活性炭动态交换分离富集光度法测定水和废水中痕量铍

丘星初　陈　军　朱盈权
（江西省赣州地区环境科学研究所）

铍及其化合物对人类的毒性极大，并且有致癌作用．目前已成为人们较关注的环境污染物．随着铍的利用和环境保护的发展，急需解决铍的富集和测定的高灵敏度方法．文献［1］利用活性炭静态吸附铍-铬天菁S(CAS)-氯化十六烷基吡啶（CPC）三元络合物分离富集铍，且利用此三元络合物光度法测定铍．惜此法操作繁琐，且吸附回收率也不太稳定．本文在此基础上，改用活性炭动态吸附分离富集铍，操作简便，适应性广，回收率也较好．用于水样中铍的测定，结果良好．

一、仪器和主要试剂

1.仪器　751型分光光度计用于吸收曲线的绘制；72型分光光度计用于给定波长下吸光度的测定．

2.铍标准溶液

（1）准确称取0.2460g $BeSO_4 \cdot 4H_2O$，加适量水溶解，加浓硫酸1.25ml，定容至250ml，混匀．此溶液含Be50.0μg/ml；

（2）取标准（1）10ml，用水稀释至100ml．此溶液含Be 5.0μg/ml；

（3）取标准（2）10ml，加2mol盐酸2.5ml，用水稀释至500ml，配制成含Be 0.10μg/ml的标准工作溶液；

3.铬天菁S 0.1%（W/V）水溶液；

4.氯化十六烷基吡啶0.25%（W/V）水溶液；

5.氨性缓冲溶液 pH 10，每L含浓氨水230ml，氯化铵83g；

6. EDTA溶液　0.1mol二钠盐水溶液；

7.六亚甲基四胺（HMT）缓冲液　1mol六亚甲基四胺溶液，用1mol盐酸调节pH值为5.0；

8.硫酸镁溶液　0.5%（W/V）水溶液；

9.活性炭　德国E. Merck产品．

二、一般试验方法

在25ml比色管中，依次加入0.40μg铍，EDTA溶液1ml，$MgSO_4$溶液0.5ml，CAS溶液0.5ml，HMT缓冲液5ml，CPC溶液0.5ml，沿比色管壁加水至刻度．混匀后在60℃水浴上加热5min，取出后放置30min．在605nm处，以相同步骤的试剂空白为参比，用2cm比色皿测量吸光度．

三、结果与讨论

1.显色条件的选择

（1）吸收曲线

在试验方法条件下，Be-CAS-CPC三元络合物的吸收峰位于波长605nm处．试剂空白的最大吸收波长位于435nm处（见图1）．故 $\Delta\lambda = 170nm$

（2）pH值的影响

试验表明，在pH值为5.0—5.3时，该三元络合物吸光度保持恒定．本方法选在pH 5.0反应．

（3）CAS和CPC浓度的影响

试验表明，当CAS溶液加入量为0.4—

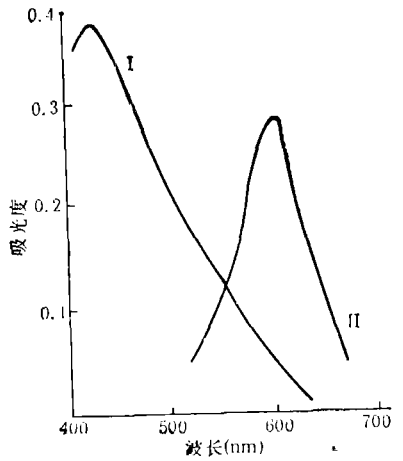

图 1 吸收曲线

I. 试剂空白,水参比

II. 络合物,试剂空白参比

0.7ml; CPC 溶液用量在 0.4—0.7ml 范围时，均可得到稳定的结果. 故本方法将 CAS 溶液及 CPC 溶液的用量均选为 0.5ml.

(4) EDTA 浓度的影响

EDTA 与 Be^{2+} 有微弱的络合作用. 当加入量为 1.0ml 时,吸光度约降低 5%. 标准系列与水样同量加入,误差基本可抵消.

(5) 络合物的稳定性

在室温下络合物显色完全需要 4 小时；而在 60℃ 水浴中，有 Mg^{2+} 存在时，加热 5min 取出，然后放置 30min，则反应已近完全,且在 2h 内吸光度保持恒定.

2. 富集条件试验

在 500ml 容量瓶中,依次加入铍 0.40μg, EDTA 溶液 2ml，氨性缓冲溶液 5ml，CPC 溶液 1ml，然后加水稀释至刻度,摇匀. 剪一张与容量瓶瓶口直径大小相仿的滤纸，用水润湿后,盖在容量瓶口上.将容量瓶倒放在架子上,使容量瓶口放在吸附柱内(见图 2). 用洗瓶向吸附柱内加水至容量瓶口处，滤纸即脱落，容量瓶中之试液便自行慢慢流经吸附柱,待试液流完后,将 25ml 比色管放在吸附柱底端,用 2mol 盐酸 6ml 分三次滴加于淋洗柱内. 淋完后取出比色管，向管内加酚酞指

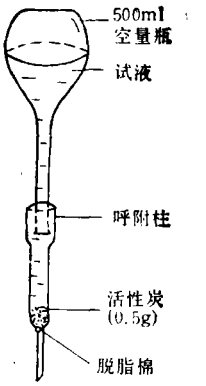

图 2 吸附装置示意图

示剂 1 滴，用 1:1 氨水中和至微红色，继用 2mol 盐酸回滴至红色刚消失,以下按直接显色法测定.

(1) 酸度的影响

按分离富集方法,改变试液的 pH 值,测定铍的回收率，所得结果列于表 1. 由表 1 看出，pH 值在 8—11 范围内均适宜. 故本方法选在 pH 10 时反应.

表 1 酸度对铍吸附回收率的影响

(铍加入量为 0.4μg)

pH	8	10	11	12
回收铍 (μg)	0.39	0.40	0.42	0.43
回收率(%)	97.5	100	105	107.5

(2) 淋洗酸用量的选择

按试验方法,改变淋洗液的用量,测定回收率,结果如表 2 所示. 由表 2 可知,当盐酸用量在 4—10ml 时,回收率较好,本方法选用量为 6ml.

表 2 淋洗酸用量对吸附回收率的影响

(加入铍量为 0.40μg)

加入 2mol 盐酸量 (ml)	2	4	6	8	10
回收铍量 (μg)	0.24	0.38	0.40	0.40	0.41
回收率(%)	60.0	95.0	100.0	100.0	102.5

(3) 活性炭再生试验

在同一根柱上,重复进行吸附回收试验,以考查活性炭重复利用的次数，所得结果列于表 3. 由表 3 可见，一根吸附柱可重复利用四次,其回收率均在 94.5% 以上.

表 3　活性炭再生试验

利用次数	1	2	3	4	5
铍回收率(%)	99.1	97.3	96.0	94.5	88.0

3. 共存离子的影响

测定 0.40μg 铍,共存离子的允许量列于表 4.

4. 方法精密度

活性炭吸附分离富集后,重复进行 10 次测定,其标准偏差为 0.00303，相对标准偏差为 2.89%.

5. 符合 Beer 定律的浓度范围及方法的灵敏度在 7 支比色管中,依次加入0.10,0.20,0.30, 0.40, 0.50, 0.60, 0.70μg 铍标准溶液,按试验方法测定吸光度,绘制工作曲线,结果见图 3.

表 4　共存离子的允许量

共存离子	允许量(mg)	共存离子	允许量(mg)	共存离子	允许量(mg)
Mg^{2+}	30	Cu^{2+}	3	Sb(III)	0.5
Zn^{2+}	20	Al^{3+}	3	Ce^{3+}	0.5
Co^{2+}	15	Fe^{2+}	5	As (III)	3
Ni^{2+}	15	Cr^{3+}	2	F^-	0.05
Pb^{2+}	15	Mo(VI)	10	PO_4^{3-}	5
Ca^{2+}	10	Mn^{2+}	0.5	EGTA (0.1mol)	5ml
Cd^{2+}	10	V(V)	0.5	DCTA (0.1mol)	5ml

表 5　水样加标回收率的测定

样品号 / 测定结果	1#	2#	3#
样品测定的个别值 (μg)	0.068 0.054 0.056 0.057 0.056 0.073	0.225 0.227 0.230 0.226 0.225 0.230	0.430 0.427 0.420 0.425 0.430 0.420
平均值 (μg)	0.061	0.227	0.425
变异系数 (%)	12.9	1.02	1.07
加标量 (μg)	0.10	0.20	0.20
回收量 (μg)	0.154	0.420	0.620
回收率(%)	93.0	96.5	97.5

四、实际样品的测定

1. 样品的预处理

若水样中铍含量适中而且干扰少，则将 pH 值调至中性后,就可直接显色测定；若样品中含有有机物质，则可用硫酸或硝酸预处理后,再显色测定;若水样中铍含量甚微或干扰严重,则采用活性炭吸附分离富集后,再显

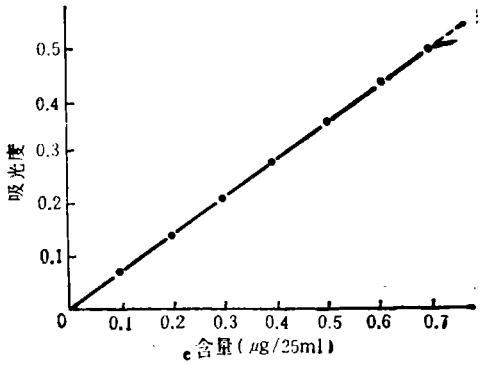

图3 工作曲线

色测定之.

2. 样品的测定

我们对三个水样进行了测定. 结果见表5.

参 考 文 献

[1] 陈炎,刘少陵,郑州大学学报(自然科学版)8(2),82,(1982).

(收稿日期: 1987 年 8 月 18 日)

(上接第33页)

9. 香樟 *Cinnamomum camphora*
10. 川桂 *Cinnamomum wilsonii*
11. 油茶 *Camellia cleosa*
12. 木荷 *Schima confertiflora*
13. 枇杷 *Eriobtrya japonica*
14. 苦槠 *Castanopsis sclerophylla*
15. 青岗 *Cyclobalanopsis glauca*
16. 枣树 *Zizyphus jujuba*
17. 柿树 *Diospyros kaki*
18. 桂花 *Osmanthus fragrana*
19. 女真 *Ligustrum lucidum*
20. 夹竹桃 *Nerium indicum*
21. 油桐 *Aleurites montana*
22. 杜仲 *Eucommia ulmoides*
23. 喜树 *Camptotheca acuminata*
24. 毛竹 *Phyllostachys pubescens*
25. 苦楝 *Melia azedarach*
26. 香椿 *Toona sinensis*
27. 侧柏 *Platycladus orientalis*
28. 圆柏 *Cupressus duclouxiana*
29. 垂柳 *Salix babylonica*
30. 泡桐 *Paulownia tomentosa*
31. 火力楠 *Michelia macclurei*
32. 马桂木 *Liriodendron chinense*
33. 柑桔 *Citrus reticulata*
34. 构树 *Broussonetia papyrifera*
35. 刺桐 *Erythrina indica*
36. 石榴 *Punica granatum*
37. 法桐 *Platanus acerifolia*

(收稿日期: 1987 年 8 月 25 日)

(上接第 76 页)

[11] Hawkes, H. A., *Chem. Ind.*, **21**, 990—1000 (1974).
[12] Hawkes, H. A., "Invertebrates as indicators of river water quality" in *Biological indicators of water quality*, Edited by James, A. and Evison, L., pp. 2, 1—45, John Wiley & Sons 1979.
[13] Hawkes, H. A., *Water Pollut. Cont.* **81**(3), 329—342 (1982).
[14] Hellawell, J. M., *Biological surveillance of river. Water Res. Cent.*, pp 332, Stevenage, UK, 1978.
[15] Herricks, E. E. and Cairns, J. Jr., *Water Res.*, **16**, 141—151 (1982).
[16] Lenat, D. R. et al., "Use of benthic macroinvertebrates as indicators of environmental quality" in *Biological monitoring for environmental effects*, Edited by Worf, E. L., pp. 97—112, Lexington Books, 1980.
[17] Matthews, R. A. et al., *Water Res.* **16**, 129—139 (1982).
[18] Pittwell, L. R., "Biological monitoring of river in community" in *Principles and methods for determining ecological criteria on hydrobiocenoses*, Edited by Amevis, R. and Smeets, J., pp. 225—261, Pergamon Press, 1976.
[19] Tittizer, T. and Kothe, P., "Possibilities and limitations of biological methods of water analysis" in *Biological indicators of water quality*, Edited by James, A. and Evison, L., pp. 4, 1—21, John Wiley & Sons, 1979.

(收稿日期: 1987 年 5 月 12 日)

The experimantal results show that under the conditions of carbon monoxide below 200 ppm within 16 hours of chambering time, there is no obvious injury on leaves of woody plants. But the ratio of photosynthesis is varied from different biocharacters of woody plants. When 100 ppm CO pollution, the relation of ratio of photosynthesis and the chambering time is exponential function, and $P_t/P_o = 5.75 \exp(0.001t)$ to *Fraxinus chinensis* and $P_t/P_o = 7.04 \exp(1.9\ 10t)$ to *Puruns davidiana*. (See pp. 27—29)

Injuries to Tree Leaves by Simulated Acid Rain and Resistant Nature of the Trees

Zhang Jiawu, Feng Zongwei et al. (Institute of Applied Ecology, Academia Sinica, Shenyang)

The paper gives a general description of the effects of simulated acid rain on tree leaves. The experiments have been done in Hunan Experimental Station of Forest Ecology. After the simulated acid rain were sprayed upon tree leaves, there appeared some symptoms: discoloration of greens, tissue necrosis, dewatering and early withering. And injurious extents on leaves were fundamentally due to the rain acidity, duration of spraying and conditions of sunlight and temperature. However, because of different tissue structures of the tree leaves, their resistant capacity were varied. (See pp. 30—33)

Toxicity of Floatation Agent S-808 of Phosphatic Ore and Mineral Wastewater to Fishes and Embryos

Zhang Fuying and Yin Yiwa (Institute of Hydrobiology, Academia Sinica, Wuhan)

Toxic test determining larvae of grass carp and guppy for 96-hour LC_{50} was 18 mg/L and 35 mg/L respectively, 10-day LC_{50} of grass carp embryo was 3.69 mg/L. For fish embryos in 1 mg/L, there appeared deformation. Deformation percentage and concentration were of positive correlation. In fish toxic test, deformed index was more sensitive than dead index. The toxic test showed that, according to classfication standard, S-808 was a "poisonous grade" of fish toxicity. S-808 in floating process was treated with physiochemical method and toxicity of dressing mineral wastewater decreased, so the value of LC_{50} in the test could not be determined, and there didn't appear deformation of fishes. (See pp. 34—37)

Tests on the Residues of 5% *Bestox* in Cotton Fields

Zhou Hou'an et al. (Institute of Zoology, Academia Sinica, Beijing)

Experiments on the residual kinetics of *Bestox* emulsion (5%) were carried out in the cotton fields. The results showed that the half-life of *Bostox* emulsion (5%) was 23 to 25 days in soil, and 3 to 5 days on leaves. The residues were not observed in cotton seeds even by using dosages 1.5 to 2.0 times of the conventional ones. *Bestox* is low toxic to mammals and there is no systemic action. The results can give a reliable basis for rationalizing the use of *Bestox* in the cotton field and limting MRL value in cotton seeds. (See pp. 38—41)

Ascertainment of Main Factors for Biological Denitrification System Using Orthogonal Test

Du Shelin et al. (Institute of Environmental Pretection, Shanghai Petrochemical Complex, Shanghai)

Hydraulic retention time (HRT), ratio of the volume of anaerobic tank to the volume of aerobic tank (I: R) and reflux ratio (r) have been established as three main factors in a biological denitrification system by using mathematically the orthogonal test method of Lg (3^4). Thus, in such a system for the treatment of a combined wastewater containing nitriles and sodium thiocyanate in high concentration, it was determined that HRT, I: R and r are 24 hours, 1:3 and 5.5 respectively, and they would be more favourable process parameters. In addition, an analysis of the whole system is made in this paper. (See pp. 42—46)

Removal of Mercury from Wastewater with Maize-Starch Dregs

Liu Manying and Kang Weijun (Hobei Medical College, Shijiazhuang, Hobei Province)

This paper deals with removal of mercury from wastewater by using maize-starch dregs. The experimental result shows that the rate of removal is 99.9%, and Saturated capacity is 45 mg/g. The method seems to be a cheap and efficient one for treating mercury-contained liquids. (See pp. 47—48)

Method for Determination of Twelve Phthalate Esters in Natural Water

Kang Junxing (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing) *Hing-biu Lee* (National Water Research Institute, Canada Center for Inland Waters)

An Analytical method was developed and validated, which permits determination parts per billion levels of twelve phthalate esters in natural water. Water sample was extracted with methylene chloride, and the extract was cleaned up by using silica gel liquid chromatographic column prior to determination of the phthalate esters by capillary column ECD-GC, (See pp. 49—54)

Spectrophotometric Determination of Trace Beryllium in Water and Wastewater after Adsorption concentration by Activated Carbon

Qiu Xingchu, Cheng Jun and Zhu Yingquan Ganzhou Institute of Environmental Science, Ganzhou, Jiangxi Province)

In this paper the optimum conditions of colour reaction of Be-CAS-CPC and adsorption concentration by activated carbon has been studied. In the buffer solution of urotropine pH 5.0. The adsorption maximum of the complex is near 605 nm. Beer's law is obeyed for 0-0.70 g *Be*/25ml (2cm cell) ranges. It is applied to determine the trace Be in Water by spectrophotometric method, which is simple exact and rapid. (See pp. 55—58)