | $y_{\text{实}}$ | $\bar{y}_{\text{实}}$ | $\bar{y}_{\text{计}}$ | $y_{\text{计}}$ |
| 1 | 1 | 1 | 1 | 1 | 3321 | 3209 | 3265 | 3267 |
| 2 | 1 | 2 | 2 | 2 | 2831 | 2850 | 2841 | 2830 |
| 3 | 1 | 3 | 3 | 3 | 2048 | 2101 | 2075 | 2047 |
| 4 | 2 | 1 | 2 | 3 | 2795 | 2697 | 2746 | 2754 |
| 5 | 2 | 2 | 3 | 1 | 3695 | 3760 | 3728 | 3719 |
| 6 | 2 | 3 | 1 | 2 | 3611 | 3650 | 3631 | 3629 |
| 7 | 3 | 1 | 3 | 2 | 1818 | 1792 | 1805 | 1819 |
| 8 | 3 | 2 | 1 | 3 | 3187 | 3278 | 3233 | 3252 |
| 9 | 3 | 3 | 2 | 1 | 3859 | 3998 | 3929 | 3930 |
| 最佳条件 | 3 | 3 | 3 | | 4260 | 4231 | 4246 | 4250 |

从表 2 中可见, 回归方程预测值和实验值能很好地符合, 说明方程(2)能准确地预测不同流量下的响应值。对方程(2)在约束条件($30 \leq x_1 \leq 50$, $30 \leq x_2 \leq 70$, $300 \leq x_3 \leq 500$)下求极大值, 即得最佳条件, 用内惩罚函数法对方程(2)求极大值, 得最佳条件 $x^* = (49.99567, 69.99941, 499.99064)^T$, $y_{\text{max}} = 4250$, 即氢气流量取 50 ml/min , 氮气取 70 ml/min , 空气取 500 ml/min 。用实验验证为 4246(见表 2), 说明优化结果是正确的。至此各种气体的流量已经确定。所有优化计算都由 JB-3000 微机完成, 具体的算法可参见献[4]。

4 定性与定量分析

4.1 定性分析

甲醇废水经无水 CaCl_2 、3A 分子筛等吸水浓缩后, 由中国药科大学分析测试中心用聚乙二醇-20M 毛细管色谱柱进行 GC/MS 定性, 醇类流失顺序为甲醇、乙醇、异丙醇、正丙醇、仲丁醇、异丁醇、正丁醇、戊醇-[2]、异戊醇、正戊醇。并在 GDX-203+5% 聚乙二醇-20M 上用标样得到了验证。(戊醇-[2]因无标样, 未该对)

4.2 定量分析

4.2.1 色谱条件

由于废水中含有 $\text{C}_1 - \text{C}_5$ 醇类, 沸程比较宽, 柱温太低, 重组分保留时间太长, 甚至不出峰, 柱温太高, 水和甲醇分不开。甲醇受水信号干扰, 所以使用程序升温法。

经过多次实验, 适宜的色谱条件为: 检测室温 160℃, 汽化室温 140℃; 柱温: 初温 80℃。

初始时间为 0，升温速率为 10 C/min，终止温度为 160℃；H₂ 流量为 50 ml/min，N₂ 为 70 ml/min，空气为 500 ml/min；进样量 4 μl。标样和甲醇废水的色谱图见图 1。

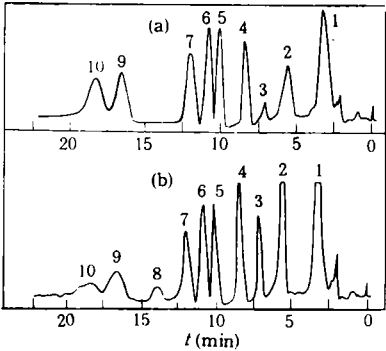


图 1 C₁—C₅ 醇色谱图

- (a) 标样色谱图 (b) 甲醇废水色谱图
1. 甲醇 2. 乙醇 3. 异丙醇 4. 正丙醇
5. 仲丁醇 6. 异丁醇 7. 正丁醇
8. 戊醇-[2] 9. 异戊醇 10. 正戊醇

4.2.2 定量方法

采用外标法定量，配制和被测物浓度相近的标准溶液，在进样量(4 μl)一定时，采用一点

法比较标样和被测物的峰面积得出被测物的浓度。不同厂家的甲醇废水，由于所用催化剂和原料的差异，有的含有戊醇-[2]，有的则没有。因无戊醇-[2]标样，定量时以异戊醇为标准。

4.2.3 分析实例

甲醇塔经过数模计算，改变现有操作条件，采用先进的侧线采出技术，可使釜底甲醇废水中的醇类总浓度降至 0.01%(即 100 μg/ml)以下，大大降低了有机物的排放量。

某化肥厂联产甲醇，经该技术改造后甲醇废水中的低碳醇含量由近 3%降为 50 μg/ml 以下(见表 3)。

5 小结

(1) 在 GDX-203 上涂 5% 聚乙二醇-20M 固定液，覆盖了高分子多孔微球表面部分极性点，使出峰时间大为缩短，峰形变窄，使用柱温也大大降低。固定液的浓度不能太小或太大。太小作用不大，太大会使水峰后移，干扰甲醇、乙醇的分析。

(2) 利用黑箱理论对 FID 检测条件进行优

表 3 甲醇废水的实测结果(μg/ml)

| 样 品 | 甲 醇 | 乙 醇 | 异 丙 醇 | 正 丙 醇 | 仲 丁 醇 | 异 丁 醇 | 正 丁 醇 | 戊 醇 [2] | 异 戊 醇 | 正 戊 醇 |
|-----------|--------|--------|-------------|-------------|-------------|-------------|-------------|---------------|-------------|-------------|
| 某厂 1 | 27000 | 6 | | 27 | 5 | | 20 | | 7 | 21 |
| 某厂 1(改造后) | 15 | 1 | | | | | 2 | | 5 | 9 |
| 某厂 2 | 26114 | 1908 | 53 | 621 | 130 | 140 | 152 | 31 | 60 | 35 |

化。先由正交试验数据用最小二乘法求得二次回归方程，然后用内惩罚函数法对二次回归方程在有约束条件下求极值，得最佳条件。该方法优于正交试验法，可弥补正交设计时未考虑因子间交互作用的不足。

(3) 建立了分析甲醇废水的分析方法。在

进样量为 4 μl 时，C₁—C₃ 醇的最小检测限为 1 μg/ml，C₄ 醇为 3 μg/ml，C₅ 醇为 4 μg/ml。

参 考 文 献

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3 秦金平, 张菊珍, 程明霄. 化学世界. 1994, 35(1): 25

ments in batch experiments. A COD removal of 98.4% was given when a gentamycin wastewater with a COD concentration of 19240 mg/L was subjected to an anaerobic treatment for 3 d and then to an aerobic treatment for 10 h. A COD removal of 95.8% was given when a mixture of gentamycin wastewater and aureomycin wastewater (1 : 2) with a COD concentration of 7740 mg/L was subjected to an anaerobic treatment for 2 d and then to an aerobic treatment for 10 h. The COD concentration in final effluent could be reduced to less than 300 mg/L when the gentamycin wastewater after an anaerobic treatment for 3 d was combined with the aureomycin wastewater after an anaerobic treatment for 6 h and then subjected to an aerobic treatment for 4 h.

Key words: gentamycin wastewater, aureomycin wastewater, refractory organics, anaerobic-aerobic treatment.

Chemical Valence States of Sulfur Measured with a High Resolution Two Crystal X-ray Fluorescence Method. Wang Qingguang et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085), Ji Ang (Shanghai Institute of silicates, Chinese Academy of Sciences, Shanghai 200050), Ma Guangzu (Institute of Rock and Mineral Analysis, Ministry of Geology and Mineral Resources, Beijing 100037); *Chin. J. Environ. Sci.*, **16** (5), 1995, pp. 48–50

With a high resolution two crystal X-ray fluorescence (HRXRF) method, the chemical valence states of sulfur in pure elemental sulfur, sulfites, sulfates and sulfides and in some of unknown samples were determined, the range of energy differences of the spectral peaks for sulfur in different valence states were identified, and then the range of energy differences was used to identify the chemical valences of sulfur in unknown samples. Each of chemical valence states of sulfur in standard samples had essentially no change after they had been subjected to repeated HRXRF measurements. Sulfur in various chemical valence states had the following ranges of energy differences for spectral peaks; S^{6+} , +1.10 to +1.25 eV; S^{4+} , +0.61 to +0.93 eV; and S^{2-} , -0.12 to -0.21 eV. This method was found useful in the measurement of sulfur in a single chemical valence state, and in the identification of different chemical valence states of sulfur.

Key words: HRXRE, chemical valence state, sulfur, sulfur-bearing compounds, energy

change.

Application of Black-box Theory to GC Analysis of Waste Containing Methanol. Qin Jinping et al. (Nanjing Institute of Chemical Technology, Nanjing 210009); *Chin. J. Environ. Sci.*, **16** (5), 1995, pp. 51–53

The GC optimal conditions were estimated based on black-box theory. GC/MS was used for qualitative analysis of methanol wastewater. On the GPX-203 (60–80 mesh) coated with 5% PEG-20 M, C_1 – C_5 alcohols in methanol wastewater were quantitatively analyzed by means of FID. The detection limits were 1 μ /ml for C_1 – C_3 alcohols, 3 μ g/ml for C_4 alcohols, and 4 μ g/ml for C_5 alcohols.

Key words: methanol, wastewater, C_1 – C_5 alcohols, black-box theory, gas chromatography.

Flame Atomic Absorption Spectrometric Determination of Copper, Lead, Cadmium, and Manganese in Natural Waters Using a Flow Injection System with On-line Ion Exchange Preconcentration. Wang Peng et al. (Dept. of Applied Chemistry, Harbin Institute of Technology, Harbin 150006); *Chin. J. Environ. Sci.*, **16** (5), 1995, pp. 54–56

The title method was developed, and some practical considerations in the design of on-line column preconcentration FIA system for FAAS were studied. The relative standard deviation was about 2.0% ($n=11$) at a sampling frequency of 45 h^{-1} with an enrichment of around 20 times. The advantages, such as high-efficiency, on-line, accuracy, precision, micro-amount of sample, automation et al., made it possible to be applied to the routine analysis of natural waters.

Key words: flow injection analysis (FIA), ion exchange preconcentration, atomic absorption spectrometry, copper, lead, cadmium, manganese.

Study on the Seasonal Variations in the Atmospheric Particulate Nitrate and Sulfate Concentrations in the Yanshan District of Beijing. Li Xin, Guo Huajie et al. (Dept. of Technical Physics, Peking Univ., Beijing 100871); *Chin. J. Environ. Sci.*, **16**(5), 1995, pp. 57–60

The title study was carried out in summer and autumn, in which the seasonal variations were also related to the atmospheric concentration of ozone as a major photochemical oxidant. The results show that the concentrations of nitrate and sulfate in atmospheric particulates varied significantly with seasons, and were higher in summer than in