

# DBS-偶氮氯膦分光光度法测定铅的研究\*

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**摘要** 为了克服用双硫脲比色法测环境样品中铅的选择性差和条件要求严等缺点, 研究了铅与 DBS-偶氮氯膦的显色反应, 并提出了用分光光度测定铅的新方法. 在稀盐酸介质中, 铅与 DBS-偶氮氯膦形成 1:2 的蓝色配合物, 最大吸收波长位于 635 nm, 表观摩尔吸光系数为  $4.7 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ , 铅量在 0—25  $\mu\text{g}/25 \text{ ml}$  范围内符合比耳定律. 应用于化妆品及铜冶炼烟尘中铅的测定, 获得了满意的结果.

**关键词** DBS-偶氮氯膦, 铅, 分光光度法.

环境样品中铅的光度法测定, 通常均采用双硫脲比色法<sup>[1, 2]</sup>, 由于该法选择性差, 条件要求较严, 且需用四氯化碳萃取或用剧毒的氰化钾掩蔽干扰离子, 因此应用不便. 本研究采用 2-(4-氯-2-膦酸基苯偶氮)-7-(2, 6-二溴-4-磺酸苯偶氮)-1, 8-二羟基-3, 6-萘二磺酸 [2-(4-chloro-2-phosphonophenylazo)-7-(2, 6-dibromo-4-sulphophenylazo)-1, 8-dihydroxy-3, 6-naphthalene disulfonic acid] 简称 DBS-偶氮氯膦 (DBS-CPA)<sup>[3]</sup>, 作为铅的显色剂, 对显色反应的条件及配合物的光度特性进行了探讨, 拟定了直接光度测定铅的新方法. 该法灵敏度高, 选择性好, 简便快速.

## 1 实验部分

### 1.1 主要试剂与仪器

(1) 铅标准溶液 称取 0.7993 g 硝酸铅, 用少量水溶解后, 再加入 2 ml 硝酸(1+1), 并以水稀释至 500 ml, 摇匀. 此溶液每 ml 含 1mg 铅, 使用时再用水稀释成每 ml 含 10  $\mu\text{g}$  铅的工作溶液.

(2) DBS-偶氮氯膦 0.1% 的水溶液.

(3) 本实验所用试剂均为分析纯以上, 分析用水为去离子水.

(4) 721 型分光光度计(上海第三分析仪器厂).

### 1.2 实验方法

准确移取一定量铅标准溶液, 于 25 ml 容量瓶中, 依次加入 3 ml 2mol/L 的盐酸溶液, 3 ml 0.1% 的 DBS-CPA 溶液, 以水稀释至刻度, 摇匀. 放置 10 min 后, 用 2 cm 比色皿, 以试剂空白为参比, 在分光光度计上, 于 635 nm 波长处, 测量吸光度.

## 2 结果与讨论

### 2.1 吸收光谱

取一定量铅标准溶液, 按实验方法显色后, 分别测定试剂空白对水和配合物对试剂空白, 在不同波长下的吸光度, 并绘制吸收光谱, 结果如图 1 所示. 铅与 DBS-CPA 形成的配合物, 最大吸收峰位于 635 nm, 试剂本身为 540 nm,  $\Delta\lambda$  为 95 nm.

### 2.2 配合物的形成条件

(1) 介质及酸度的影响 试验在不同酸介质中进行. 配合物的形成情况. 结果表明, 在稀硫酸、盐酸、高氯酸介质中, 配合物均能形成, 吸光度相近. 本实验采用盐酸介质, 当 2 mol/L 盐酸溶液的用量在 1—3.5 ml 内, 吸光度基本一致, 试验中加入 3 ml.

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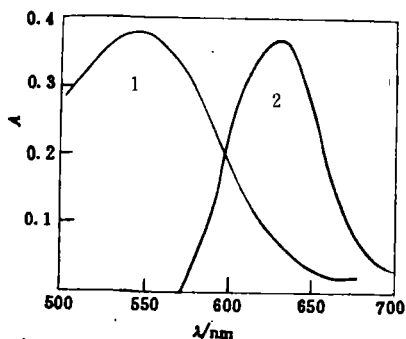


图1 吸收光谱  
1. 试剂空白(HCl 0.24 mol/L 稀释 10 倍)对水  
2. 配合物对试剂空白

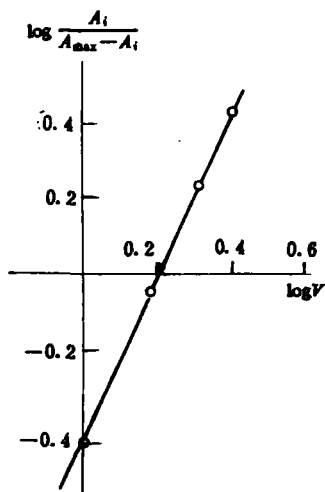


图2 平衡移动法

(2) 显色剂用量 配合物的吸光度随 0.1% 的 DBS-CPA 用量增加而上升, 当用量大于 2.5 ml 以后, 吸光度最大且保持定值, 本试验选用 3 ml.

(3) 显色时间及配合物稳定性 实验结果表明, 配合物在室温下显色, 10 min 内吸光度达最大值, 且在 5 h 内吸光度保持不变.

### 2.3 配合物的组成

用体积因素平衡移动法和直线法, 测定了铅与 DBS-CPA 生成的配合物的组成比(见图 2, 3). 2 种方法测得结果均表明, 在配合物中  $\text{Pb} : \text{DBS-CPA} = 1 : 2$ .

### 2.4 工作曲线及测定灵敏度

分别取不同量的铅标准溶液, 按实验方法显色, 测定吸光度并绘制工作曲线. 结果表明, 在 25 ml 体积中, 铅量在 0—20  $\mu\text{g}$  内服从比耳定律, 用最小二乘法求得线性回归方程为:  $A = 0.0189c - 0.010$  ( $c$  为  $\mu\text{g}/25\text{ ml}$ ), 相关系数  $r = 0.9998$ , 计算得表观摩尔吸光系数  $\epsilon_{635} = 4.7 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ .

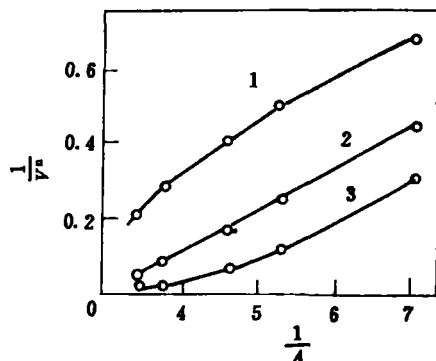


图3 直线法  
1.  $n=1$  2.  $n=2$  3.  $n=3$

### 2.5 共存离子的影响

在本实验条件下, 测定 10  $\mu\text{g}$  铅, 相对误差不超过  $\pm 5\%$  时, 共存离子和允许量列于表 1.

从表 1 可以看出, 稀土、 $\text{Ca}^{2+}$ 、 $\text{Nb(V)}$ 、 $\text{Bi}^{3+}$ 、 $\text{Ti(IV)}$ 、 $\text{Sr}^{2+}$  等离子的允许量甚少. 在实际样品测定过程中, 若上述离子超过允许量时, 可采用巯基棉预先分离除去<sup>[4-6]</sup>.

表1 共存离子的影响

共存离子	允许量/mg	共存离子	允许量/mg
$\text{Co}^{2+}$	5	$\text{Mo(V)}$	0.1
$\text{Zn}^{2+}$	3	$\text{Mn}^{2+}$	0.1
$\text{Mg}^{2+}$	3	$\text{Sn}^{2+}$	0.07
$\text{V(V)}$	1.2	$\text{Zr(IV)}$	0.01
$\text{Cu}^{2+}$	1	$\text{Nb(V)}$	0.005
$\text{Ni}^{2+}$	1	$\text{Ca}^{2+}$	0.005
$\text{Cd}^{2+}$	1	$\text{Bi}^{3+}$	0.002
$\text{Cr}^{3+}$	0.5	$\text{Ti(IV)}$	0.002
$\text{Al}^{3+}$	0.5	$\text{Sr}^{2+}$	0.001
$\text{Fe}^{2+}$	0.2	$\text{Ce}^{4+}$	0.001
$\text{W(V)}$	0.2		

### 3 样品分析

#### 3.1 化妆品中铅的测定

准确称取化妆品试样 1 g 于 100 ml 瓷蒸发皿中, 加入 10 ml 硝酸, 低温加热消解, 并蒸发至 2—3 ml, 取下冷却后, 加入 2—5 ml 高氯酸, 继续加热至冒白烟, 此时试液呈淡黄色或无色, 并蒸发至 1 ml 左右. 冷却至室温后, 用少量水冲洗皿壁, 并将试液转入 50 ml 容量瓶中, 以水稀释至刻度, 摇匀.

移取上述试液 10 ml 于 25 ml 容量瓶中, 然后依次加入 4 ml 2% 的抗坏血酸溶液, 3 ml 2 mol/L 的盐酸溶液和 3 ml 0.1% 的 DBS-CPA 溶

液, 以水稀释至标线, 摇匀. 放置 10 min 后, 在分光光度计上, 用 2 cm 比色皿, 以试剂空白为参比, 于 635 nm 波长处, 测量吸光度. 查工作曲线求得铅的含量, 结果见表 2.

#### 3.2 铜冶炼烟尘中铅的测定

准确称取 0.1 g 试样于 200 ml 烧杯中, 加入 10 ml 王水, 在低温电炉上加热至试样全溶, 冷却后转入 500 ml 容量瓶中, 以水稀释至标线, 摇匀. 分取一定量试液于 25 ml 容量瓶中, 以下按 3.1 同样操作, 测定结果列于表 2.

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表 2 样品中铅的测定结果/ $\mu\text{g} \cdot \text{g}^{-1}$

样品	AAS 法测定值	本法测定值 ( $n=5$ )	R · S · D /%
化妆品-1	89.80	90.43	0.6
化妆品-2	68.75	68.57	0.7
铜冶炼烟尘/%	9.55	9.69	1.0

## 《环境科学》征稿简则

1 《环境科学》由中国科学院环境科学委员会和中国科学院生态环境研究中心主办、中国环境科学研究院、清华大学环境工程设计研究院和北京市环境保护科学研究院协办. 创刊于 1976 年, 是我国最早正式出版的关于环境科学的学术期刊. 本刊宗旨是报道我国环境科学领域中的最新科技成果, 促进国内外学术交流. 读者对象为环境科学研究人员、工程技术人员、环境管理干部和大专院校有关专业的师生等.

2 《环境科学》以发表实验研究论文为主, 力求及时报道我国环境科学领域的具有创造性的 高水平的、有重要意义的基础研究和应用研究方面的成果以及阶段性科技成果. 也发表科研成果的专题评述和学科最新进展的综合评述以及反映控制污染, 清洁生产 and 生态环境建设战略思想的专论等.

#### 3 来稿要求和注意事项

(1) 来稿要求论点明确、数据可靠、层次分明、结构完整, 文字图表精练. 研究报告一般不超过 5000 字(含图、表和文献), 专论综述不超过 6000 字. 文首给出中文文摘和关键词, 英文文摘另附, 包括题目、作者姓名汉语拼音和工作单位的英文名.

(2) 来稿务必做到清稿定稿. 稿中外文缩写在第一次出现时应写明文中含意、外文全称; 外文字母、符号, 必须分清大小写; 上、下角的字母、数码和符号, 其位置高低应区别明显; 容易混淆的外文字母、符号, 请在第一次出现时用铅笔批清. 计量单位一律使用《中华人民共和国法定计量单位》, 非许用单位务请加以换算.

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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  $\mu\text{g}$  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  $\mu\text{m}$  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  $\text{CS}_2$  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 mg/L.

**Key words:** wastewater, fast determination, spectrophotometry,  $\text{CS}_2$ .

**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-