

监测与分析

石墨探针采样/石墨探针炉原子吸收光谱 测定 APM 中痕量铜

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摘要 采用一定规格的石墨探针可直接收集大气微粒物质(APM)。然后,立即采用石墨探针炉原子吸收光谱测定收集在探针上的 APM 中痕量铜。方法简便,快速。在 0—550 ng/mL 范围内,铜的浓度与峰面积吸光度呈良好的线性关系。铜的特征量为 22.0 pg,检出限为 6.6 ng/mL。分析标准参比材料,铜的回收率达 98%,相对标准偏差为 3.3%。

关键词 痕量铜,大气微粒物质,石墨探针,原子吸收光谱。

燃料的燃烧是大气微粒物质中痕量元素的主要来源,且以铜、铅、锌为其特征^[1]。人体吸入一定量 APM 中的铜将危害其健康。目前,一般采用玻璃纤维滤膜^[2,3]及其它滤膜(如纤维素酯、聚酰胺等)^[4,5]来收集 APM,酸溶、稀释定容后,用石墨炉原子吸收光谱(GFAAS)测定痕量铜。虽然方法的灵敏度、准确性较高,但分析速度慢。对于 APM 来说,多孔的电石墨是一个理想的过滤材料,有着很高的收集效率^[6,7]。本文采用一定规格的石墨探针过滤器收集 APM,然后,立即用石墨探针炉原子吸收光谱(GPFAAS)测定收集在探针上的 APM 中的痕量铜。本法省去了繁杂的化学预处理步骤,避免了预处理过程中可能出现的样品的玷污和分析物的损失,除保持了常规的滤膜收集, GFAAS 法灵敏度、准确性高的特点外^[8],分析速度大大加快,既可对 APM 中铜含量的波动进行快速监测,也可在较长时间内对某一地区 APM 中铜含量的变化进行连续监测,只要合理布点,定期更换过滤器中的石墨探针即可。

1 实验部分

1.1 仪器和试剂

Perkin-Elmer 5000 型原子吸收分光光度计(钨/氘灯背景校正);HGA-500 石墨炉;Perkin-Elmer 7500 型计算机。石墨探针规格:长 25mm、宽 5mm、厚 0.5mm(由 5 种不同类型的电石墨块

加工制成,石墨等极/气孔性分别为 7716/34%、9429/30%、3494/26%、8826/20%和 9236/16%,美国)。在石墨炉接触圆柱体及石墨管上各开一个长 5mm、高 1.8mm 狭槽,以便探针插入。

金属铜为光谱纯、HNO₃ 优级纯,其余试剂均为分析纯;二次蒸馏水;标准参比材料(SRM 1648,城市微粒物质,美国国家标准局)。

1.2 原子吸收测定条件

波长:327.4nm;光谱带宽:0.2nm;灯电流:15mA;保护气体(氩气)流量:300mL/min,原子化期间中断流动。石墨探针炉升温程序:原子化前 20℃,斜坡 5s,保持 5s;原子化(阶梯)2650℃,5s;冷却 20℃,斜坡 5s,保持 5s。

1.3 步骤

(1)溶液 在石墨炉内空烧除残一次后的探针前部准确移入 5μL 试验溶液,在红外线灯下蒸干,将探针后部附在探针系统上。当原子化步开始时,通过气动装置将探针前部快速插至石墨炉中部,在恒定的温度下加热。

(2)APM 将空烧除残一次后的探针放入过滤器收集 APM。将收集了 APM 的探针后部附在探针系统上,以下步骤同前,按下式计算铜含量:

$$c_i = \frac{10^6 [(c_2 - c_1)(A_r - A_1) / (A_2 - A_1) + c_1] V}{Ft}$$

式中, F 是过滤流速 (mL/min), t 是采样时间 (min); c_1, c_2 分别为一号标液和二号标液的铜浓度 ($\mu\text{g}/\text{mL}$); A, A_1, A_2 分别为样品, 一号, 二号标液中铜的峰面积吸光度; V 是移至探针前部的标液体积 (μL)。

2 结果和讨论

2.1 记忆效应试验

在无基体改良剂存在下, $0-550\text{ng}/\text{mL}$ 范围的铜没有记忆效应产生, 即在此含量范围的铜, 测定后探针只需空烧除残一次就可重复使用。

2.2 分析校正曲线

图 1 表明: 铜的浓度 (c) 在 $0-550\text{ng}/\text{mL}$ 范围内与峰面积吸光度 (A) 呈良好的线性关系, 线性范围宽。通过对分析校正曲线进行计算机回归分析, 得出回归方程: $y = 0.2367x + 0.0011$, 相关系数 0.999 , 相关性显著。对含铜 $25\text{ng}/\text{mL}$ 的标准溶液平行测定 10 次, 其检出限 (3σ) 为 $6.6\text{ng}/\text{mL}$, RSD 为 3.25% 。图 2 是 $250\text{ng}/\text{mL}$ 铜的吸收轮廓和空白信号。

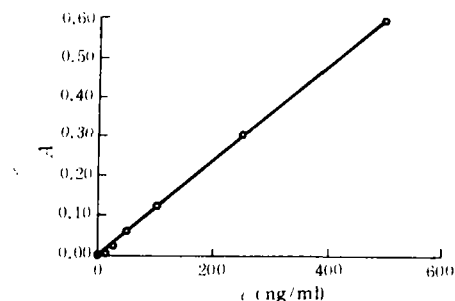


图 1 铜的分析校正曲线

2.3 收集效率和回收率试验

试验上述过滤和分析系统的总体性能是困难的, 因为这需要同时采用良好的分析方法和常规的空气过滤装置来测定 APM 中的铜。目前, 后者仍然是不成熟的。因此, 本试验分两部分研究此系统。首先, 采用双探针过滤器研究石墨探针的收集效率。其次, 通过 GPFAAS 测定标准参比材料 (SRM) 中铜的回收率, 研究分析测试的可行性。

本试验选择了 5 种大小, 厚度相同 ($25 \times 5 \times 0.5, \text{mm}$), 但石墨类型不同的探针, 每次试验将两种类型的探针放入过滤器, 上探针的气孔性应大于下探针, 用真空泵抽滤收集 APM。按前述仪器工作条件, 测得的上探针与上, 下探针铜量的比值, 即为上探针的收集效率。试验表明: 由气孔性为 20% 、8826 等级的电石墨加工制成的探针对 APM 中铜的收集效率接近 100% (见表 1)。经透射电镜分析, 此类探针的孔径为 $0.01-2\mu\text{m}$ 。

GPFAAS 对 SRM3 次独立分解制得的 3 种标液的分析表明, 铜的回收率达 98% (见表 2), 对铜的测定有很高的灵敏度 (见表 3)。

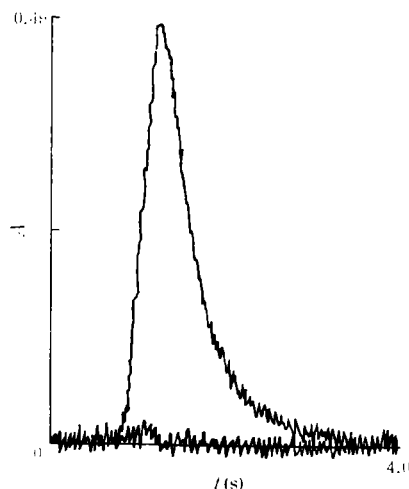


图 2 铜的吸收轮廓和空白信号

2.4 干扰试验

对 10 种共存离子进行试验, 当测定误差小于 5% 时, 各共存离子的允许量如表 4 所示。

2.5 样品分析

表 5 为采用石墨探针及过氯乙烯滤膜 ($\phi: 80\text{mm}$) 在不同日期收集的学校上空 APM 中痕量铜的 5 次分析结果。采用探针法收集 APM, 每

表 1 不同类型石墨探针对 APM 中铜的收集效率

上探针	7716/34% ¹⁾	9429/30%	3494/26%	8826/20%
下探针	9236/16%	9236/16%	9236/16%	9236/16%
收集效率	62.2%	75.8%	85.5%	99.9%

1) 石墨等级/气孔性

表 2 SRM3 次独立分解制得的 3 种标液中铜的回收率

标液 No.	保证值 ¹⁾ ($\mu\text{g/ml}$)	实验值 ($\mu\text{g/ml}$)	回收率 (%)	精密度($n=10$) (%RSD)
1	2.40	2.38	99	3.2
2	2.32	2.25	97	3.4
3	2.45	2.40	98	3.2
平均值			98	3.3

1) 由 SRM 中的铜的分析保证值($609 \pm 27 \mu\text{g/g}$)算得

表 3 SRM 中铜的特征量和检出限

标液	特征量($n=10$) (μg)	检出限(3σ)($n=10$) (ng/mL)
1	23.0	6.9
2	22.5	6.5
3	21.0	6.4
平均值	22.0	6.6

表 4 共存离子的干扰试验

(Cu: $2.50 \mu\text{g/ml}$, $5 \mu\text{l}$)

共存离子	共存离子加入量(μg)	倍数 ¹⁾	测得值 (ng)	相对误差 (%)
Al^{3+}	6250	5×10^5	12.1	-3.2
As^{III}	125	1×10^4	12.7	1.6
Cd^{2+}	625	5×10^4	12.9	3.2
Cr^{3+}	12.5	1×10^3	13.0	4.0
Fe^{3+}	10000	8×10^5	12.0	-4.0
Ni^{2+}	1250	1×10^5	12.4	-0.8
Pb^{2+}	750	6×10^4	12.2	-2.4
Cl	0.1mol/L		12.0	-4.0
K^+	0.1mol/L		12.2	-2.4
Na^+	1.4mol/L		12.8	2.4

1) 倍数 = 共存离子加入量/Cu 量

次分析都将 3 个独立的探针过滤器平行联入过滤收集系统,过滤流速均保持 79ml/min ,收集时间都为 30min ,以测量方法的精密度。滤膜法收集的 APM,用稀 HNO_3 浸出法溶样,稀释定容后,再用 GFAAS 测定铜,仪器工作条件与 GPFAAS 相同;过滤流速、收集时间分别为 90L/min 和 1h ;每次测定结果应扣除滤膜空白值。试验表明:同一日期收集的 APM,两种收集方法的分析结果相近,其相对偏差为 $4.80\% \sim 8.51\%$ 。不同日期采用探针法收集、测得的 APM

中铜含量虽在 $1.5 \sim 8.3 \text{ng/m}^3$ 范围变化,但同一日期 3 个探针平行收集,测定的铜含量,其相对标准偏差均低于 5% ,结果令人满意。

表 5 APM 中痕量铜的分析

样品	探针法收集 含量(ng/m^3)	RSD(%)	滤膜法收集 含量(ng/m^3)	相对偏差 (%)
1	5.70	3.86	5.15	4.92
	5.53			
	5.82			
2	8.29	1.99	7.44	4.80
	8.20			
	8.07			
3	4.59	4.68	4.06	5.47
	4.38			
	4.62			
4	1.50	3.90	1.29	8.51
	1.52			
	1.58			
5	3.32	3.19	2.90	6.76
	3.25			
	3.40			

3 小结

采用一定规格的石墨探针直接收集 APM 以及采用 GPFAAS 测定其中的痕量铜,是一项准确、灵敏、简便、快速的分析方法。采用此过滤收集与分析系统,还可试验、测定 APM 中其它痕量元素,有着广阔的应用前景。

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The environmental deterioration caused by human activities and overlapped by the natural changes has become one of the major problems for current environmental protection cause. The desertification of large lands and the sand-dust storms occurred in the deserts and the desertified regions are such typical problems. This paper describes the major sources of the sand-dust storms in China and the transportation path of the Kosa aerosol. A brief description of the transportation path of the sand-dust storm generated around the region of Jinchang City, Gansu Province on May 5, 1993 is also given.

Key words: Sand-dust storms, Northwest Region, China, high—altitude transportation.

New Type Nonpollution Antifouling Coating for Marine Application. Tian Jun et al. (Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000); *Chin. J. Environ. Sci.*, **14**(5), 1993, pp. 65—68

This paper deals with the major affecting factors of the fouling living things, the present development situation of antifouling coating for marine application and the important role of initial mucosa in the adherent mechanism. The antifouling mechanism and application of the new type nonpollution antifouling coating have been emphatically discussed, based on the material of low surface free energy, hydrophilic material, biochemical material, and low toxic material. It is suggested that the low toxic material is the recent goal to solve the marine organotin pollution, but nontoxic antifouling coating of the new generation, particularly the material of low surface free energy, is at the initial stage of development. The application of this material is almost impossible in the near future.

Key words: marine nonpollution antifouling coating, antifouling mechanism, marine environment.

Effects of Cobalt (II) and Nickel (II) on *Catharanthus roseus* Cell Suspension Cultures. Zhu Lizhong (Department of Chemistry, Hangzhou University, Hangzhou 310028); *Chin. J. Environ. Sci.*, **14**(5), 1993, pp. 69—71

The effects of cobalt(II) and nickel(II) on the growth of *catharanthus roseus* (*C. roseus*) cell suspension cultures at pH 5.5 were investigated. Cell growth and cobalt or nickel uptake were monitored. When the concentrations

of Co(II) and Ni(II) were more than 4.0 $\mu\text{g/ml}$ and 2.0 $\mu\text{g/ml}$ respectively, the growth of *C. roseus* was inhibited. Minimum lethal concentrations of Co(II) and Ni(II) were 50.0 $\mu\text{g/ml}$ and 10.0 $\mu\text{g/ml}$ respectively. Cobalt (II) was more easily to be uptaken and enriched by *C. roseus* cells than nickel(II).

Key words: *Catharanthus roseus*, cell culture, cobalt, nickel, toxicity test.

Study on the Some Environmentally Chemical Natures of Ether Amines $\text{R-O}-(\text{CH}_2)_3\text{NH}_2$ in Mineral Separation Wastewater. Tao Yinhe et al. (General Prospecting and Research Institute, Ministry of Metallurgical Industry, Baodin 071069); *Chin. J. Environ. Sci.*, **14**(5), 1993, pp. 72—75

Some tests have been made on soil-column leach, degradation and adsorption to study some environmentally chemical natures of the ether amines $\text{R-O}-(\text{CH}_2)_3\text{NH}_2$ in mineral separation wastewater. The results indicated that: ① in water, the $\text{R-O}-(\text{CH}_2)_3\text{NH}_2$ was degraded by following an equation of first-order biochemical reaction, $c=c_0\exp(-kt)$, where the temperature and pH value are two major factors affecting the degradation coefficient; ② the soil adsorbed the ether amines $\text{R-O}-(\text{CH}_2)_3\text{NH}_2$ at a rate of over 92% and the adsorption equilibrium equation was $q=5.335+63.29C$; and ③ in soil, the ether amines $\text{R-O}-(\text{CH}_2)_3\text{NH}_2$ moved in the vertical direction by following the $c=a\exp(-b/t)$. These results provided a scientific basis for water quality calculation and environmental protection designing.

Key words: ether amines, $\text{R-O}-(\text{CH}_2)_3\text{NH}_2$, degradation law, degradation coefficient, soil adsorption ratio, distribution coefficient, vertical direction movement.

Collection with a Graphite Probe Filter/Determination of Trace Copper in Atmospheric Particulate Matter by Graphite Probe furnace Atomic Absorption Spectrometry. Zhang Bicheng (Department of Chemistry, Hubei University, Wuhan 430062); *Chin. J. Environ. Sci.*, **14**(5), 1993, pp. 76—78

Direct determination of trace copper in atmospheric particulate matter was done by graphite probe furnace atomic absorption spectrometry after collection with a graphite probe filter. The new method was simple and rapid. The concentration of copper and absorbance (peak-area mode) showed excellent linear relation in the range of 0—550

ng/ml. The characteristic mass and detection limit of copper were 22.0ng and 6.6ng/ml, respectively. The results of analysis of the National Bureau of Standard (NBS), Standard Reference Material (SRM) No. 1648, urban particulate matter, gave recovery of 98% and a precision of 3.3% RSD.

Key words: trace copper, atmospheric particulate matter, graphite probe, atomic absorption spectrometry.

Distribution Pattern of Polycyclic Aromatic Hydrocarbons in the Atmosphere in Huhhot City. Gao Chunmei et al. (Inner Mongolian Scientific Research Institute of Environmental Protection, Huhhot 010010); *Chin. J. Environ. Sci.*, **14**(5), 1993, pp. 79—81

The PAHs in the vapor phase and on the particulates have been collected simultaneously through PUF and fiberglass filter film. The batch collecting samples have been carried out respectively in both inhabited areas and clean meadow areas in the two seasons of winter and summer. The contents of PAHs, such as anthracene, pyrene, chrysene, perylene, benzo(a) pyrene, dibenz(a, h) anthracene and benzo[ghi]-perylene, have been determined by using HPLC. The results show that over half of the PAHs of below four rings were found in the vapor phase and most of the PAHs of over four rings were found in particulates; the percentage of each of PAHs in the vapor phase in summer was higher than that in winter; the percentages of the PAHs in the vapor phase and on particulates in clean meadow areas were different from those in inhabited areas; and in winter the time at which the pollution in inhabited areas was most serious was 10:00-11:30 and 17:30-21:30 but in summer the time was 6:00-10:00 and 18:00-22:00.

Key words: polyurethane foam (PUF), polycyclic aromatic hydrocarbons, vapor phase and particulates, high performance liquid chromatography (HPLC).

Determination for Valence Distribution of Iron with a Stopped Flow-Kinetic Spectrophotometric Method. Wang Jianhua et al. (Department of Chemistry, Yantai Teacher's College, Yantai 640000); *Chin. J. Environ. Sci.*, **14**(5), 1993, pp. 82—84

A stopped flow-kinetic spectrophotometric method for the determination of Fe(II) was proposed based on the inductive effect of Fe(II)-Cr(VI) reaction on the Cr(VI)-iodide redox reaction systems under the optimal conditions

of: $[Cr(VI)] = 1.8 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[I^-] = 2.0 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\text{pH} = 1.9$ 590nm. The calibration graph is linear for 0-2.2 $\mu\text{g} \cdot \text{ml}^{-1}$ Fe(II) and the detection limit is 0.009 $\mu\text{g} \cdot \text{ml}^{-1}$ Fe(II). 25 times higher concentrations of Fe(II) do not interfere with the determination of Fe(II). Fe(II) was reduced to Fe(II) and total iron content was measured after the determination of Fe(II) content and the recovery of Fe(II) was greater than 98%. Valence distributions of iron of several samples were analysed with the proposed method and the results are satisfactory.

Key words: iron, valence distribution, kinetic spectrophotometry.

A Review on the Methods for Determining Partition Coefficient (K_d). Ye Yanmei et al. (Chengdu College of Geology, chengdu 616059); *Chin. J. Environ. Sci.*, **14**(5), 1993, pp. 85—89

The factors affecting partition coefficient (K_d) were discussed, based on experimental data. It is considered that the key to precisely determining a partition coefficient is to have an experimental model which is sufficiently imitable to the natural system. An experimental method for determining K_d by dynamical simulation is suggested. The K_d values calculated with this method are close to the real values in many cases and the method is found to be simple, convenient and practical. In some cases such as quick reaction, the K_d values may be determined by using a static simulation experiment which is more simple and a special case of the dynamical simulation experiment, and the results are also close to the real situation.

Key words: partition coefficient, dynamical simulation experiment, affecting factors.

Use of Dimethyl Silicone Oil for Defoaming in the Measurement of Aniline. Zhang Qun et al. (Yancheng Environmental Monitoring station, Jiangsu 224002); *Chin. J. Environ. Sci.*, **14**(5), 1993, pp. 90

This paper deals with the use of a dimethyl silicone oil (Silicone Oil I) as a defoaming agent in the measurement of aniline present in a textile dyeing and printing wastewater which has a quite dark colour and a higher content of phenols. In the pre-distillation-diazotization-colorimetric determination of the above aniline, a large volume of foams formed during the distillation is an important factor affecting the precision of results and can be defoamed by adding the above silicone oil. It has been