监测分析

硒化氢发生-硒化银溶胶法测定微量硒

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摘要　人体内微量硒的存在对人的健康至关重要，缺硒会引起一些严重的疾病．本文基于在酸性介质中，用硼氢化钾片将硒离子转变为硒化氢，再以硝酸银-阿拉伯胶溶液吸收显色，形成的硒化银溶胶在紫外区有最大吸收，从而建立了一个测定微量硒的新的分光光度法．此方法的特点是：操作简便快速，有较高的选择性和灵敏度，检出限为 0.04ppm．本方法用于硒酵母、人发、大米和人尿等样品中硒的测定，取得了满意的结果．

硒是生物体内所必需的微量元素之一，缺硒与人类的某些疾病密切相关[1]．硒及其化合物的药理及分析方法的研究，已引起环境化学、分析化学、医学、生物学等方面科研人员的充分重视．常用测定硒的方法有分子荧光法[2]、阳极溶出伏安法[3]、气相色谱法[4]等，利用氢化物发生原子吸收测定微量硒，近年来也取得了很大进展[5,6]．

本文在 0.1molH_2SO_4-2% 酒石酸介质中，加入硼氢化钾片将 Se(IV) 还原成 H_2Se，用硝酸银-阿拉伯胶溶液吸收，硒化氢与硝酸银反应生成硒化银溶胶[7]，此溶液在 246nm 处有最大吸收，从而建立了新的测定微量硒的分光光度法。采用片状固体还原剂发生硒化氢，较用硼氢化钾溶液操作更为方便．本方法一般共存离子均不干扰硒的测定，具有较高的选择性和灵敏度，检测限为 0.04ppm (按取样量克计)．用于硒酵母、人发、米、尿等样品中硒的测定，取得了满意结果。

实　验　部　分

一、仪器

日本岛津 UV-200 分光光度计，上海 791 型电磁搅拌器．

二、试剂

1. 四价硒标准溶液　准确称取 100.0mg 硒粉于 100ml 烧杯中，加入 10ml 硝酸。盖上表皿，加热使之完全溶解，蒸至近干．加入 1:1 盐酸 20ml，加热煮沸 5 分钟．冷却，移入 100ml 容量瓶中，用水稀释至刻度．浓度为 1.0mgSe(IV)/ml．用 0.5mol 盐酸将此溶液稀释配制成 1.0μgSe(IV)/ml 的工作溶液．

2. 阿拉伯胶　0.7% 的水溶液．

3. 硝酸银溶液　准确称取 0.500g 硝酸银于 100ml 烧杯中，用少量去离子水溶解后，移入 100ml 容量瓶中，加入 1.0ml 浓硝酸，用去离子水稀释至刻度．

4. 吸收显色液　在 100ml 锥形瓶中，依次加入 40.0ml 阿拉伯胶、1.0ml 硝酸银溶液及 20.0ml 无水乙醇，混合均匀．

5. 硼氢化钾片　硼氢化钾与氯化钠以重量比 1:5 压制而成，每片重 1.4—1.6g．

所用试剂均为分析纯，所用水未经说明均为蒸馏水．

三、实验方法

实验装置见图 1．

在反应瓶中加入待测溶液，1 滴 0.05% 甲基橙，用 1:1 氨水中和变黄，再滴加 0.5mol 硫酸至溶液刚变红．加入 2.0ml 2.5 mol

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H_2SO_4、5.0ml 20% 的酒石酸溶液，加水至50ml.在吸收管中加入3.0ml吸收显色液后，往反应瓶中加入2片硼氢化钾片，迅速塞紧塞子．反应完毕后，将吸收液移入4cm石英比色皿中（如果硒含量较高，可用1cm比色皿），放入带有特制遮光板的液槽中，在246 nm处以原吸收显色液为参比，测量吸光度．

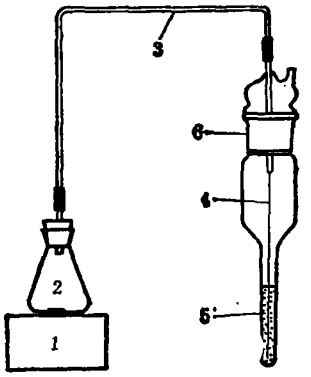

图1　实验装置示意图

1.电磁搅拌器　2.反应瓶　3.聚四氟乙烯导管　4.细聚四氟乙烯管(直径 0.4mm)　5.吸收显色液　6.吸收管

结果与讨论

一、硒化氢发生介质的选择

硒化氢的发生需要在较强的酸性介质中进行，但酸度过高，空白值明显增大．我们比较了多种无机酸和有机酸对产生硒化氢的影响，并给出了它们吸光度的相对强度，见图2．用低浓度的硫酸与2%的酒石酸共同做为反应介质，可使氢离子浓度得到适当控制，使还原反应不致过于激烈，降低了空白值.在固定酒石酸浓度为2%的条件下，我们试验了硫酸酸度对硒化氢发生的影响．图3表明，硫酸酸度为0.05—0.15 mol时，满足空白值小，灵敏度高的要求，故选择硫酸酸度为0.1mol.

二、吸收显色条件

1.分散剂及其浓度的选择

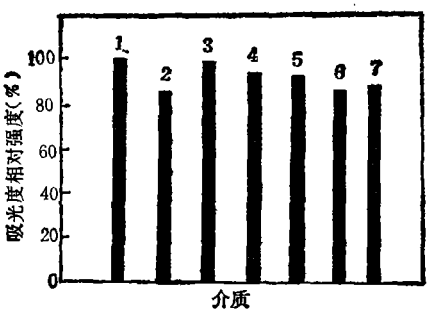

图2　硒化氢发生介质的选择

1. 0.1mol H_2SO_4-2% 酒石酸　2.5% 柠檬酸　3.5% 酒石酸　4. 0.2mol HNO_3-2%酒石酸　5. 0.1 mol H_2SO_4-2% 柠檬酸　6.5% 草酸　7. 0.2mol HCl-2% 酒石酸

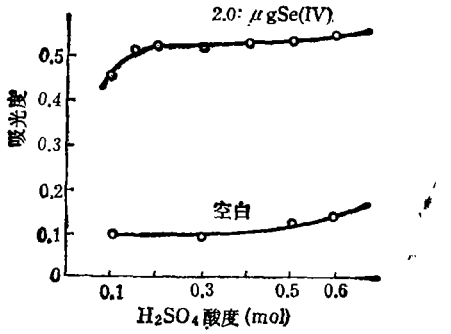

图3　硫酸酸度的影响

在OP、Triton X-100、明胶、聚乙烯醇、阿拉伯胶等分散剂中，以阿拉伯胶效果最好．用0.3—1.5%的阿拉伯胶的水溶液配制吸收液，所得吸光度最高并保持稳定．我们选择0.7%的阿拉伯胶溶液配制吸收液．

2.硝酸银浓度的影响

吸收液吸收硒化氢后的吸光度随其中硝酸银浓度的改变而产生相应的变化，但变化的幅度不大．当硝酸银浓度在 $2—5\times10^{-4}$ mol/L 时，灵敏度最高．选择硝酸银浓度为 2.413×10^{-4}mol/L.

3.吸收液酸度的影响

硒化氢与硝酸银的反应受酸度的影响较大，酸度的增高，会阻碍反应的进行．图4给出了酸度对显色灵敏度的影响．从提高灵敏度方面考虑，吸收液的酸度应越低越好．根据我们的试验结果，酸度过低，吸收液将不稳

定，同时空白值也会增高．本文选择吸收液的酸度为 1.248×10^{-3}mol 硝酸，既保证了灵敏度，又使空白值低，结果稳定。

三、显色液的稳定性

吸收液对硒化氢的吸收显色完全、迅速。硒化氢发生完毕，吸收液也同时显色完毕且达到最高吸光度，并在半小时内保持不变。

四、共存元素干扰试验

在被试验的三十多种共存离子中，阳离子 K^+、Na^+、NH_4^+、Ca^{2+}、Mg^{2+}、Mn^{2+}、Zn^{2+} 等；阴离子 F^-、Cl^-、Br^-、NO_3^-、SO_4^{2-}、ClO_4^- 等不干扰 Se(IV) 的测定．用 EDTA 做掩蔽剂，大部分过渡元素的允许量可达到被测元素的 500—5000 倍．共存元素的影响情况列于表 1 中．除砷、锑外，其它可生成氢化物元素的允许量都较高，硫的干扰在用 HNO_3-$HClO_4$ 湿法消解过程中生成挥发性硫化物除去。故本方法具有较高的选择性。

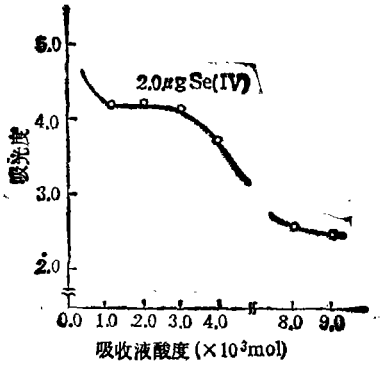

图 4　吸收液酸度的影响

五、工作曲线

在反应瓶中依次加入含 Se(IV) 0.0、0.5、1.0、1.5、2.0、3.0μg 的标准溶液，按实验方法进行硒化氢的发生、吸收显色及吸光度的测量。得到工作曲线参数为：$r=0.9997$、$a=0.0060$、$b=0.205A/\mu g$。

样品分析

一、人发、米、面包

表 1　共存元素的影响*

共存元素及加入量，μg		测得 Se^{4+} 的回收率，%	共存元素及加入量 μg		测得 Se^{4+} 的回收率，%
a Ni^{2+}	5000	100	Mo^{6+}	100	100
W^{6+}	5000	100	b Cu^{2+}	50	91
a Fe^{3+}	5000	95	Ge^{4+}	50	100
a Fe^{2+}	5000	100	a Sn^{2+}	50	100
a Cr^{6+}	5000	96	Sn^{4+}	20	103
a Cr^{3+}	3000	95	a Pb^{2+}	10	96
a Co^{2+}	3000	100	a Ag^{+}	5	91
Bi^{3+}	500	102	As^{5+}	2.5	101
a Al^{3+}	500	100	As^{3+}	2.5	101
b Cd^{2+}	500	93	Sb^{5+}	2	105
Te^{4+}	100	105	Sb^{3+}	2	105
a Hg^{2+}	100	100			

* 每一试验加入 1.0μgSe(IV)
a 加入 5ml 0.1mol EDTA 掩蔽
b 加入 0.1g 亚铁氰化钾掩蔽

称取 0.5—1.0g 样品于 100ml 烧杯中，加入 15ml 硝酸，放置过夜后，加入 2ml 高氯酸．盖上表皿，低温消解蒸去硝酸，慢慢升温至冒高氯酸白烟，保持半分钟．取下，冷却后移入反应瓶中，加入少许尿素后，用固体氢氧化钠大致中和，加入 5 ml 0.1 molEDTA，再按实验方法操作步骤进行硒的测定。

二、硒酵母

称取 2—10mg 样品于 100ml 烧杯中，加入 10ml 硝酸，放置过夜，加入 2ml 高氯酸．其余操作同上。

三、尿样

取 20ml 尿样于 100ml 烧杯中，加入 10ml 硝酸、2ml 高氯酸，加热至冒高氯酸白烟．然后按人发样品的操作进行测定。

以上样品我们还做了加标试验，并与其它方法的测定结果做了比较．从表 2 可以看出，测定回收率高，结果令人满意。

表 2　样品测定结果

样品	加入 Se(IV)量 (ppm)	单次测得值 (ppm)	平均值 (ppm)	变异系数 (%)	回收率(%)	参考值(ppm)
人发	0.0	0.57, 0.66, 0.63 0.61, 0.57, 0.54	0.60	7.5		
	1.0	1.59　　1.63	1.61		101.6	
硒酵母-1	0.0	685, 680, 678 690, 695, 676	684	1.1		680**
	100.0	786　　781	784		100	
硒酵母-2	0.0	498, 500, 510 485, 505, 494	501	1.7		499**
	200.0	687,　　694	691		98.0	
硒酵母-3	0.0	120, 118, 125 131, 115, 120	122	4.7		
	200.0	315　　323	319		97.5	
米	0.0	0.31, 0.28, 0.36 0.36, 0.29, 0.35	0.33	10.9		0.34*
	0.50	0.83　　0.80	0.82		97.0	
面包	0.0	0.44, 0.38, 0.41 0.36, 0.38, 0.46	0.41	9.3		0.41*
	2.0	2.43　　2.40	2.42		102.4	
尿-1	0.0	0.066, 0.056, 0.060 0.056, 0.059, 0.061	0.060	6.2		0.058*
尿-2	0.0	0.042, 0.044, 0.048 0.039, 0.047, 0.018	0.045	8.2		0.046*

* 分子荧光法测得值

** 氢化物发生 -Fe(III)- 邻菲罗啉法测得值

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Chen Zhongliang et al. (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing)

Total suspended particulates (TSP) and their chemical composition in Beijing-Tianjin Area have been analyzed. There were 12 elements (Cd, Cu, K, Mn, Pb, Zn, Fe, Na, Ni, Cr, Sr, Ba), 5 kinds of ions (F, Cl, NO, SO, NH) and 26 kinds of organic pollutants in the regional distribution. The sources of TSP were estimated by means of orgenic odd/even carbon number rates. Atmospheric pollution affected mutually among Beijing, Tianjin, Lanfang anf Gixian County were studied with identification analysis of inorganic elements. (See pp. 24—27)

Economie Optimization in Noise Reduction by Sonnd-Absorbing Treatment

Kang Jian (Architecture Department, Tsinghua University, Beijing)

In the design of noise reduction by sound-absorbing treatment, there may be several schemes that can attain the goal of anticipated noise reduction under approximate decorative level. However, the costs are very different. So it is necessary to choose an optional one. This paper presents a maths model to solve the optimization problem. The corresponding computer program and a case study are also given. (See pp. 30—33)

Removal of Cd^{2+} and Cu^{2+} Ions in Water Solution by the Modified CARIX Ion-Exchange Technology

Ma Shishen (The Institute of Atomic Energy, Beijing);

W. H. Hoell and S. H. Eberle (Institute of Radiochemistry, Karlsruhe Nuclear Research Center, Federal Republic of Germany)

This paper reports a new technology of ion exchanges in removing Cd^{2+} and Cu^{2+} from the dilute solutions of cadmium sulfate and copper sulfate. Its advantages are derived from the use of carbon dioxide and magnesium compounds as regenerats. As carbon dioxide is a non-polluting chemical, it could diminish saline loads in water bodies. The experimental results show that a partial conversion of the resin to magnesium is achieved and the effect of desalination is satisfied. In addition, the concentration of magnesium ions in the regenerant is higher than that of carbonic acid and calcium ions during regeneration. It increases effective cation exchange capacity of the weakly acid cation exchange resins. (See pp. 36—40)

Petroleum-Sulfoxide Extract-Leach Resin: A New Resin for Treatment of Wastewater Containing Methylmercury

Jia Jinping (Department of Applied Chemistry, Shanghai Jiao Tong University); Zhou Yi (Department of Applied Chemistry, China University of Sciences and Technology, Hefei, Anhui Province); Peng An (Research Center for Eco-Environmental Sciences, Beijing)

This paper presents the study on possibilities of treating low-concentrated methylmercury in wastewater by petroleum solfoxide (PSO) extract-leach resin, in which PSO as a cheap extractant, can be obtained from raw oil containing high sulfur content. The experimental results were as follows: (1) the resin was avaiable to sorb more than 99% methylmercury (concentrations 10-20ppb) in pH range 5—8; (2) current velocity of effuent affected sorption capacity. As the velocity increased from 0.5 ml/min to 5.0 ml/min, the sorption capacity decreased from 99.66% to 98.90% in bed column (diameter 0.8 cm, length 10.3 cm, resin weight 3.0 g); (3) the resin could be regenerated easily by means of eluting it with the regenerant (4mol HCl); (4) Mg(II), Fe(II), Fe(III), Ag(I), Cu(II), Hg(II), FA(fulvicacid) and Cl^- ions had no influence on sorption capacity of the resin except Hg(II) and Ag(I). (See pp. 40—44)

Determination of Trace Selenium Using Hydride Generation-Silver Selenide Sol Method

Niu Jianjun and Wang Bingwu (Changchun Institute of Applied Chemistry, Academia Sinica)

A new method for determination of trace selenium has been presented. Se(IV) was converted into H_2Se by reaction with KBH_4 pellet in 0.2 mol H_2SO_4-2% tartaric acid solution and the escaped hydride was absorbed and colored by silver nitrate solution in the presence of gum arabic. Beer's law was obeyed in the range of 0—3 μg Se(IV)/3ml, the colored solution gave an absorption maximum at 246 mm with detection limit 0.04ppm, most of the foreign ions did not interfere with the determination of selenium. The method has high sensitivity and selectivity and has been applied to analyse urine selenium yeast and other samples. (See pp. 45—48)

Determination of Trace Lead in Animal Organs Using Direct Sampling Flameless Atomic Absorption Spectrophotometry

Xu Tonming et al. (Department of Chemistry, East China Normal University, Shanghai)

The animal organs were ground to be very fine particles, with which suspended solution was prepared and then it was analyzed in graphite atomizer by direct sampling. Because the whole procedure would be completed without sample dissolution, separation and concentration, and no reagents were used during sample preparation, the samples so were avoided from contamination. In the experiment, several parameters were investigated, for example, the effects of particle sizes of the samples and of temperature program of atomizer. The results showed that the precision of this method for analyzing different animal organs covered a range of 3.5—8.6% and recovery ratio a range of 90—108% with spiked 20—60 ng/ml of lead. (See pp. 49—51)

(Continued on page 51)