

地下水中 H 酸衍生污染物的对照分析

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摘要 对地下水中一种染料中间体 H 酸(4-氨基-5-羟基-2, 7-萘二磺酸)的污染进行了提取、分离、碱熔融试验, 并与已知可能的污染物进行薄层色谱和红外光谱对照分析, 确定该地下水中棕红色污染物为 H 酸长期氧化的衍生产物。

关键词 地下水污染, H 酸, 薄层色谱。

H 酸(4-氨基-5-羟基-2, 7-萘二磺酸)及其一钠盐是合成染料的重要中间体。它们的废液排放对附近河流和地下水会造成污染, 特别是对碱性土壤或与工厂(如造纸厂)排放的碱性废液合流, 这种污染现象尤为显著。某地一造纸厂附近两口地下井水均呈棕红色, 类似酱油, 严重影响人畜饮水和农田灌溉。原以为是造纸厂废液所致, 后经对照分析, 发现污染来自 H 酸(及其一钠盐)在排污中长期氧化的衍生污染物。本工作采用已知可能的污染物与井水中棕红色物质作薄层色谱, 红外光谱等对照分析, 寻找出导致该 2 口井水呈棕红色的污染源。

1 实验部分

1.1 仪器和试剂

UV-3000 型紫外/可见分光光度计, 1700 型 PERKIN-ELMER 傅立叶变换红外光谱仪。薄层色谱所用的展层剂以及分离提取用的试剂均为分析纯。薄层色谱用硅胶 G, 柱层析用氧化铝(中性 200-300 目)。

1.2 实验方法

(1) 地下水样的采集和处理 水样取自某地邻近排污河的造纸厂内地下井水, 呈棕红色, 略有异味, 在紫外灯下略呈黄绿色荧光, pH 为 7.5 左右。水样在水浴上减压浓缩, 冷却后析出大量的无机盐类残渣, 棕红色物和荧光物仍留在溶液中。经氧化铝柱色谱分离, 用蒸馏水洗

脱荧光物质。棕红色物质吸附在色谱柱上, 然后用稀氨水将其洗脱, 在水浴上蒸干棕红色洗脱液, 用含少量水的甲醇反复提取棕红色物质, 蒸去溶剂得棕红色固体试样(其中仍含有少量无机盐)。

(2) 棕红色物质的薄层色谱分离 将甲醇提取的棕红色物质用 3 种不同的展层剂进行薄层色谱试验。薄层板: 硅胶 G 板。展层剂: a. 丙醇-浓氨水(2: 1), b. 乙酸乙酯-浓氨水-乙醇-水(2: 1: 2.5: 2), c. 丙醇-浓氨水-吡啶-乙醇(4: 3: 2: 1)。

(3) 碱熔融乙醚提取条件及其薄层色谱 将棕红色物质和可能污染物分别与过量固体 NaOH 混匀, 在硅油浴上, 加热搅拌至 280℃, 3 h 后, 冷却加水溶解, 用盐酸调至中性、乙醚提取, 将乙醚提取物进行薄层色谱分离。

薄层板: 硅胶 G 板

展层剂: d 苯-二氧六环-乙酸(9: 2.5: 0.4)

显色剂: 1% 对硝基苯重氮氟硼酸盐的乙醇溶液。

2 结果和讨论

2.1 棕红色污染物的特性

(1) 棕红色污染物热稳定性强, 经薄层色

谱试验, 浓缩前后两者的 R_f 值相同, 色泽不变.

(2) 极易溶于水, 微溶于甲醇, 不溶于乙醇、乙醚、丙酮、二氧六环、氯仿等溶剂.

(3) 经柱色谱分离, 含水甲醇提取的棕红色物质用展层剂(a, b, c)进行薄层色谱分离均呈现单一棕红色斑点, R_f 值分别为 a. 0.04, b. 0.89, c. 0.09.

(4) 棕红色物质熔点高(加热至 300°C 不熔化), 对其进行质谱试验不出峰. 红外光谱试验(见图 5)和碱熔融乙醚提取物的薄层分离显色试验均证明含有芳香磺酸基^[1].

2.2 薄层色谱

棕红色物质与几种可能污染物的薄层色谱见图 1.

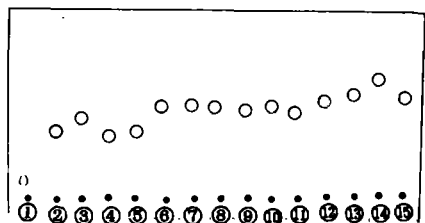


图 1 棕红色物质与几种可能污染物的薄层层析图(展层剂 a)

- ① 棕红色物 ② H 酸 ③ 变色酸 ④ 1-萘酚-3,6-二磺酸
⑤ 2-萘酚-6,8-二磺酸钾 ⑥ 1-氨基-2-萘酚-4-磺酸
⑦ r 酸 ⑧ J 酸 ⑨ 分散剂 NNO ⑩ 分散剂 MF
⑪ 分散剂 CNF ⑫ 分散剂 S ⑬ 造纸厂
废液(酸不溶部分) ⑭ 造纸厂废液(酸溶部分)
⑮ 萘醌-2,6-二磺酸钠

可能污染物是根据当地环保局提供的资料. 色谱分离时, 个别不显色的化合物可在紫外灯下观察其荧光. 从斑点的颜色、荧光和 R_f 值, 说明棕红色物质不属于这些可能的污染物.

2.3 经碱熔融乙醚提取物的薄层色谱

薄层层析见图 2.

从图 2 中看出, 棕红色物质经碱熔融乙醚提取物的薄层色谱分离, 出现 4 个酚类斑点. 而在可能的污染物中仅 H 酸和变色酸的碱熔融乙醚提取物有与棕红色物相近的酚类色谱斑点和 R_f 值, 因而需作以下进一步验证.

2.4 H 酸和变色酸氧化产物与红棕色物的薄层色谱

将相同摩尔浓度的 H 酸(及其一钠盐)和变色酸的水溶液分别添加地下井水中所含的主要无机盐以模拟水样, 在同一室温下, 经 4 周以上的空气氧化, 然后与棕红色污染物相同的条件进行柱色谱分离和提取, 再做薄层色谱对照试验(图 3).

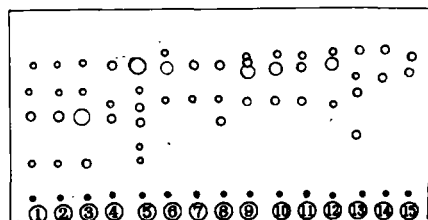


图 2 棕红色物质与几种可能污染物经碱熔融乙醚提取物的薄层层析图(展层剂 d)
序号含义同图 1

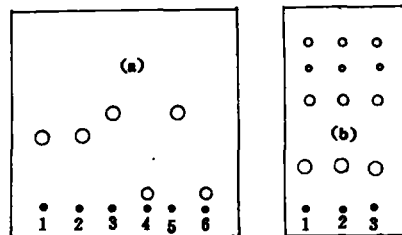


图 3 薄层色谱图

- (a) H 酸和变色酸以及经氧化的产物与棕红色物(展层剂 a), 其中: 1. H 酸一钠盐 2. H 酸
3. 变色酸 4. H 酸(及其一钠盐)的氧化产物
5. 变色酸的氧化产物 6. 棕红色物

- (b) H 酸(及其一钠盐)氧化产物和棕红色物经碱熔融乙醚提取物(展层剂 d), 其中: 1. H 酸(及其一钠盐)碱熔融乙醚提取物 2. H 酸(及其一钠盐)氧化产物碱熔融乙醚提取物 3. 棕红色物碱熔融乙醚提取物

图 3(a)表明, 变色酸氧化产物的 R_f 值与棕红色污染物不同, 而 H 酸(及其一钠盐)氧化产物的 R_f 值则相近. 因此, 棕红色物有可能是 H 酸(或其一钠盐)的氧化产物.

2.5 H 酸氧化产物碱熔融乙醚提取物与棕红色物的薄层色谱对照

H 酸(及其一钠盐)和棕红色物在相同条件下碱熔融乙醚提取物的薄层色谱出现酚的斑点数

目和 R_f 值相互对应, 见图 3(b).

经上述对照鉴定证明, H 酸(及其一钠盐)的碱熔乙醚提取物, H 酸(及其一钠盐)氧化产物碱熔乙醚提取物的薄层色谱均与棕红色物碱熔乙醚提取物相似.

2.6 棕红色物质和 H 酸(及其一钠盐)氧化产物的光谱分析

紫外-可见吸收光谱见图 4.

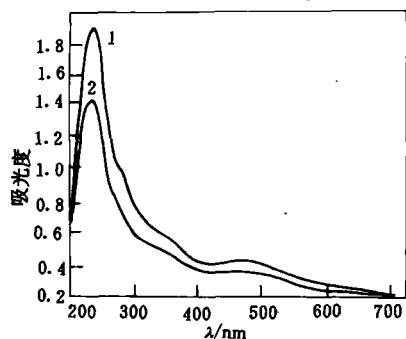


图 4 H 酸(及其一钠盐)氧化产物与棕红色物的紫外/可见光谱图(甲醇为溶剂)

1. H 酸(及其一钠盐)的氧化产物(3.68×10^{-2} mg/ml)
2. 棕红色污染物(2.98×10^{-2} mg/ml)

从图 4 中看出, 二者的吸收曲线走向相同, 且最大吸收峰的位置与强度都能很好吻合. 红外光谱见图 5.

由图 5 看出, 棕红色污染物和 H 酸(或其一钠盐)的氧化产物有相似的红外光谱, 在 3400 cm^{-1} 、 1200 cm^{-1} 、 1100 cm^{-1} 和 1040 cm^{-1} 均有羟基, 芳环和磺酸基特征峰^[2].

3 结论

棕红色污染物为芳香磺酸盐类, 熔点高且难与无机盐完全分离, 若进行质谱分析需用电

子冲击质谱法或离子束质谱法^[3]等. 进行核磁共振实验也未得到清晰的图谱. 依据当地实际情况选择可能的污染物标样, 经直接薄层色谱和碱熔乙醚提取物的薄层色谱, 找出与棕红色污染物相近的标样, 然后将近似的标样经过氧化, 薄层色谱, 紫外/可见光谱、红外光谱等手段进一步对照分析, 发现只有 H 酸(及其一钠盐)的氧化产物与棕红色污染物相吻合, 因此确定该地下水的棕红色物质为 H 酸(及其一钠盐)长期氧化后的衍生产物.

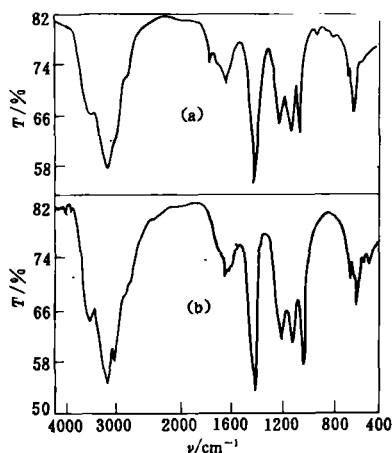


图 5 红外光谱图(KBr 压片)

(a) 棕红色物质 (b) H 酸(或其一钠盐)氧化产物

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Longsheng et al. (Institute of Marine Environmental Protection, SOA, Dalian 116023); *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 56—58

In this paper, the residue of pollutants in economical shellfish along the coast of Huanghai and Bohai Seas during July 1990 and December 1991 was investigated. The background value of concentration of the petroleum hydrocarbons in mollusc along the coast has been calculated. Its overall range is 3.47—19.7 mg/kg (wet), and upper limit of the background value was utilized as assessment standard for the pollution level of oil in shellfish along the coast, the sea area division on pollution degrees of oil in mollusc was done. The results showed that content of oil in shellfish of Dalian bay and Changjiang River estuary and west Jinzhou bay is higher, and the coast of north Huanghai Sea from Yalujiang River mouth to Dayao bay is lower.

Key words: economical shellfish, petroleum hydrocarbons, background value, the coast of Huanghai and Bohai Seas.

Study on the Spectrophotometric Determination of Lead with DBS-Chlorophosphonazo. Zhao Shulin et al. (Shenyang Institute of Chemical Technology, Shenyang, 110021); *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 59—61

In acidic solution, lead forms a blue colour complex with DBS-chlorophosphonazo. This complex exhibits absorption maximum at 635 nm with apparent molar absorptivity of $4.7 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. The molar ratio of lead to DBS-Chlorophosphonazo has been found to be 1 : 2. Beer's law is obeyed in the concentration range of 0—20 μg per 25 ml. This colour reaction has been used directly for the spectrophotometric determination of lead in cosmetics and dust of smelting copper with satisfactory results.

Key words: DBS-chlorophosphonazo, lead, spectrophotometry.

Determination of RH-5992 in Aquatic Environment by Liquid Chromatography. Zhu Jiusheng. (Institute of Plant protection, Shanxi Academy. of Agri. Sci., Taiyuan 030031), K. M. S. Sundaram and R. Nott (Forestry Canada, Forest Pest Management Institute Ste., Marie P6A 5M7); *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 62—64

A method was developed to determine RH-5992 in some aquatic environment matrixes. The procedure included solvent extration, liquid-liquid partition, column cleanup and liquid chromatographic determination. RH-5992 was analyzed on a liquid chromatograph equipped with a diode-array UV detector set at 236 nm, using a RP-8, 10 μm column with a mobile phase of acetonitrile-dioxane-water. Mean recoveries for analyte ranged from 85% to 98%, with coefficient of variation from 6% to 9%. Limits of detection were 0.050 mg/kg for natural waters and from 0.009 to 0.028 mg/kg for other matrixes.

Key words: RH-5992, aquatic environment, residual analysis, high performance liquid chromatography.

A Comparative Analysis for the Pollutants Derived from H Acid in Underground Water. Liu Meijun et al. (Dept. of Chem. Zhengzhou University, Zhengzhou 450052); *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 65—67

The brown red pollutants in underground water derived from a dyestuff intermediate-H acid (4-amino-5-hydroxy-2,7-naphthalene disulfonic acid) were extracted by means of reduced pressure concentration, column chromatographic separation. The extracted pollutants were primarily tested by alkali fussion, and then undertaken the comparative analysis between the pollutants and some standard samples which were selected as possible pollutants in the light of the actual conditions. According to the thin layer chromatography and IR spectrometry of them. It can be established that the brown red pollutants were the derivatives of H acid oxidized by air for a period of time in underground water.

Key words: pollution in underground water, H acid, thin layer chromatography.

Fast Determination of Carbon Disulfide in Wastewater.

Fang Haijun et al. (Shanghai Jiao Tong University, Shanghai 200240); *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 68—71

This paper studied an improving method using spectrophotometry to determine CS_2 in wastewater. By using tube-strip system instead of washing gas bottle, the stripping efficiency was raised, and the stripping time was reduced greatly. Nearly no declining sensibility and accuracy of analysis, the time of analysis was shortened from 1—2 hours to several minutes. The carbon disulfide in wastewater can be determined quickly. Analytical precision is $<3\%$ of RSD, mass of detection limit $<5 \mu\text{g}$, recovery $>90\%$. If the wastewater sample is 10 ml, the lowest detection consistence is $<0.5 \text{ mg/L}$.

Key words: wastewater, fast determination, spectrophotometry, CS_2 .

The Studies and Assessment for Ecological Environment and Social Economic Conditions in the Upper Reaches of the Changjiang River. Zhong Xianghao et al. (Institute of Mountain Hazards and Environment, Chinese Academy of Sciences and Ministry of Water Conservance, Chengdu 610041); *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 72—75

The area is distributed in the watersheds of the Wujiang River and the Changjiang River which includes the Jialingjiang River, the Qujiang River, the Fujiang River, the Tuojiang River and the upper reaches of Minjiang River in the upper reaches of the Changjiang River. Applied the integrated standpoint under guidance of the theory of systems science, the characteristics of natural and social economic environment and the assessment for their effects on the forests, ecological economic divisions and macroscopic overall arrangement of the ecology-economic protection forest system, and quantitative forecast for development prospects of the protection forests in each of the ecological economic divisions have been studied. A great quantity of technological data, and quantitative and qualitative assess-