β修正孔雀绿光度法测定工业废水中银

郜洪文

（安徽省淮北环境保护监测站，淮北　235000）

摘要　在pH 5醋酸盐缓冲溶液中，银(Ag^+)与孔雀绿(MG)和碘化钾作用生成绿色缔合物。β修正光度法利用该显色反应能完全消除反应体系中过量MG干扰，计算缔合产物真实吸光度。分析灵敏度、精密度和准确度均比普通单波长光度法有明显提高。结果表明：银浓度0－2.0 mg/L内符合比耳定律，方法检出限0.05 mg/L；废水加标回收率97.3%－107%，相对标准偏差(RSD)6.2%。

关键词　β修正原理，分光光度法，银，孔雀绿，真实吸光度。

银是一种贵金属，在制镜、电镀和印相行业废水中含量较高。目前用于银测定的分光光度法包括双硫腙[1]、3，5-Br_2-PADAP[2]、试银灵罗丹宁[3]等显色。研究发现，在pH5醋酸盐缓冲介质中，银(Ag^+)与孔雀绿(MG)和碘化钾作用，反应液由蓝色变绿色。当应用该反应使用普通单波长法测定银时，由于反应体系中过量MG吸收干扰，分析灵敏度低，测定误差大。本文应用β修正光度分析理论研究该反应体系中银的测定，该方法通过吸光度修正可消除过量MG干扰，准确计算出Ag^+-MG-I^-缔合产物真实吸光度，提高分析灵敏度、精密度和准确度。该理论和方法已用于铁、铍、铝等测定[4-6]。

1　实验部分

1.1　β修正光度分析理论

以显色剂(R)与金属离子(Me)的反应为例来阐述β修正分析理论。显色反应为：

$$a\mathrm{R} + b\mathrm{Me} \longrightarrow b\mathrm{MeR}_\gamma + c\mathrm{R}$$

a、b分别是R、Me初始加入浓度，c是反应平衡后过量R的浓度，γ是R与Me络合比。因此$a=c+b\gamma$。R与MeR_γ及混合体系吸收光谱示意如图1。曲线3是过量R的吸收曲线。

在λ_2波长下，MeR_γ产物真实吸收度(A_C)应等于MN而不是MO(MO=ΔA)。A_C由下式计算：

$$A_C = \frac{\Delta A - \beta \Delta A'}{1 - \alpha\beta} \qquad (1)$$

α、β均是常数，称修正系数。分别由下式计算：

$$\alpha = A'_\infty / A_\infty \qquad (2)$$

$$\beta = A_0 / A_0' \qquad (3)$$

ΔA、$\Delta A'$是(aR+bMe)体系当以试剂空白即aR为参比时在λ_2、λ_1下吸光度，由曲线1和2知ΔA=MO；$-\Delta A'$=PQ；A_∞、A_∞'是任一浓度缔合产物MeR_γ以水为参比时在λ_2、λ_1下吸光度，由曲线4计算；A_0、A_0'分别是试剂空白当水参比时在λ_2、λ_1下吸光度，由曲线1计算。一般情况下，$\alpha \cdot \beta \approx 0$，由式(1)得：

$$A_C = \Delta A - \beta \Delta A' \qquad (4)$$

A_C值与Me浓度b成正比。

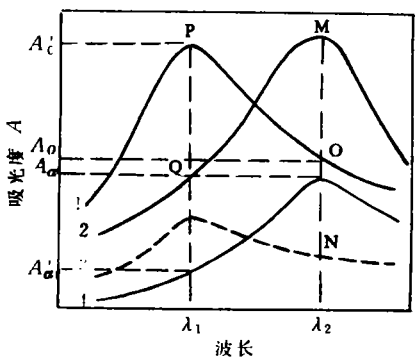

图1　R与Me显色吸收示意(水参比)

1. 显色剂R，浓度a　2. R-Me显色液，(aR+bMe)

3. 过量显色剂R，浓度c　4. MeR_γ缔合产物

1.2　实验仪器与试剂

收稿日期：1994-08-01

722 型光栅分光光度计(上海第三分析仪器厂)，25.0 ml 比色管；10 mm 比色皿。

银标准贮备液：准确称取 0.7875 g 硝酸银溶解于 1%硝酸溶液 10 ml，加水定容至 500 ml。混匀后贮存于棕色瓶中。该溶液 1.00 ml 含银(I)1.00 mg。

10.0 mg/L 银标准溶液：由贮备液配制。

pH5 缓冲溶液：称取 100 g 乙酸钠($CH_3COONa \cdot 3H_2O$)溶于 250 ml 水中，加入 60 ml 1mol/L 乙酸溶液，加水定容至 1000 ml，混匀。

5%EDTA-Na_2 溶液；0.050%孔雀绿(MG)溶液；10%碘化钾溶液。

1.3 测定方法

对颜色和浊度较高样品应预先用硝酸消化除去干扰，然后取适量分析。对较清洁水可直接取样测定。

取一定体积样品于 25 ml 比色管中，加 2 ml pH5 缓冲溶液，2 ml 碘化钾溶液，1 ml EDTA-Na_2掩蔽剂及 1.0 ml MG 显色剂。加水至刻线混匀放置 5 min。以试剂空白为参比用 10 mm 比色皿分别在 620、670 nm 波长下测定吸光度，由式(4)计算 A_C。

2 结果与讨论

2.1 吸收光谱

MG、MG-Ag^+-I^-缔合物及(Ag^++MG+I^-)混合液吸收曲线如图 2 所示。由曲线 2 可知，在 620 和 670 nm 波长下，显色液吸光度绝对值达到最大，测定灵敏度最高。从曲线 1 和式(3)计算 $\beta=0.076$；从曲线 2 和式(2)计算 $\alpha=0.81$。因此 $\alpha\beta=0.062\ll1$。Ag^+-MG-I^-缔合产物真实吸光度可由式(4)计算，不会引起误差。

2.2 MG 溶液用量影响

改变 0.05%MG 加入量，对 0.80 mg/L Ag^+标液进行实验，结果如图 3 所示。可见在 620 nm 波长处，曲线 3 吸光度变化灵敏。但当 MG 溶液加入量大于 1.0 ml 时，从曲线 1 知，MG-Ag^+-I^-缔合物 A_C 值趋于平衡。因此本实验选择 0.05% MG 显色剂加入量 1.0 ml。

2.3 其他条件影响

实验表明，改变 10%碘化钾用量，加入 0.5－3.0 ml，A_C 无明显改变。本实验选择加入量 2 ml。

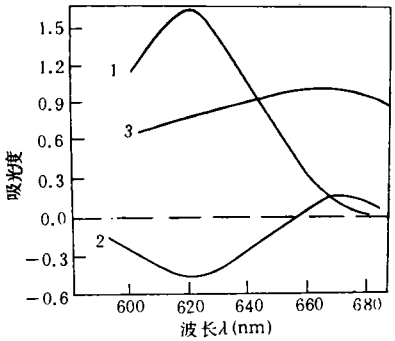

图 2 MG 与 Ag-MG 等吸收曲线

1. MG(0.002%)＋KI(0.8%)，水为参比 2. Ag^+(0.8 mg/L)＋MG(0.002%)＋KI(0.8%)，试剂空白为参比 3. Ag^+-MG-I^-缔合物，水参比

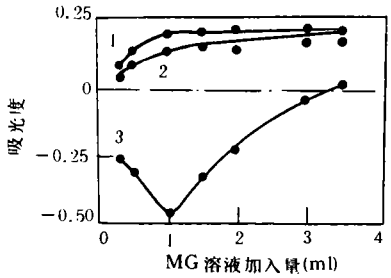

图 3 MG 溶液加入量对吸光度的影响

1. 缔合物 A_C，670 nm 2. 反应液测定吸光度 ΔA，670 nm，以试剂空白参比 3. 同 2，620 nm

Ag^+-MG-I^-反应在 pH4－6 条件下，产物与空白颜色对比度较大，反应速度快，而且 EDTA能有效掩蔽其他金属离子。本实验选择使用 pH5 醋酸-醋酸钠缓冲溶液。

Ag^+-MG-I^-反应在 pH5 条件下 2 min 即反应完成，30 min 后，A_C 值有所下降。本实验选择显色 5 min 后测定。

2.4 银标准溶液实验

2.4.1 标准曲线

分别对 0、0.20、0.40、0.80、1.20、1.60、2.00 mg/L 银标准溶液系列进行实验，在 670 nm 波长下，A_C、ΔA 银浓度(x)关系如图 4。曲线 1 的直线性和斜率均高于曲线 2，因此 β 修正

光度法的分析准确度和灵敏度高于普通单波长法。

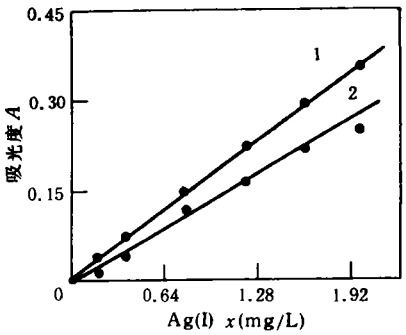

图4　银测定标准曲线(670 nm)

1. A_C-x　2. ΔA-x

2.4.2　干扰实验

在pH5和EDTA-Na_2存在下，对0.8 mg/L银标液分析误差<10%时，发现400 mg/L的K^+、Na^+、Ca^{2+}、Mg^{2+}、SO_4^{2-}、Cl^-、F^-、Ti^{4+}，40 mg/L的Zn^{2+}、Pb^{2+}、Fe^{2+}、Mn^{2+}、Al^{3+}，20 mg/L的Sn^{2+}、Ni^{2+}、Co^{2+}、Cd^{2+}、Cu^{2+}、Be^{2+}、As^{3+}，8 mg/L的Bi^{3+}、Hg^{2+}不影响直接测定。

2.4.3　方法精密度和检出限

对0.40 mg/L银标准液10次重复测定，相对标准偏差RSD和最大相对误差MRE分别是3.1%和5.8%。而普通单波长法的RSD、MRE分别是：11%和18%。

以A_C=0.010计算方法检出限[7]。则银检出限0.05 mg/L

2.5　废水样品测定

分别对印相(1#)、实验室(2#)、制镜(3#)及制药(4#)废水进行测定，结果见表1。1#样相对标准偏差RSD6.2%，废水加标回收率为97.3%—107%。

表1　工业废水中银测定结果

样品	银(mg/L) 加标量	测定值			回收率(%)
1#	0	0.211	0.215	0.196	107
		0.224	0.207	0.189	
	0.200	0.428	0.431	0.407	
2#	0	0.081	0.078	0.075	97.3
	0.100	0.171	0.179	0.176	
3#	0	0.316	0.317	0.328	104
	0.300	0.636	0.645	0.616	
4#	0	0.091	0.084	0.086	97.3
	0.100	0.184	0.192	0.177	

3　结论

β修正光度法是一种能够消除过量显色剂干扰的新方法，它不同于其他双波长分析法[8-13]。测定参数均比普通光度法有所改善。应用于行业废水痕量银测定，精密度和准确度能满足分析要求。银浓度在0—2.0 mg/L范围内，修正吸光度有良好线性。方法检出限0.05 mg/L。对印相、制镜等废水加标回收率97.3%—107%，相对标准偏差6.2%。

参考文献

1　Pierce T B. The Analyst. 1960, 85: 166
2　国家环保局. 水和废水监测分析方法. 第3版，北京：中国环境科学出版社，1989：120
3　郜洪文. 浙江冶金. 1993,(2)：53
4　郜洪文. 卫生研究. 1994, **23**(2)：147
5　Gao H W and Zhang P F. Anal. Proc.. 1994, **31**(3)：85
6　郜洪文. 环境科学研究. 1994, **7**(2)：59
7　中国环境监测总站. 环境水质监测质量保证手册. 北京：化学工业出版社，1984：234
8　郜洪文. 环境科学. 1993, **14**(2)：82
9　Hiroto Watanabe and Hideki Ohmori. Talanta. 1979, **26**: 959
10　陈静仪，林园等. 分析化学. 1990, **18**(10)：970
11　Ratzlaff K L and Natusch D F S. Anal. Chem.. 1977, **49**: 2170
12　Chen D et al.. Anal. Chim. Acta. 1989, **222**: 205
13　铁安年，张勇. 地质实验室. 1991, **7**(6)：325

Hygienic Evaluation of Indoor Air Pollution Caused by Domestic Natural Gas. Wang Juning et al. (Institute of Environmental Health and Engineering, Chinese Academy of Preventive Medicine, Beijing 100050): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 44—48

Natural gas (NG) combustions was compared with coal gas and liquid petrol gas (LPG) in the causation of indoor air pollution. The routine pollutants including B(a)P have been monitored and the 1-hydoxy pyrene in urine of the representative subjects measured. Radon concentration and its change in the NG used, starting from the source plant through transfer station to the end users, has been investigated and measured during the four seasons of the year. To analyse organic components in 3 gases, a big volume sample collector has been designed. The semi-volatile organic components contained in the combustion products of the 3 gases have been identified by GC/MC. The results show that the levels of particles and CO in the heating season were much higher than the standards, but they were the lowest in NG; NO_2 and CO_2 were a little higher in NG; B(a)P in particles and the 1-hydoxy pyrene were the lowest in NG. The organic compositions of coal gas and LPG were more complicated than that of NG. Radon in the NG from Beijing contributed less than 1‰ of effective dose to indoor air quality of the population. Compared with the traditional fuels, the gas fuel are the cleanest ones, and the NG is cleaner than other two.

Key words: natural gas, indoor air pollution, organic components, radon, 1-hydoxy pyrene.

Rapid Determination of Trace Arsenic in Water and Wastewater by Using an Arseno-antimono-molybdenum Blue Spectrophotometric Method. Qiu Xingchu et al. (Ganzhou Prefectural Institute of Environ. Sci. Research, Ganzhou, Jiangxi 341000): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 49—51

It was found that the colour producing products have a Soret band at 865 nm, an apparent molar absorptivity of 2.1×10^4, an over 24 hour stability at room temperature, a linearity range of 0—80 μg As in a volume of 10 ml and a correlation coefficient of 0.9990. The use of the Qiu's Arsenic Analyzer allows arsenic in water to be reduced as AsH_3 giving off from water. None of Al, Mn, Zn, Cd, Fe, Co, Ni, Cu, Sn, Sb, Bi and S^{2-} in a reasonable amount can interfere with the determination. This method has been applied to determining arsenic at a microgramme level in surface water and wastewater with satisfactory results.

Key words: arsenic, Qiu's Arsenic Analyzer, arseno-antimono-molybdenum blue, spectrophotometry, surface water, wastewater.

Enzyme Ticket and Chromophoric Substrate Ticket for the Convenient and Rapid Detection of Organophosphorus Pesticides. Huang Yan et al. (Guangzhou Medical College, Guangzhou 510182): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 52—54

The cholinesterase inhibition test made it possible to detect organophosphorus pesticides (OPs) compounds in water at 25—35℃ in 15—20 min, and the sensitivity of the method was in the range of 0.01—10 mg/L. Most thiophosphorus pesticides, such as methamidophos and optunal, can also be detected in those levels after they are oxidized with bromine water. This enzyme inhibition assay has been applied to the detection of pesticide in natural waters, and it was found that the positive results were quite obvious as soon as the concentration of OPs were not lower than the detection limits. The method is particularly suitable for field dtection because there is no need for expensive instruments and preparation of reagents.

Key words: organophosphorus pesticides, detection, enzyme ticket, substrate ticket.

β-Correction Spectrophotometric Determination of Silver in Wastewater with Malachite Green. Gao Hongwen (Huaibei Environ. Monitoring Station, Anhui 235000): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 55—57

Silver has been found to react with both malachite green (MG) and potassium iodide to form a green chelate at pH 5. β-correction spectrophotometry was studied for the determination of trace amounts of silver. This method can eliminate completely the excess MG in its Ag(I) colored solution to give out the real absorbance of produced Ag-MG-I^- chelate. The reaction of Ag-MG-I^- is selective in the presence of EDTA to mask other metal ions. The β-correction method has higher sensitivity, precision and accuracy than a conventional single wavelength spectrophotometry. Beer's law was obeyed over the concentration range of 0—2.0 mg/L of silver and the detection limit for Ag is 0.05 mg/L which is suitable for the analysis of wastewater. The recovery was found to be between 97.3%—107%,

with a RSD of 6.2%.

Key words: β-correction, spectrophotometry, silver, malachite green, real absorbance.

Study on a Synthetical Index Method for Air Quality Assessment. Wu Limin et al. (Fuxin College of Mining, Fuxin 123000): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 58—60

A synthetical index method for air quality was developed, where the principles followed are: ① each of pollution factors has an equal contribution to the synthetical assessment index; and ② the air pollution becomes heavier when multiple pollution factors exist simultaneously. Finally, the rationality of the method is proven based on an assessment prototype.

Key words: air pollution, environmental quality assessment, synthetical index.

Preliminary Study on the Pollution Assessment of Cd in Soil by the Concentration of Cd in Plant Seedling. Yang Linshu et al. (Resources and Environ. College, Beijing Agriculture Univ., Beijing 100094): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 61—63

Pot experiments were conducted to study the feasibility for the pollution assessment of Cd in soil by the concentration of Cd in seedlings of *Triticum aestivum* L., *Glycine max* L. and *Brassica camspestris* L. The results show that Cd concentrations in the three plant seedlings were higher than those of their later growth stages or havested parts. The seed Cd concentrations of *Triticum aestivum* L. and *Glycine max* L. were highly positively correlated to Cd concentrations in their seedlings, respectively. Cd concentration in havested *Brassica camspestric* L. was also highly correlated to its seedling Cd concentration. According to the National Criterion for Public Health, the critical Cd concentrations for threeleave *Triticum aestivum* L., seedlings of *Glycine max* L. and *Brassica camspestris* L. were 0.72 mg/kg, 0.5 mg/kg and 0.16 mg/(kg • fw) respectively.

Key words: Cd concentration in seedlings, soil Cd pollution, *Triticum aestivum* L., *Glycine max* L., *Brassica camspestris* L..

Study on the Information System for Management of Solid Waste Exchange. Wang Jue et al. (Institute of Environ. Sci., Beijing Normal Univ., Beijing 100875): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 64—67

An information system has been developed for the management of solid waste exchange which is a means of waste recycling and recovery and a kind of exchange between waste generators and potential waste users, based on the relativity of waste. Based on the analysis of solid waste exchange patterns, the exchage types were classified and their effects were summarized. By expounding the links of waste exchange and using the method of system analysis, the basic functions and components of such an information system were analyzed. Computer technology system design and system implement action were used to set up the information system for management of solid waste exchange by using a modern database as its system core. According to the basic demands of waste exchange, this system realizes functions such as data input, output, transport, retrieval and statistics. A theoretical discussion on system intellectualization was made based on the development of the system.

Key words: waste exchange, system analysis, information system.

Criteria of Centralization or Decentralization for Use in a Regional Planning of Wastewater Treatment System. Wang Yonghang and Fu Guowei (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 68—71

A simple and efficient methodology was developed for use in a regional planning of wastewater treatment systems. The criterion for eliminating nonoptimal treatment plant sites for every wastewater source in a region took into account the critical distance parameter derived from the interrelation between the lower limit of transportation cost and the upper limit of regionalization efficiency. The developed method was able to significantly reduce the number of candidate locations of shared facilities for regionalized wastewater treatment. In addition, a case study was given. Enhancement of regional systems management would be a principal benefit of the suggested methodology.

Key words: wastewater treatment, critical distance, centralization, decentralization.

Investigation on the Current Status of Sewage Discharge from Beijing and the Response Strategy. Wang Yan et al. (Beijing Municipal Research Academy of Environment Protection, Beijing 100037): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 72—74