

单阀 FIA 氢化物发生分光光度法测定水中砷的研究

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摘要 利用自行设计制造的新型氢化物发生及吸收装置, 将流动注射技术同氢化物发生分光光度法有机地结合在一起。设计了一种单阀 FIA 氢化物发生分光光度测砷的流路系统, 该系统不需载气, 选用 $\text{AgNO}_3\text{-HNO}_3$ -聚乙烯醇-乙醇混合液作为吸收液及 KBH_4 溶液作为砷发生反应试剂。实验证明将该方法用于各种水样中痕量砷的测定, 具有简便、快速(30 次/h)、灵敏度高、重现性好($R.S.D. = 3.04\%$)、检出限低($c_L = 1.82 \times 10^{-9} \text{g/ml}$)等优点, 可以广泛地用于各种环境污水中砷的测定。

关键词 流动注射, 氢化物发生, 分光光度, 水质, 砷。

现在已有许多测砷方法^[1-2], 其中以氢化物发生分光光度法应用最广泛^[4,5]。由于该方法的操作烦杂, 速度慢(约 2h 测定 1 次样品), 因此有许多不便, 并不能用于大量样品的快速测定。本文利用自行设计制造的氢化物发生及吸收装置, 设计一种单阀 FIA (Flow Injection Analysis) 氢化物发生分光光度测砷系统, 该系统充分发挥 FIA 技术和氢化物发生分光光度法两者的优势。

1 实验部分

1.1 主要仪器及试剂

氢化物发生及吸收装置(自制);

721 型分光光度计(上海第三分析仪器厂);

JB-4 型通用蠕动泵(泰县分析仪器厂);

LZ-1020 型多功能阀(沈阳电影反光镜厂)。

砷标准贮备液: 称取 0.6600g As_2O_3 溶于 5ml 20% NaOH 溶液中, 用酚酞作指示剂, 以 1mol/L H_2SO_4 中和至中性后, 加入 15ml 1mol/L H_2SO_4 溶液, 再用去离子水定容至 500ml 备用。此溶液含砷量为 1.00mg/ml。

1% KBH_4 溶液配制^[6]: 称取 2.5g KBH_4 (分析纯) 于 100ml 烧杯中, 用 0.1% NaOH 溶液溶解, 将溶液过滤并转移到 250ml 容量瓶中定容。此溶液现用现配。

AgNO_3 溶液配制: 称取 4.07g AgNO_3 (分析纯) 于 200ml 烧杯中, 加 100ml 去离子水, 用玻璃

棒搅拌至 AgNO_3 全部溶解后, 再加入 30ml 浓 HNO_3 , 将该溶液转移到 500ml 棕色容量瓶中, 用去离子水定容至刻度。

聚乙烯醇溶液配制: 称取 1g 聚乙烯醇于 500ml 烧杯中, 加入 500ml 去离子水, 将烧杯置于电炉上加热, 在不断搅拌下使聚乙烯醇全部溶解, 盖上表面皿继续保持微沸 10min, 自然冷却至室温后, 转移至 500ml 容量瓶中, 用去离子水定容至刻度。

吸收液配制: 取 AgNO_3 溶液 40ml 于带塞玻璃瓶中, 加入 40ml 聚乙烯醇溶液, 混匀, 再加入无水乙醇 80ml 充分摇匀待用。此溶液需临用时配制。

醋酸铅脱脂棉: 将脱脂棉侵入 10% PbAc_2 溶液中, 2h 后取出, 自然干燥后备用。

1.2 实验方法

1.2.1 实验流路设计(见图 1)

1.2.2 实验步骤

按图 1 流路安装好仪器, 打开分光光度计电源预热并调节吸收波长为 400nm, 将醋酸铅脱脂棉装入滤管中, 将吸收液 R_2 注入液槽内, 开启进样阀并使之处于状态 I, 调节吸收液体积, 使之在吸收池内的体积为 0.1ml; 将 R_1 及 S 管放入相应容量瓶内, 开启泵 P 注入 R_1 及 S 到氢化物

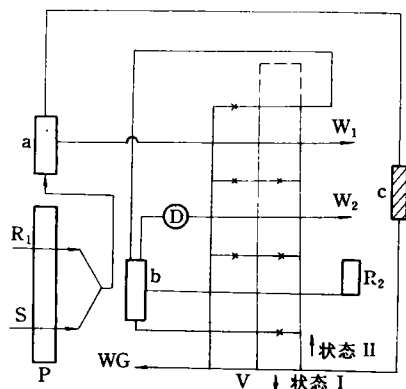


图1 单阀FIA系统测砷流程

P. 蠕动泵 D. 分光光度计 V. 多功能进样阀

a. 氢化物发生器 b. 吸收池 c. 脱脂棉管

R₁. KBH₄ 溶液 R₂. 吸收液 S. 样品溶液 W₁—W₂. 废液 WG. 废气

发生器中, 冲洗2次反应器后, 放掉废液并停泵; 调节分光光度计零点, 将进样阀状态打到状态Ⅱ, 开启泵P, 此时样品与R₁反应生成的AsH₃气体经气路抵至吸收池中被吸收, 待反应液充满反应器后(20ml), 将进样阀V打到状态Ⅰ并停泵, 此时, 吸收AsH₃气体的吸收液进入比色池进行比色测定。而反应器中的废液被排放; 待两者进行完毕后, 又重新将阀V打到状态Ⅱ并启动泵P进行下一次测定。

2 结果及讨论

2.1 实验条件的选择

2.1.1 采样体积的影响

采样体积的大小直接决定了测定的灵敏度, 采样体积越大, 产生AsH₃的总量就越多, 测定的灵敏度就越高, 反之, 测定的灵敏度就越低。为保证测定灵敏度的要求, 要根据试样中砷含量的高低, 选择较合适的进样体积。一般情况下, 当试样液浓度为10⁻⁷g/ml数量级时, 进样量约5ml, 而当试样中砷浓度为10⁻⁸g/ml数量级时, 进样量为10ml即可完成测定。本实验测定取进样体积为10ml。

2.1.2 流路系统残留死体积的影响

实验发现流路系统残留死体积的影响来源于2方面, 其一, 残留于反应器内壁的上次反应

液; 其二, 残留于气路之中的上次反应的少量气体。这2方面的残留对下次测定有一定的影响, 影响情况见图2。由图2知, 重复测定2次就可消除残留死体积的影响。

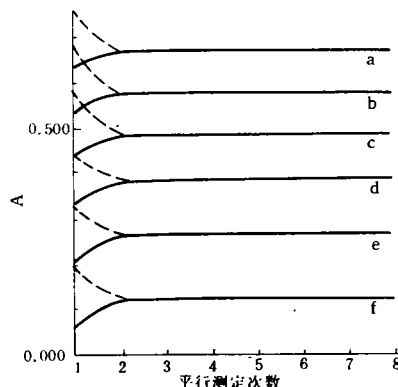


图2 流路系统残留死体积的影响

[As](g/ml): a. 6.00×10^{-8} b. 5.00×10^{-8} c. 4.00×10^{-8}
d. 3.00×10^{-8} e. 2.00×10^{-8} f. 1.00×10^{-8}

2.2 FIA系统稳定性考察

在采样体积10ml, 砷标准液浓度 $c = 2.00 \times 10^{-8}$ g/ml的条件下, 平行测定8次, 得信号平均值为 $\bar{A} = 0.250$, 相应的标准偏差 $S = 0.0076$, 由此可计算出相对标准偏差(RSD)及检出限 c_L 如下:

$$RSD = \frac{S}{\bar{A}} \times 100\% = \frac{0.0076}{0.250} \times 100\% = 3.04\%$$

$$c_L = \frac{3S}{\bar{A}} \cdot c = \frac{3 \times 0.0076}{0.250} \times 2.00 \times 10^{-8} \\ = 1.82 \times 10^{-8} (\text{g/ml})$$

2.3 样品测定

2.3.1 工作曲线绘制

采用逐级稀释法配制砷标准溶液浓度不高于 6.00×10^{-8} g/ml, 在上述给定的实验条件下测定其信号值, 采用线性回归方式求得工作曲线方程: $y = 0.103x - 0.010$, 相应的相关系数 $r = 0.9950$ 。

2.3.2 样品分析

将水样过滤得清亮水样, 准确取. 95.00ml水样于100ml容量瓶中, 加入1.00ml浓盐酸, 用去离子水定容至刻度后, 上机测定。对某化肥厂净化车间的水样取10.00ml于100ml容量瓶中,

(下转第82页)

(2)街道内 CO 浓度不均匀使得街道内真正的污染水平难以评价,即使是相距较近的两点,测量数据有时相差较大。所以,难以确定街道真正的污染水平。国外采用如下办法:以街道内行人呼吸带(距地面 1.55m)内的最高 CO 浓度做为评价指标。一般情况下,最高浓度出现在背风面。

(3)CO 空间分布的不均匀影响汽车排放污染状况的监测精度。固定设备测量的 CO 浓度只代表监测站及其周围 CO 浓度,并不能代表其它点的浓度。因此,评价城市汽车排放 CO 污染需要密集的固定移动监测网。目前,国内城市汽车排放 CO 污染监测网不能满足这一要求,所以直至今日,国内汽车排放污染水平仍不十分清楚。

(4)CO 空间分布的高度不均匀性关系到汽车排放 CO 污染控制措施的有效范围。通常,CO 浓度升高是由其附近车辆及固定排放源排放造成的。所以控制 CO 污染只需控制小范围内的排

放即可。因此,当街道内 CO 浓度升高后,可以通过调整路段上的车流密度及汽车运行工况降低本地街道 CO 排放量,从而降低 CO 污染。因此,通过城市规划、交通规划与交通管理措施,可有效控制城市汽车排放污染,改善道路交通大气环境质量。

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(上接第 72 页)

加入 1.00ml 浓盐酸后,用去离子水稀释至刻度上机测定。样品测定结果见表 1(每个试样平行测定 5 次)。

采用加标方式测定回收率。取同上述相等体积分的样品液,加入含砷 1.00×10^{-6} g/ml 标液 2.00ml(砷量值为 2.00 μ g)与样品液混合,加入 1.00ml 浓盐酸,用去离子水定容至 100ml 刻度

表 1 水质样品中砷测定结果(95%置信度)

样品来源	样品中砷测定值 ($\times 10^{-8}$ g/ml)	加标砷量值 (μ g)	加砷测得值 (μ g)	砷加收率 (%)
某厂净化车间	18.1 $\pm$ 0.4	2.00	2.06	103.0
某厂污水排放口	2.98 $\pm$ 0.14	2.00	1.90	95.0
东明桥水样	0.85 $\pm$ 0.05	2.00	2.06	103.0
焦化厂水样	0.66 $\pm$ 0.05	2.00	1.98	99.0
自来水样品	0.18 $\pm$ 0.08	2.00	1.70	85.1

后上机测定。通过计算得各种测定的回收率,结果列于表 1 中。

该方法不适用于含高铈,铋的样品,如遇此类试样,可以将二甲基甲酰胺(50%),乙醇胺(20%)和三乙醇胺(30%)的混合液分散于脱脂棉内,可以清除约 20 倍于砷的铈和铋的干扰。

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Key words: beryllium, morin, fluorescence.

environmental quality classification.

Study on the Determination of Arsenic in Wastewater by Using Single Valve FIA combined with Hydride Generation Spectrophotometry. Liu Guoquan and Wang Chunxu (Dept. of Environ. Eng., Hebei Institute of Chemical Technology and Light Industry, Shijiazhuang 050018), He Yuaping (Shijiazhuang Chemical Fertilizer Factory, Shijiazhuang 050018); *Chin. J. Environ. Sci.*, **15** (5), 1994, pp. 71—72

A Single Valve FIA (Flow Injection Analysis) system with hydride generation spectrophotometric detection was designed for the determination of the trace arsenic in wastewater. This FIA system had no need for any carrying gas. The new hydride generator and the absorbing device made by the authors were used in the FIA system. The KBH_4 solution and the mixed silver nitrate-polyvinyl alcohol-ethanol solution were used for the generation and absorption, respectively, of arsenic hydride. The experimental results show that this method was very good for the determination of trace arsenic in wastewater. The FIA system had main advantages, including simple equipment, easy operation, high sensitivity, rapid determination (30 samples/h), good reproducibility ($R. S. D = 3.04\%$) and low detection limit ($1.82 \times 10^{-9} \text{ g/ml}$).

Key words: flow injection analysis, hydride generation, spectrophotometry, arsenic, wastewater.

Reversed-phase High Performance Liquid Chromatographic Determination of Methomyl in Soils. Chen Yanjun et al. (Jining Medical College, Jining 272113); *Chin. J. Environ. Sci.*, **15** (5), 1994, pp. 73—74

A reversed-phase HPLC method was described for determination of methomyl in soils. The detection limit of methomyl in soils was $0.1 \mu\text{g}$, and the linear range was $1.0\text{--}20 \mu\text{g/ml}$. The average recovery of methomyl as standard added to soils was in the range of $96.1\% \text{--} 100.2\%$. The relative standard deviations were below 5% . This method was simple with a higher sensitivity and a better accuracy.

Key words: methomyl, reversed-phase, HPLC, soil.

Study on Environmental Quality Classification Based on B-P Neural Network. Li Zuoyong (Chengdu Institute of Meteorology, Chengdu 610041); *Chin. J. Environ. Sci.*, **15** (5), 1994, pp. 75—77

Based on the back-propagation (B-P) algorithm of neural network, the classification models of water quality with 3 and 4 parameters were developed by taking the data on water quality indexes of 25 lakes as training samples. The verification of models for water quality classification of 6 lakes indicated that B-P neural network possessed not only good practicability, but also superiority over other classification methods of environmental quality because of its self-learning and self-adaptability.

Key words: neural network, B-P algorithm,

Qualitative Analysis on the Urban Vehicular Emission Pollution Model. Zhou Hongchang and Yang Peikun et al. (Dept. of Road & Traffic Eng., Tongji University, Shanghai 200092); *Chin. J. Environ. Sci.*, **15** (5), 1994, pp. 78—82

Based on the physical process of the vehicular emission dispersion in the urban street canyon, the monitored data of CO concentration near the urban traffic roads were analysed. The microscale near field dispersion model was particularly discussed, including the initial conditions, boundary conditions and the scope of the model as well as the problems that the model might deal with.

Key words: urban transportation, air pollution model, dispersion.

Current Status of Hazardous Waste Pollution and the Strategy for Its Control in China. Chen Liqui (Dept. of Science and Technology, National Environmental Protection Agency, Beijing 100035); *Chin. J. Environ. Sci.*, **15** (5), 1994, pp. 83—87

Hazardous waste pollutions in soils, waters, air and organisms are very serious in China, have caused negative effects and threats to human health in some parts of China, and have become a major environmental problem which urgently need to be solved at present. This paper deals with the current status of hazardous waste pollution in China, a comprehensive analysis and comparison on the pollution control technologies and management competencies for hazardous wastes in home and abroad, and the response strategies and recommendations on pollution control of hazardous wastes which are proposed according to the local conditions in China.

Key words: hazardous waste, pollution control, response strategy.

Development of Catalytic Oxidation Technology for the Treatment of Highly Concentrated and Refractory Organic Wastewater. Wen Donghui, Zhu Wanpeng (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, **15** (5), 1994, pp. 88—91

Four branches of the catalytic oxidation process have been formed, i. e., wet catalytic oxidation; photocatalytic oxidation; homogeneous catalytic oxidation and heterogeneous catalytic oxidation. Substantially, they all catalyze the decomposition of oxidant so as to speed up the chemical reactions between organic matters and oxidant in wastewater. Some powerful oxidants can produce much stronger radicals by catalysis to oxidate and decompose some highly concentrated and refractory organic matters. Therefore, catalytic oxidation becomes important as a new technology for the treatment of highly concentrated and refractory organic wastewater.

Key words: catalytic oxidation, organic wastewater, oxidants.