卡尔曼滤波分光光度法同时测定钴、镍、铜、锌、镉

李志良 石乐明
（湖南大学化学化工系） （中国科学技术大学近代化学系）

微量元素对动物、植物，尤其是人类都具有重要的生理及病理意义，对其检测在生物学与环境科学上均具有重要的实际意义．多元素的同时分析日显迫切与重要．本文报道利用卡尔曼滤波这一有效的化学计量学方法借分光光度法同时测定微量钴、镍、铜、锌和镉五种元素的工作，结果令人满意．

一、卡尔曼滤波分光光度法的原理与算法

卡尔曼滤波(Kalman Filter，简称 KF)方法基于最小二乘原理，借一套递推算法解决统计估计问题，使之能从带噪声的测量讯号中提取有用的信息[1]．卡尔曼滤波最早主要用于通讯与控制问题，1976 年引入分析化学中[2]，1979 年 Poulisse 将卡尔曼滤波方法用于分析化学中的多组分同时分析[3]．原理如下：

对于几个相互干扰的组分，根据 Lambert-Beer 定律与吸光度的加和性原理：

$$A_k = \sum_{i=1}^{n} A_{ki} = \sum_{i=1}^{n} \varepsilon_{ki} X_i \qquad (1)$$

式中 k 表示在第 k 个波长处进行测量，$k = 1, 2, \cdots m$，m 代表所选定的波长数目，ε_{ki} 表示第 i 个组分在第 k 个波长处的摩尔吸光系数（设比色池厚度为 1cm），X_i 表示第 i 个组分的摩尔浓度．ε_{ki} 可用单一组分的纯样分别求得．

卡尔曼滤波的原理是，根据新获得的测量值 A_k，对前 $k-1$ 次测量所估计的 $\hat{X}_{k-1}$ 值进行校正：

新估计值 $\hat{X}_k$ = 旧估计值 $\hat{X}_{k-1}$ + 校正值 (2)

算法为：

$$P_{k/k-1} = P_{k-1} \qquad (3)$$

$$K_k = P_{k-1}\varepsilon_k^T(\varepsilon_k P_{k-1}\varepsilon_k^T + R_k)^{-1} \qquad (4)$$

$$\hat{X}_k = \hat{X}_{k-1} + K_k(A_k - \varepsilon_k \hat{X}_{k-1}) \qquad (5)$$

$$P_k = (I - K_k\varepsilon_k)P_{k/k-1} \text{ 或} \qquad (6)$$

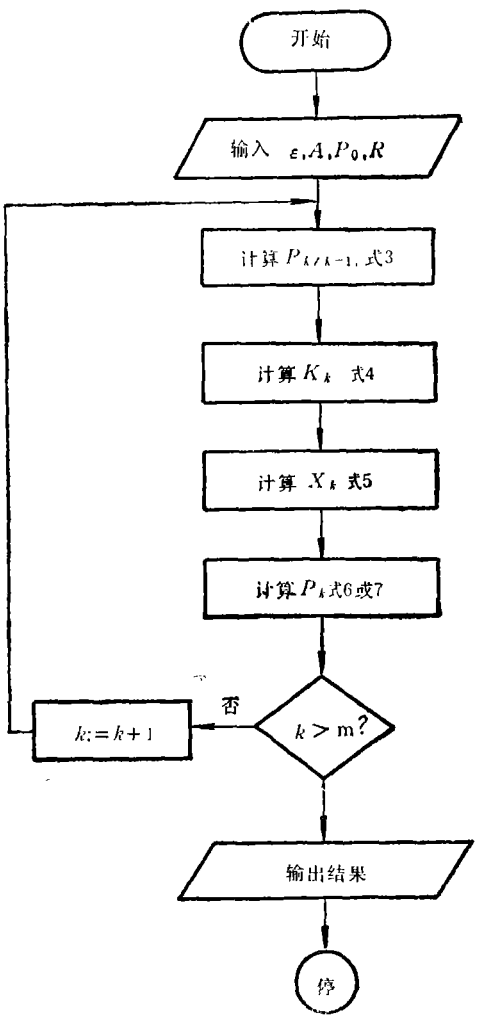

图 1 卡尔曼滤波程序框图

$$P_k = (I - K_k\varepsilon_k)P_{k/k-1}(I - K_k\varepsilon_k)^T + K_kR_kK_k^T \quad (7)$$

此处 $P_{k/k-1}$ 为预测误差协方差矩阵 $(n \times n)$，K_k 为卡尔曼增益矩阵 $(n \times 1)$，P_k 为估计误差协方差矩阵 $(n \times n)$，T 表示矩阵转置，I 表示 $n \times n$ 阶单位矩阵，R_k 表示在第 k 个测量点处的测量噪声方差，在分光光度分析中可取 $R_k = 10^{-6}(k = 1, 2, \cdots, m)$[3]。

由上述算法可知，在开始滤波时需知道 P_0 与 $\hat{X}_0$，常设 $P_0 = 10^{-12} \cdot I$，$\hat{X}_0 = 0$[3]。

基于以上算法，我们分别用 BASIC 语言或 PASCAL 语言编写了适合于微机运行的计算机程序，框图如图 1 所示。

二、实 验 部 分

1. 主要试剂与仪器

钴、镍、铜、锌和镉标准溶液按常法配制；0.02% 的 5-Br-PADN 乙醇溶液，本室新近合成[4]；10%(V/V) 的 Tween-80 (CP) 水溶液；pH 10.0 的 NH_3-NH_4Cl 缓冲溶液(0.40 mol/l)；UV-120 紫外-可见分光光度计；821 型数字式 mV/pH 离子计 (中山大学电子仪器厂)；IBM PC/XT 微机。

2. 实验方法

(1) $\varepsilon_{m\times n}$ 矩阵的确定　分别取一定量的钴、镍、铜、锌和镉标准溶液于 25ml 容量瓶中，依次加入 5.0 ml 缓冲溶液，2.5 ml Tween-80 溶液和 2.5ml 5-Br-PADN 溶液，以去离子水稀释至刻度，逐次摇匀，15 分钟后，用 1cm 比色池于 UV-120 分光光度计上测量吸光度，记录 500—620 nm 范围内间隔 5,2 或 1nm)的吸光度值共 52 个，求得吸收系数矩阵 $\varepsilon_{52\times5}$。吸收光谱如图 2 所示。

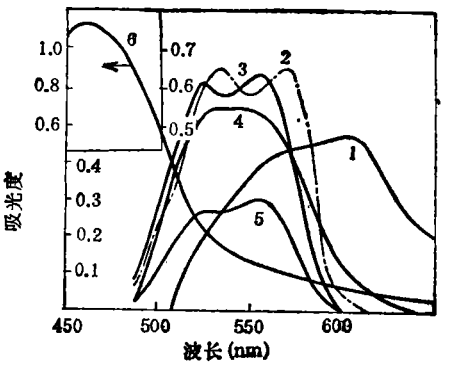

图 2　吸收光谱. 1,2,3,4,5 分别为 Co、Ni、Cu、Zn、Cd 对 R; 6: R(5-Br-PADN) 对水. 金属离子含量均为 22.5μg/25ml

(2) 标准混合样分析　将五种金属离子标准溶液按一定比例混合，按 (1) 的条件显色，读取相应波长处的吸光度，得 A 矩阵。

(3) 湘江水样分析：提取湘江水样，经过滤后准确移取 100ml 于 250ml 烧杯中，加入数滴浓 HNO_3 处理，蒸发至近干，依次加入柠檬酸盐 200mg，NaF 饱和溶液 1ml，移

表 1　标准混合样分析结果 (μg/25ml)

合成样编号	标准加入量					分析结果				
	Co	Ni	Cu	Zn	Cd	Co	Ni	Cu	Zn	Cd
1	5.0	2.0	8.0	4.0	0	4.8	2.1	8.8	4.2	0.0
2	6.0	8.0	4.0	4.0	0	5.6	8.4	4.3	4.4	0.1
3	1.0	5.0	2.0	2.0	5.0	1.0	5.1	1.9	2.2	4.7
4	2.0	5.0	4.0	4.0	0	1.9	5.3	4.2	3.8	0.0
5	4.0	1.0	2.0	5.0	2.0	3.9	1.1	2.0	5.2	1.9
6	2.0	2.0	3.0	8.0	0	2.0	1.9	3.0	8.3	0.02
7	8.0	3.0	5.4	1.0	2.0	8.2	2.9	5.6	0.9	2.1
8	6.0	0	1.0	2.5	1.5	6.2	0.03	1.0	2.7	1.4
9	4.0	5.0	5.0	4.0	0	4.1	5.4	5.2	4.4	0.2
10	4.0	4.0	0	4.0	0	4.0	4.3	0.1	3.7	0.0

表 2 湘江水样分析结果 (μg/100ml)

测得量					加入标准量					测得量与回收率(%)				
Co	Ni	Cu	Zn	Cd	Co	Ni	Cu	Zn	Cd	Co	Ni	Cu	Zn	Cd
0.26	1.62	1.25	16.1	0.5	2.0	2.0	2.0	2.0	2.0	2.40	3.53	3.46	17.9	2.54
2.6	16.2	12.5	161.0	5.0*						107.0	95.5	110.5	90.0	102.0

* 表示湘江水样中金属离子的含量(ppb)

入 25ml 容量瓶中，用 1mol NaOH 调节酸度至近中性，按(1)显色，测量相应波长处的吸光度。为测定回收率，加入标准金属离子溶液各 2.00μg，进行同样的处理与测量。

三、结果与讨论

从图 2 可以看出，钴、镍、铜、锌和镉的络合物吸收光谱严重重叠，当它们共存时，无法用常规方法定量。本文利用卡尔曼滤波方法进行计算，结果令人满意(见表 1，表 2)，优于共轭梯度法的计算结果[4]。

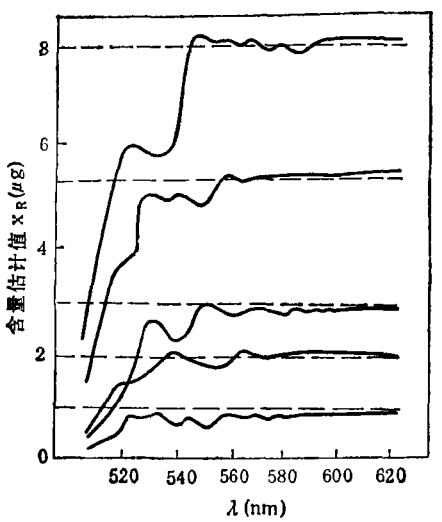

图 3 卡尔曼滤波趋势图。图中虚线代表真实浓度

图 3 表明估计值 $\hat{X}_k$ 随测量点数 k 或波长 λ_k(nm) 的变化规律，当滤波到一定次数时，各组分浓度的估计值 $\hat{X}_k$ 即趋于稳定，这一稳定值即可作为最后的计算结果输出。

本文所提出的卡尔曼滤波分光光度法可以不经分离直接用于钴、镍、铜、锌和镉的同时测定，为多元素的同时分析提供了一条新途径。

参 考 文 献

[1] 贾沛璋，朱征桃编著，最优估计及其应用，33—50 页，科学出版社，北京，1984 年。
[2] Seelig, P. F., Blount, H. N., *Anal. Chem.*, **48** (2), 252 (1976).
[3] Poulisse, H. N. J., *Anal. Chim. Acta*, **112**, 361 (1979).
[4] 石乐明，李志良，青年化学，**2**(1)，48(1987)。

(收稿日期：1987 年 11 月 2 日)

(上接第26页)

参 考 文 献

[1] Baker, C. K. et al., *Nature*, **299**, 149—151 (1982).
[2] Matsuoka, Y., *Special Bulletin of Chiba Experiment Station*, (7), 63 (1978).
[3] Jäger, H-J. et al., *Angewandt Botanik*, (54) 337—348 (1980).
[4] 张耀民等，中国环境科学，**6**(1)，36—39(1986)。
[5] 李振国等，植物生理学报，**13**(1)，27—34(1987)。
[6] 舒俭民等，中国环境监测，(2)，11—14(1985)。
[7] Bull, J. N. et al., *Nature*, **250**, 443—444 (1974).
[8] 宋秉彝，北京农业科学，(2)，1—20(1984)。

(收稿日期：1987 年 7 月 8 日)

Academia Sinica, Beijing)

Zinc is an important element for life. Studying its background values in aquatic environment is significant for evaluation of water quality. This work describes that zinc contents in water samples taken from Xiangjiang River in Hunan Province and from from the rivers in Beijing-Tianjin area have been analysed by flame AAS. The distribution types of background values of zinc were handled by mathematical statistic method. The results show that the background values of zinc in the waters above mentioned are in normal ranges compared with world levels. The chemical speciation of zinc in water and sediments of Xiangjing River were studied as well. ASV-labile zinc in dissolved zinc were found as predominant forms in water. The bound to Fe-Mn oxides are major speciations of Zn in the sediments except residual. The background values of zinc and its different species in water are mainly affected by its geochemical charater and environmental factors. (See pp. 30—33)

Effects of Alkali and Alkaline Earth Groups of Population Growth of *Chlamydomonas Reinhardtii*

Shi Jinyuan et al. (Department of Tech. Physics, Peking University); Li Yunzhen (Department of Biology, Peking University)

The influence of alkali and alkaline earth group elementes of different concentrations on the population growth of green algae that is employed as a biological model. A certain regularity between biological effects of the elements and their position in the periodic table has been discussed. *Chlamydomonas reinhardtii* were cultured in the solution containing some inorganic salts. Based on relation rate of proliferation (R) on each element of IA and IIA Groups, the stimulating concentrations (when $R > 100\%$) and inhibitory concentrations (when $R < 100\%$) have been obtained. The results show that the toxicity of the elements on the algae will increase with the increase of their atomic number (Z) in the same group except Li and Mg. (See pp. 33—35)

Determination of the Quantity of Nonbiodegradable/Nonremoval Substances in Industrial Wastewater

Zhou Xiaojian (Environmental Protection Institute of the Ministry of Light Industry, Beijing)

According to the kinetics of biological process, this paper has proposed the determination of the quantity of nonbiodegradable substances in wastewater, which is then applied to the process of an anaerobic treatment and an aerobic treatment respectively. The results are as follows:

(1) In the anaerobic treatment of cotton pulp black liquor with an UASB reactor, when the COD concentration of the influent is 10—13g/L, the concentration of nonbiodegradable subsctances, through measuring and calculating, is 4.147g COD/L. Thus, the average value of the maximum COD removal is 63.3%. Meanwhile, in the batch experiment of the anaerobic treatment of cotton pulp black liquor, the result obtained in the same way is the maximum COD removal can be 63.9%, which further supports this result.

(2) As for the wine lees with the activated sludge process, the average value of the maximum COD removal can be expected to be 86.8%. (See pp. 36—39)

A Study on the Conditions for Treating Wastewater Containing Copper Complex by Reduction-Coagulation Method

Zhang Zhongyan, Yu Shouhui and Zhu Rongfen (Shanghai University of Industrial Technology, Shanghai)

The conditions for treating copper-containing complex wastewater by Fe^{2+} reduction coagulation have been studied. In the mean time, coprecipitation with other inorganic coagulants [$CaCl_2$, PAC, $Fe_2(SO_4)_3$] has been discussed. The results in lab and productive experiments show that when EDTA citric acid or tartaric acid exists in wastewater, the effect of single chemical precipitation on removing copper is very poor. As the unstability of complex copper in acidic solution, Cu^{2+} can be reduced to be Cu^{+} with Fe_2^{+} at $pH = 4.5—5$, and then by increasing pH to 8—9, coprecipitation will take place, In this way the residual copper in outflow is always less than Img/L. Thus, an economical and efficient technology will be presented for treating of cooper-containing complex wastewater. (See pp. 44—48)

Simutaneous Determination of Cobalt, Nickel, Copper, Zinc and Cadmium Using Kalman Filtering Spectrophotometry

Li Zhiliang (Hunan University, Changsha) and *Shi Leming* (China University of Sciences and Technology, Hefei)

A method for simultaneous determination of cobalt, nickel, copper, zinc and cadmium by Kalman Filtering Spectrophotometry has been proposed based on their chelate-forming reactions with 5-Br-PADN in the presence of Tween—80, Satisfactory results were obtained for the analysis of synthetic and river water samples by the method. (See pp. 56—57)

Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans in the Environment

Kang Junxing and Bao Zhicheng (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing)

Because of the extreme toxicity of some of the polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF), the concerns for the health hazards of exposure to PCDD and PCDF led to growing Studies of PCDD and PCDF. The purpose of this review is to provide the information of toxicity, construction, major sources, pollution and human professional exposure of PCDD and PCDF. The current status of PCDD and PCDF in China was also discussed primarily in this article. (See pp. 59—67)