

逆流流动注射在线萃取火焰原子吸收法 测定水样中的铜、铁、铅、锰*

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摘要 采用逆流流动注射在线萃取, 用 APDC+DDTC 为络合剂, MIBK 作萃取剂, 与火焰原子吸收光谱仪联用测定 Cu、Fe、Pb、和 Mn 的灵敏度, 分别提高了 35.7、34.3、48.7 和 41.6 倍, 检测限分别为 1.6、7.5、3.3、2.1 $\mu\text{g/L}$. 该法用于含这些重金属很低的饮用水和环境水样的测定, 获得了满意的结果.

关键词 逆流流动注射萃取, 火焰原子吸收法, 铜, 铁, 铅, 锰.

Pb、Fe、Cu、Mn 等元素在饮水、河水等环境水样中含量很低, 不能用火焰原子吸收法直接检测, 往往需将被测元素预浓缩分离, 溶剂萃取^[1-4]是人们常采用的一种有效方法, 但手工萃取费时、费试剂、操作繁琐及有机溶剂污染环境, 常常限制了此法的广泛使用. 用流动注射在线萃取可避免此法的这些缺点. 本工作采用逆流流动注射在线萃取可降低流动注射在线萃取的分散度, 而使在线萃取流动注射火焰原子吸收法测定灵敏度进一步提高, 可以满足饮水、河水等水样中痕量重金属的测定.

1 实验部分

1.1 仪器与试剂

PE-3100 原子吸收分光光谱仪; LZ-1010 型蠕动泵; LZ-1020 型自动/手动多功能阀; LP-2A 变速蠕动泵; 自制柱型膜相分离器和玻璃毛细管分段器.

1% DDTC + 1% APDC 溶液: 称取 1.0g DDTC (二乙基二硫代氨基甲酸钠) 和 1.0g APDC (吡咯啉二硫代氨基甲酸铵) 溶于 100ml 去离子水中, 如有浑浊 (APDC 分解产物) 需过滤. 4 1HNO₃, 4 1NaOH, MIBK. Cu、Fe、Pb、Mn 的工作溶液均由 1000 $\mu\text{g/ml}$ 的标液逐级稀释而成.

所用试剂至少为分析纯级.

1.2 逆流流动注射在线萃取的管道设计和操

作步骤

流路管道设计见图 1.

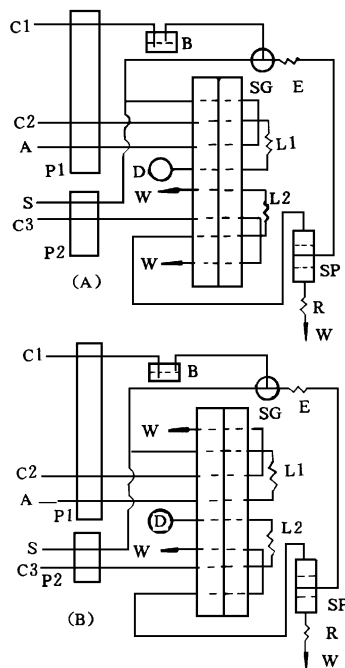


图 1 流动注射萃取流路

C1, C3. 载液(去离子水) C2. 去离子水 S. 样品
A. 1% DDTC + 1% APDC 溶液 P1, P2. 蠕动泵 B. 置换瓶
SG. 分段器 E. 萃取环 SP. 相分离器 R. 阻尼管
W. 废液 L1. 水环 L2. 有机相采样环 D. 原子吸收光谱仪

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图 1(A) 为采样阶段, 持续时间为 50 s. 试样中的金属离子与络合剂络合后, 被有机相萃取, 富集了被测元素的有机相经相分离器分离后收集在采样环中.

图 1(B) 为进样及清洗阶段, 持续时间为 10 s. 载流 C3 送有机采样环中的样品进入原子

吸收光谱仪进行检测, 同时水环中的去离子水可清洗整个流路.

1.3 流动注射各参数的选择

文献[5]中已详细研究过流动注射在线萃取各参数选择的规律, 本工作选择的参数见表 1.

表 1 流动注射实验参数

样品流速 / $\text{ml} \cdot \text{min}^{-1}$	有机相流速 / $\text{ml} \cdot \text{min}^{-1}$	载液流速 / $\text{ml} \cdot \text{min}^{-1}$	试剂 R 流速 / $\text{ml} \cdot \text{min}^{-1}$	有机相采样体积 / ml	采样频率 / $\text{次} \cdot \text{h}^{-1}$
6.8	0.35	5.0	0.50	0.20	60

2 结果与讨论

2.1 萃取体系

DDTC 和 APDC 是常用的萃取络合剂, 它们各有其优缺点^[6]: DDTC 水溶液在低 pH 值不易分解, 但易溶于水, 与金属离子的络合速度相对较快. 流动注射在线萃取由于短时间内完成, 既要考虑萃取的热力学, 又要考虑萃取的动力学, 因此用 DDTC+ APDC 作混合络合剂可充分利用两者优点. 有机萃取剂 MIBK 不仅对火焰的稳定性无影响, 而且对测定有增敏作用.

2.2 在线萃取方式对灵敏度的影响

要使在线萃取增大富集倍数, 必须增加两相流速比, 因此总流速不可能太低, 另外为了萃取完全, 萃取管又不能太短, 再加上流路中的分段器和相分离器, 这些都造成分散度的增大, 而使灵敏度将低. 采用逆流萃取(直接泵入样品), 可使分散度大大降低, 但逆流萃取需样品量相对较多, 一般对生物样品及其它量小的样品不适宜, 而水样不受样品量的限制可适用此法. 虽然实验中水相和有机相流速比接近 20 倍, 但是一般富集倍数不会达到这个倍数, 这是由于分散度和萃取不完全所致, 如以前工作^[5,7]中采用正常进样方式, 加上有机溶剂的增敏作用, 灵敏度仅提高 14.5–23 倍, 本法由于采用逆流进样

方式大大降低了分散度, 使灵敏度比正常进样方式又提高了 1 倍以上. 各元素的灵敏度提高倍数见表 2.

表 2 灵敏度的变化

测定元素	直接吸入测定灵敏度 / $\mu\text{g} \cdot (\text{L} \cdot 0.0044\text{A})^{-1}$	萃取后测定灵敏度 / $\mu\text{g} \cdot (\text{L} \cdot 0.0044\text{A})^{-1}$	灵敏度提高倍数
Cu	54.32	1.52	35.7
Fe	209.52	6.11	34.3
Pb	382.61	7.86	48.7
Mn	78.57	1.89	41.6

2.3 样品酸度的选择

采用流动注射在线萃取时, 萃取仅在几十秒内完成, 因此平衡时达到最大萃取率的酸度不一定是在线萃取时萃取率达到最大值的酸度. 测定灵敏度不仅与达到平衡时萃取率有关, 而且与萃取速度有关. 酸度对两者都有较大的影响. 本研究比较了不同酸度对灵敏度的影响, 结果见图 2 和图 3.

从图 2 和图 3 中可看出, pH= 3–4 时上述元素测定都能获得较高的灵敏度, 并且比较稳定, 因此选定 pH 值为 3.5 左右.

2.4 精密度和线性范围

实验各离子经 FIA 萃取后, 精密度及线性范围如表 3.

表 3 精密度和线性范围¹⁾

测定元素	Cu	Fe	Pb	Mn
精密度/ %	3.23	3.52	4.19	2.36
线性范围/ $\mu\text{g} \cdot \text{ml}$	1.6×10^{-3} –0.20	7.5×10^{-3} –0.50	3.3×10^{-3} –0.50	2.1×10^{-3} –0.20

¹⁾精密度为 Cu²⁺ 0.02 $\mu\text{g}/\text{ml}$ 、Fe³⁺ 0.05 $\mu\text{g}/\text{ml}$ 、Pb²⁺ 0.05 $\mu\text{g}/\text{ml}$ 、Mn²⁺ 0.05 $\mu\text{g}/\text{ml}$ 的 9 次测定值计算结果

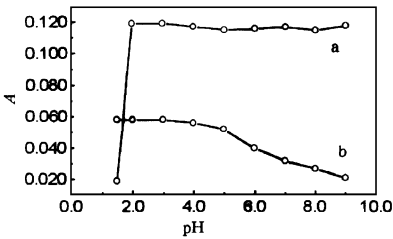


图2 pH 值对铜、锰灵敏度的影响
a. Mn 0.05 $\mu\text{g}/\text{ml}$ b. Cu 0.02 $\mu\text{g}/\text{ml}$

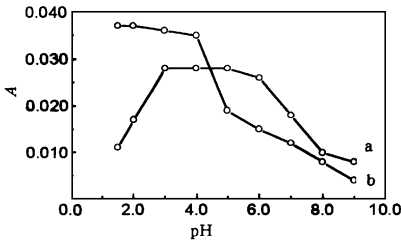


图3 pH 值对铁、铅灵敏度的影响
a. Fe 0.05 $\mu\text{g}/\text{ml}$ b. Pb 0.05 $\mu\text{g}/\text{ml}$

2.5 干扰离子实验

火焰原子吸收法直接测定 Cu、Fe、Pb、Mn

时,通常干扰不太严重,但当碱金属、碱土金属的盐类太高时,会影响测定的准确度^[4]. 萃取不仅起到富集作用,而且也是分离的一种手段. 不被萃取的离子不再对测定有干扰. 例如: 水中大量存在的 K^+ 、 Na^+ 、 Ca^{2+} 、 Mg^{2+} 等, 在 0.02 $\mu\text{g}/\text{ml}$ Cu^{2+} 、0.05 $\mu\text{g}/\text{ml}$ Mn^{2+} 、0.05 $\mu\text{g}/\text{ml}$ Fe^{3+} 、0.05 $\mu\text{g}/\text{ml}$ Pb^{2+} 中分别加入 1000 $\mu\text{g}/\text{ml}$ K^+ 、 Na^+ 、 Ca^{2+} , 500 $\mu\text{g}/\text{ml}$ Mg^{2+} 、100 $\mu\text{g}/\text{ml}$ PO_4^{3-} , 20 $\mu\text{g}/\text{ml}$ Zn^{2+} , 1 $\mu\text{g}/\text{ml}$ Ni^{2+} 未发现干扰. 另外在测定时分别加入 2 $\mu\text{g}/\text{ml}$ Cu^{2+} 、1 $\mu\text{g}/\text{ml}$ Mn^{2+} 、2 $\mu\text{g}/\text{ml}$ Pb^{2+} 和 2 $\mu\text{g}/\text{ml}$ Fe^{3+} 时对被测元素不产生干扰,而一般水样中的干扰离子不会超过上述加入值.

2.6 回收率试验及水样分析

(1)回收率试验 采集了本校自来水样、学校池塘水样、合肥市环城河水样和安医附院排污水(对浑浊的水样要加酸,在低温加热板上加热处理并过滤),并对自来水和环城河水样进行了回收率试验,结果见表4.

表4 样品的回收率

水样	加入值/ $\mu\text{g} \cdot \text{L}^{-1}$				测定值/ $\mu\text{g} \cdot \text{L}^{-1}$				回收率/%			
	Cu	Fe	Pb	Mn	Cu	Fe	Pb	Mn	Cu	Fe	Pb	Mn
自来水	0.0	0.0	0.0	0.0	4.5	36.9	6.8	18.4				
	5.0	10.0	10.0	5.0	9.3	45.8	16.9	23.6	96.0	89.0	101.0	104.0
	10.0	20.0	20.0	10.0	14.6	59.4	29.6	28.4	101.0	112.5	114.0	100.0
	20.0	40.0	40.0	20.0	23.1	82.4	46.0	37.1	93.0	113.7	98.0	93.5
环城河水	0.0	0.0	0.0	0.0	8.3	17.4	2.2 ¹⁾	10.9				
	5.0	10.0	10.0	5.0	12.8	28.5	12.1	16.1	90.0	111.0	99.0	104.0
	10.0	20.0	20.0	10.0	18.0	37.9	22.4	21.0	97.0	102.5	101.0	101.0
	20.0	40.0	40.0	20.0	27.0	53.8	47.3	30.4	93.5	91.0	112.8	97.5

¹⁾标准加入法

(2) 样品测定结果 对采集的不同水样进行了测定,结果如表5.

表5 水样测定结果/ $\mu\text{g} \cdot \text{L}^{-1}$

水样	Cu	Fe	Pb	Mn
自来水	4.5	36.9	6.8	18.4
环城河	8.3	17.4	2.2 ¹⁾	10.9
城市污水	4.3	16.4	10.9	48.2
校池塘	5.4	28.1	14.5	23.9

1) 标准加入法

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Determination of Trace Fe, Cu, Pb and Mn in Water Using FAAS with Reverse Flow Injection Extraction System. Chen Shuyu, Wu Ronghu et al. (The Center of Structural and Elemental analysis, University of Science and Technology of China, Hefei 230026): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 70–72

FAAS with reverse flow injection analysis technology of on-line extraction was used to make the determination of trace Cu, Fe, Pb and Mn in drink water and environmental water. APDC and DDTC, MIBK were used as chelating, extracting agent respectively. The sensitivity of determination increase 35.7, 34.3, 48.7 and 41.6 times for Cu, Fe, Pb and Mn respectively. The detection limits for Cu, Fe, Pb and Mn are 1.6, 7.5, 3.3 and 2.1 $\mu\text{g/L}$ respectively. The results are satisfactory.

Key words FAAS, reverse flow injection extraction, copper, iron lead, manganese.

Beijing Water Resource Database Management System. Li Da and Su Wenhui (Beijing Municipal Research Academy of Environ. Protection, 100037): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 73–75

This paper described the outline of Beijing Water Resource Database Management System. A water resource macroscopic database management system with space character was developed. The system can offer various information involving in social economic activities, water resource exploitation, city drainage, water environmental quality and so on.

Key word: water resource, database, management system, grid net.

Research on Environment Management Information System in Nanshan District, Shenzhen City. Pan Yaozhong, Li Xiaobing et al. (Dept. of Resources and Environmental Science, Beijing Normal University, Beijing, 100875), Li Jixun, Hujing et al. (Environment Protect Agency of Nanshan District, Shenzhen City, Shenzhen, 518059): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 76–79

An region environment management information system (REMIS) was designed and implemented on network of microcomputer based on database and geography information system (GIS) software. The system software with the characteristics of friendly interface common needs for hardware configuration can rapidly extract the results on assessment of environment quality. The system included different level model, such as, database model, basic service management model, environment quality assessment model, statistics and analysis model and spacial analysis model. In the end of

the research, some applications of REMIS were given.

Key word: environment management, database, GIS.

The Design and Some Technical Characteristics of Environmental Multimedia Information Management System in Longgang District, Shengzhen City. Li Ya et al. (Chinese Research Academy of Environmental Sciences, Beijing 100012): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 80–82

In this paper, the design thought, the design methodology, the research content and the main function of the Environmental Multimedia Information System in Longgang Region, Shenzhen City was described in details. Some technical characteristics was also analyzed.

Key words: environmental multimedia information system, multimedia design, longgang region, Shenzhen City.

Research Progress in Fluidized Bed Reactor for Immobilized Microbial Cell. Zhao Xingli and Lan Shucheng (Beijing Municipal Research Academy of Environmental Protection, Beijing 100037): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 83–85

A review was given on the development and application of fluidized bed reactor for immobilized microbial cell. Including the attribute and development of fluidized bed reactor in waste water treatment; several types and attribute of immobilized microbial cell reactor; the application of fluidized bed reactor in industrial production and waste water treatment; a multiplicity of fluidized bed reactor for immobilized microbial cell; trend of needed research.

Key words: immobilized microbial cell, fluidized bed reactor, wastewater treatment.

Cumulative Impacts Research and Its Significance. Peng Yingdeng (Beijing Municipal Research Academy of Environmental Protection, Beijing 100037), Wang Huadong (Institute of Environmental Science, Beijing Nomoal University, 100875): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 86–88

The recognition of cumulative impact can be largely attributed to the development in environmental impact assessment. This article reviews definitions and conceptual frameworks of cumulative impact and describes analytical approaches to cumulative impacts assessment (CIA). Based on this review, the flexible application of CIA to policies, plan or programs were proposed and some immediate research needs were suggested.

Key words: cumulative impacts, cumulative impact assessment, environmental impact assessment.