导数光谱法同时测定人发中微量铜和锌

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摘要　研究了以 5-Br-PADAP 作显色剂，利用三阶导数光谱法，在碱性介质中同时测定铜和锌. 该法测定铜、锌的表观三阶导数摩尔吸光系数分别为 1.0×10^5 和 3.0×10^5，同时解决了谱带相互重叠干扰问题. 对人发中铜和锌进行测定，得到满意结果.

关键词　5-Br-PADAP，导数光谱，铜、锌测定，人发.

以 5-Br-PADAP 作显色剂，用线性回归法同时测定铜和锌已有报道[1]，但条件实验繁琐、费时，对实际样品测定误差较大；也可用双波长法同时测定铜和锌[2]，但方法的灵敏度较低；本研究以 5-Br-PADAP 作显色剂，利用三阶导数光谱，在碱性介质中同时测定铜和锌，对人发中铜和锌进行测定，与原子吸收法相比基本吻合.

1　实验部分

1.1　仪器与试剂

UV-557 型分光光度计；pHS-3C 型酸度计. Cu^{2+}、Zn^{2+} 标准溶液：分别准确称取纯度为 99.9% 以上的金属铜和金属锌，用适量酸溶解后配成 1.00 mg/ml 储备液，用时稀释至所需浓度；0.02% 5-Br-PADAP 乙醇溶液；pH8.5 的 $NH_3 \cdot H_2O\text{-}NH_4Cl$ 缓冲液；50% 柠檬酸三铵；10% 的三乙醇胺.

1.2　实验方法

取适量水样于 25 ml 容量瓶中，分别加入 3.00 ml 5-Br-DAPAP、5.00 ml $NH_3 \cdot H_2O\text{-}NH_4Cl$、8.00 ml 和 1.0 ml 柠檬酸三铵、1.00 ml 三乙醇胺，稀释至刻度，摇匀. 10 min 后，在 600—500 nm 做三阶导数光谱，读取 563 nm 和 553 m 处的导数值（仪器参数：横坐标放大因子为 2.0，$\Delta\lambda = 7$ nm，扫描速度为 120 nm/min）.

2　结果与讨论

2.1　Cu^+、Zn^+ 络合物的导数光谱

把 Cu^{2+}、Zn^{2+} 络合物作 0—4 阶导数光谱. 实验表明：三阶导数光谱分辨好，在 553 nm 处测定 Zn^+、563 nm 处测定 Cu^+，用"峰-零"法测量，两者互不干扰，见

图 1.
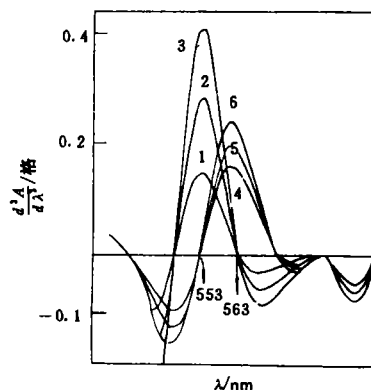
图 1　Cu^{2+} 和 Zn^{2+} 的导数光谱

1，2，3 浓度分别为 2.0、4.0、6.0 $\mu g/ml(Zn^{2+})$，

4，5，6 浓度分别为 6.0、8.0、10.0 $\mu g/ml(Cu^{2+})$

2.2　测定条件

（1）显色剂用量　在 $NH_3 \cdot H_2O\text{-}NH_4Cl$ 缓冲体系中，5-Br-PADAP 的用量在 1.50—3.00 ml 时，三阶导数值稳定且加合性良好. 本实验取 3.00 ml.

（2）显色酸度　实验表明：一定的 Cu^{2+}、Zn^{2+} 同时与 5-Br-PADAP 反应的 pH 为 8.0—10.0 时的三阶导数值基本不变，本实验选 pH 为 8.5.

（3）乙醇用量　乙醇对 Zn^{2+} 影响大，对 Cu^{2+} 影响小，但综合考虑对二者的影响，本实验用乙醇 8.00 ml.

（4）络合物的稳定性　在上述条件下 Cu^{2+}、Zn^{2+} 与 5-Br-PADAP 在 10 min 内反应完全，稳定时间在 2 h 以

上.

2.3 工作曲线和检出限

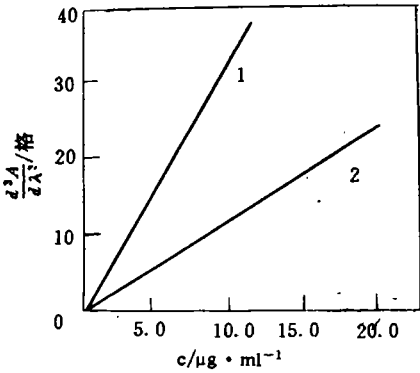配制一系列不同浓度的混合标准液,按实验方法操作,根据测定值绘制工作曲线(见图2),线性范围 0—20 和 0—10 $\mu g/ml$,Cu^{2+}、Zn^{2+} 的表观摩尔吸光系数分别为 1.0×10^5 和 3.0×10^5.

图 2　工作曲线
1. Zn^{2+}　2. Cu^{2+}

对空白溶液实验 20 次,测绘三价导数光谱,取 563 nm 和 553 nm 处的三阶导数光谱标准偏差的 3 倍,计算出本法测定 Cu^{2+}、Zn^{2+} 的最低检出限分别为 0.03 $\mu g/ml$ 和 0.01 $\mu g/ml$.

2.4 共存离子的影响

对人发中常见干扰元素进行实验,在 8.00 $\mu g/25\ ml$ Cu^{2+} 和 5.00 $\mu g/25\ ml$ Zn^{2+} 的存在下,误差不超过 ±5%,加入 1 ml 三乙醇胺、1 ml 柠檬酸三铵后,见表 1.

根据文献[3],人发中主要元素有:Ca、Mg、Fe、Cu、Zn、Mn、Pb、Ni、Cr. 在东营市范围内,上述元素的平均值分别为($\mu g/g$),Ca:822;Mg:142;Fe:13.7;Cu:10.3;Zn:196;Mn:1.2;Pb:1.5;Ni:0.26;Cr:0.12. 因此,当加入掩蔽剂后,共存离子均不干扰测定.

2.5 样品分析

(1)合成试样的回收率　准确移取适量 1.00 mg/ml Cu^{2+}、Zn^{2+} 储备液于 25 ml 容量瓶中,控制 Cu/Zn 比值在 20:1—1:20 之间,按实验方法进行测定,测得 Cu、Zn 回收率分别为 95%—105%、95%—103%.

(2)样品的测定　将发样剪成 1 cm 长,先用去离子水漂洗,再用 5% 白猫牌洗洁精洗涤 0.5 h,再用去离子水把头发上的洗涤剂洗净,倾净余水,将发样置于 100℃ 下烘干,冷却. 准确称取处理好发样 0.5000 g,在 550℃ 下炭化、灰化,然后用适量 6mol/L HCl 将残渣溶解,再定量转移至 10 ml 容量瓶中,定容. 移取上述溶液 3.00 ml 于 25 ml 容量瓶中,按实验方法进行测定,结果见表 2.

从表 2 看出,本方法与原子吸收法相比,测定误差

表 1　加掩蔽剂后各离子允许量[1]

被测离子	干扰离子及允许量/$\mu g \cdot 25\ ml^{-1}$									
	Ca^{2+}	Mg^{2+}	Fe^{3+}	Fe^{2+}	Mn^{2+}	Pb^{2+}	Ni^{2+}	Cr^{3+}	Na^+	K^+
Cu^{2+}	1000	500	150	140	80	200	80	400	1500	1800
Zn^{2+}	1000	500	100	110	85	140	50	360	1500	1800

1) Ca^{2+}、Mg^{2+}、Na^+ 和 K^+ 不是最大值

表 2　样品测定结果及方法对照

发样	本法/$\mu g \cdot g^{-1}$		原子吸收法/$\mu g \cdot g^{-1}$		相对误差/%	
	Cu	Zn	Cu	Zn	Cu	Zn
发样 1	10.81	195.2	10.65	192.8	1.44	1.24
	10.65	194.8	10.85	197.4	−1.84	−1.77
	10.64	193.8	10.98	192.7	−3.10	0.60
发样 2	11.35	198.1	11.50	194.0	−1.30	2.06
	11.45	197.2	11.30	196.0	1.33	0.61
	11.40	199.1	11.00	194.2	3.64	2.47

均小于 ±0.5%. 同时对某发样做了 8 次平行测定,其相对标准偏差:Cu 为 2.3%;Zn 为 2.1%.

3 结论

(1)在 pH 为 8.5 的碱性介质中,利用三阶导数光谱,可同时测定人发中的铜和锌.

(2)本法与原子吸收法的测定结果基本一致.

参 考 文 献

1 倪永年. 分析化学,1987,**15**(11):995
2 张明英,沈要文. 理化检验,1992,**28**(3):136
3 冯成武等. 石油大学学报,1990,**3**:97

copper in the solution reacted with T (4-MOP) PS₄ to form Cu-T(4-MOP)PS₄. Acidifing about pH2. 3 by dilute hydrochloric acid, the solution was determined by spectrophotometry. The content of S^{2-} in the sample was calculated. The effect of interference ions was studied. The Beer's law is obeyed in the range of $0-0.20 \mu g/ml$. The correlation coefficient is 0.9995 and the recoveries of sulfide are in range of 94.02% — 100.8%. The proposed method was used to determine the soluble sulfide in waste water and the results are agreed with the standard method.

Key words: copper, T (4-MOP) PS₄, sulfide, spectrophotometry.

Simultaneous Determination of Zinc and Copper With Derivative Spectrophotometry.

Liu Guangdong et al. (Dept. of Chem. Eng., University of Petroleum, Dongying 257062): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 75—76

In this paper the simultaneous determination of zinc and copper with 5-Br-PADAP at pH8. 5 by using derivative spectrophotometry has been studied. The malar derivative absorption coefficients of zinc and copper are 3.0×10^5 and 1.0×10^5 respectively. The interference of overlapped spectra was overcome. Satisfactory results were obtained in the determination of zinc and copper in hair.

Key words: 5-Br-PADAP, derivative spectrophotometry, zinc, copper, determination, hair.

Principles and Methods to Assess the Relative Sensitivity of Ecosystems to Acidic Deposition.

Hao Jiming et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 77—80

The conceptions of sensitivity, the absolute sensitivity and the relative sensitivity of ecosystems to acidic deposition have been described. Also an approach to assess the absolute sensitivity of water and soil to acidic deposition has been developed. According to the comparison of each ecological factor's buffering ability to acidic deposition, a basic principle to establish a method to assess the relative sensitivity of ecosystems to acidic deposition has been provided. Besides, the article had an introduction to the established assessment methods and their recent development.

Key words: acidic deposition, ecosystems, sensitivity.

Dissertation on Environmental Immigration.

Xu Jiang, Ouyang Ziyuan et al. (State Key Laboratory of Environ. Geochemistry, Chinese Academy of Sciences, Guiyang, 550002): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 81—86

Because of environmental degradation, some areas have arisen a kind of new special type of immigration—— environmental immigration. Environmental immigration is the inevitable outcome of the contradiction between population growth and environmental capacity. The concept, factors and essence of environmental immigraiton initially were studied in this article, and an example of environmental immigration in Guangxi Province, China, was given.

Key words: environmental immigration, population, environmental capacity.

Technique and Application of Biological Treatment of Gaseous Emissions.

Qiang Ning (School of Environ. Eng., Tongji University, Shanghai 200092): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 87—90

Three biological processes to treat waste gases are the bioscrubber, the biofilter and the biotrickling. Selecting the best biological processes suited for one paticular application depends on the contaminant concentration, stream composition etc. The biological treatment of gaseous emissions offers an inexpensive and environmentally safe alternative to conventional air treatment technologies such as absorption, adsorption and incineration. At first, the biological treatment of gaseous emissions are used to deodorize, and more recently, to remove volatile organic compounds from waste gases emited from chemical processe of industries. In Germany, Netherlands and Japan, there are nearly 1000 biological gaseous treatment systems in service.

Key words: biological treatment, gaseous emissions, biofilter, bioscrubber, biotrickling.