

反相流动注射法连续测定工业废水中的铜和镍

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摘要 采用反相流动注射光度分析技术, 以能形成颜色相近产物的化学反应为基础, 建立了工业废水中 Ni 和 Cu 的连续测定方法和装置。测定频率 60 样/h, Ni 和 Cu 的最低检出浓度分别为 0.03 $\mu\text{g/ml}$ 和 0.04 $\mu\text{g/ml}$ 。

关键词 环境监测, 流动注射分析, 镍, 铜。

早期的研究工作表明^[1, 2], nFIA 技术可成功地用于工业废水中 Cr^{6+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , CN^- 等污染离子的监测。反相流动注射分析(rFIA)^[3]更有实际意义。本文在前人工作的基础上, 采用 rFIA 技术, 设计出多离子连续自动监测系统, 建立了工业废水中微量 Ni 和 Cu 的连续测定方法。

1 实验部分

1.1 仪器装置

LZ1010 型八通道蠕动泵和 LZ1020 型自动采样阀, 由沈阳肇发自动分析研究所生产; 双向切换阀; 721 分光光度计(配有池体积为 18 μl 的流通比色皿); 采样环, 反应盘管及其它 FIA 流路连结采用 PTFE 盘管($\Phi=0.7$ mm)。

1.2 FIA 流路及工作过程

体系统路如图 1 所示。图 1 中采样阀 G 处于取样状态, 显色试剂 R 被蠕动泵 P 吸入并充满采样环 L_s ; 当 G 转换到注入状态时, L_s 中的 R 被注入到载液 C 中, R 与 C 在 R_c 内相互扩散混合, 当混合带进入二次采样环 L'_s 时(Δt 秒), G 又返回到初始取样状态, 将在 L'_s 中的试剂混合带注入样品流 S 中。在 R_c 中 S 与试剂发生显色反应。生成的有色络合物进入配有流通比色皿的 721

分光光度计 D 测定。该系统的测定频率为 60 样/h。

不同的显色试剂 R 和载液 C 通过双向切换阀 V 流入路系统, 以对水样中不同的污染组分进行连续自动监测。

1.3 试剂

测 Ni 试剂: R_1 : 丁二酮肟(0.05%)-碘(5.0 mmol/L)混合液; C_1 : 氨(5.0%)-柠檬酸铵(0.5%)混合液。测 Cu 试剂: R_2 : NaDDC(0.2%)-pH 缓冲液(pH8.2); C_2 : EDTA(0.2%)-柠檬酸铵(0.5%)混合液。标准溶液: 分别以 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 和金属铜制备。所用化学试剂均为分析纯, 溶液配制采用去离子水。

2 结果与讨论

2.1 rFIA 与 nFIA 法灵敏度比较及规律探讨

Johnson 等人^[3]首次提出反相流动注射分析(rFIA)技术, 并将其应用到海水中磷酸盐的测定。Johnson 的实验结果表明, 对于相同的显色反应体系, 由于注入方式的不同, 注入试剂的 rFIA 法较注入试样的 nFIA 的测定灵敏度将提高 5 倍; 他还采用“多釜串联”模型讨论了在 rFIA 系统的检测器中试样和试剂浓度随时间的分布情况, 并结合化学平衡原理, 从理论上解释了上述实验结果的合理性。

本实验表明, 在同一 FIA 流路系统中对于相同的显色反应, rFIA 与 nFIA 2 种测定方法的响应值之比(即 rFIA 较 nFIA 灵敏度提高的倍数)与 FIA 系统的分散度(D 值)呈现良好的线性关系(图 2), 其相关系数达 0.9973, 此现象可借注入试样(或试剂)塞在载流中的分散规律来解释, 该规律较 Johnson 的结论更具普遍性。

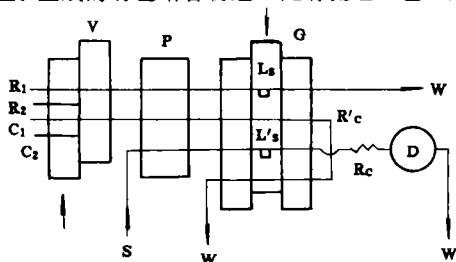


图 1 连续自动监测系统 FIA 流路图

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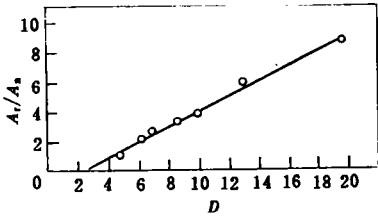


图2 FIA 测定灵敏度与分散度的关系

2.2 工业废水中微量 Ni 和 Cu 的 rFIA 连续测定

2.2.1 测定的化学体系及参数确定

在有氧化剂存在的碱性条件下, Ni(Ⅱ)与丁二酮肟形成酒红色络合物, 最大吸收波长为 460 nm。以此作为镍 FIA 测定的基础。由于显色反应需在碱性介质中进行, 铬铁等离子可能因生成氢氧化物沉淀而干扰测定, 采用柠檬酸盐络合掩蔽消除^[1]。通过实验确定的试剂组成及最佳浓度如 1.3 所示。

微量 Cu 的测定选用 N, N-二乙基二硫代氨基甲酸钠(NaDDC)作为显色剂。在弱碱性条件下 Cu(Ⅱ)与 NaDDC 形成有色络合物, 最大吸收波长为 470 nm。在此实验条件下, Zn、Ni 和 Fe 等离子对测定产生正干扰, 可用 EDTA 和柠檬酸盐掩蔽消除^[1]。通过实验确定的试剂组成及最佳浓度如 1.3 所示。

2.2.2 rFIA 流路设计及技术参数确定

探索实验结果表明, Ni 和 Cu 测定的 FIA 体系参数非常接近, 将它们统一到一个流路系统中完成不会造成各自测定灵敏度的明显降低。测定波长的选择, 由于铜吸收曲线峰形变化较缓, 综合考虑将光度计的波长固定在 460 nm。

关于 FIA 流路设计, 本文没有选择目前常见的将 2 个采样阀串联到流路中的结构, 而采用一个切换阀与采样阀配合将特定的显色试剂引入测定系统实现顺序测定(如图 1)。这种结构方法使得试剂得到充分利用, 消耗量降至最低; 而且由于将切换阀安置在蠕动泵之前, 使管道数减少, 流路设计简化, 容易实现自动化。通过实验确定的 FIA 体系参数最佳值列于表 1。

表 1 污染离子连续监测系统设计参数

流量(ml·min ⁻¹)	Q _R 2.3	Q _C 1.5	Q _S 2.0
采样环体积(μl)	L _S 30	L _S 100	
混合管长度(cm)	R _C 30	R _C 100	
Δt(s)	4		
测定波长(nm)	460		

2.2.3 微量 Ni 和 Cu 的连续测定

在前述最佳的实验条件下, 微量 Ni 和 Cu 的测定范围, 以及方法的灵敏度, 精密度等技术指标列于表 2。结果优于 nFIA 法^[2, 3]。

表 2 污染离子连续监测的技术指标

指 标	Ni	Cu
测定方程	$A=0.15C+0.03$	$A=0.12C+0.02$
回归系数(r 值)	0.9998	0.9998
测定范围(μg·ml ⁻¹)	0—4.0	0—4.0
检出限(μg·ml ⁻¹)	0.03	0.04
变异系数 ¹⁾ (%)	0.53	0.75

1) 对浓度为 2.0 μg·ml⁻¹ 的水样平行测定 11 次的结果

实验还考查了工业废水中可能存在的 20 余种离子对测定的影响, 其加入量均高于它们在废水中的正常含量。结果表明在上述确定的体系中, 共存离子对 Ni 和 Cu 的测定无明显干扰。

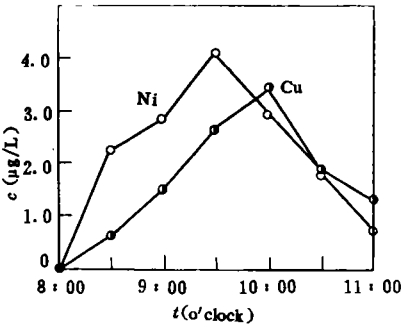


图3 污染物浓度随时间的变化情况

表 3 本法与原子吸收法数据对比(μg·ml⁻¹)

时间	本法		AAS 法		相对误差(%)	
	Ni	Cu	Ni	Cu	Ni	Cu
8:30	0	0	0	0	0	0
8:30	2.21	0.64	2.10	0.63	5.2	1.6
9:30	2.85	1.50	2.79	1.47	2.2	2.0
9:30	4.07	2.68	4.03	2.59	1.0	3.5
10:00	2.94	3.42	2.75	3.27	6.9	4.6
10:30	1.78	1.86	1.71	1.90	4.1	-2.1
11:00	0.74	1.30	0.74	1.28	0	1.6

为考查该系统在实际废水监测中的可行性, 进行了现场监测的实验室模拟^[4], 并同时取样与原子吸收法进行了数据对比, 结果如图 3、表 3 所示。本文建立的微量 Ni 与 Cu 的连续测定方法可被应用于电镀等工业废水的水质监测, 其前处理方法参见文献^[2]。

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to fluidize easily in the reactor. The treatment system can resist the loading fluctuation and possess high dehydrogenase activity.

Key words: fluidized, biofilm, treatment, phenolic wastewater, carrier.

Development of a New Type Dispelling Smoke Silencer of Diesel Engine. Zeng Defang (Turbine College, Wuhan University of Science and Technology of Traffic, Wuhan 430063); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 63—64

This paper introduces a kind of method of making a new type dispelling smoke silencer of diesel engine. The method includes adding a kind of solution which can clean the end gas of diesel engine to the bottom of the old silencer of diesel engine. The end gas of diesel engine can be both cleaned and silenced by passing through the dispelling smoke silencer. A comparison of new silencer with the old one under the same condition on the type 135 diesel engine has shown that the dispelling smoke silencer can reduce 80% of smoke and 14.1% of noise (from 99 dB to 85 dB).

Key words: diesel engine, dispelling smoke silencer, noise, end gas of diesel engine.

A Study on Treatment of Traditional Chinese Medicine Wastewater by SBR Process. Han Xiangkui et al. (Jilin Architectural and Civil Engineering Institute, Changchun 130021); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 65—67

Experimental results showed that at the concentration range of COD in influent from 1000 mg/L to 2500 mg/L, effluent COD can be reduced to less than 250 mg/L, BOD₅ and SS less than 100 mg/L. These levels conform to discharge permission standard of pharmaceutical wastewater. The variation behavior of dehydrogenase during the process of aeration is also discussed in this paper.

Key words: SBR process, wastewater treatment, traditional Chinese medicine wastewater.

Dioxins in Stack Ash from PCBs Incinerator. Ke Jiang et al. (Research Center for Eco-environmental Sciences, CAS, Beijing 100085); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 68—71

The PCDD/Fs in stack ash from a experimental incinerator for destruction of PCBs waste have been determined by ¹³C isotope HRGC/HRMS method. Seventeen 2, 3, 7, 8-substituted toxic dioxins congeners were quantitatively measured. The TEQ value of the stack ash is 47.2 ng/g.

Key words: stack ash, PCBs, dioxins.

Releasing of PAHs from Coal-ash in Seawater. Fu Yun-na and Liu Yiwen (Inst. of Mar. Environ. Prot., SOA, Dalian 116023); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 72—74

Releasing of PAHs from coal-ash in seawater was determined by fluorescence spectrophotometer. The amounts of PAHs from coal-ash soaked before and after in seawater were also analysed by reversed high performance liquid chromatography with UV or fluorescence detectors. The results show that the static state releasing and adsorption

of PAHs from coal-ash in seawater are reversible, releasing of PAHs is pool, and PAHs in the fine coal-ash dumped into sea from heat and power plant have little effect to the marine environment.

Key words: coal-ash, PAHs, releasing, seawater.

Spectrophotometric Determination of Anionic Surfactants in Water with Bromocresol Green and Cetylpyridinium Bromide. Wang Yongsheng et al. (Hengyang Medical College, Hengyang 421001); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 75—77

In this paper a spectrophotometric method has been developed for the determination of anionic surfactants in water with bromocresol green (BCG) and cetylpyridinium bromide (CPB). Sodium dodecylbenzenesulfonate (SDBS) and sodium dodecylsulfate (SDS) were determined at 614 nm and pH range of 5.5—9.0. In the concentration range of 0—80 µg/10 ml for SDBS and 0—75 µg/10 ml for SDS, both of them obey Beer's law in the presence of 86 µg CPB. The apparent molar absorptivities are $2.9 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for SDBS and $3.1 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for SDS. The proposed method has been applied to the determination of anionic surfactants in river water and wastewater. The average recovery of environmental water samples was 99.3% and the relative standard deviation was less than 3.0%.

Key words: anionic surfactants, bromocresol green, cetylpyridinium bromide, spectrophotometry.

Photometric Determinations of Nickel and Copper in Wastewater by Reversed Flow Injection Analysis. Wang Peng et al. (Department of Applied Chemistry, Harbin Institute of Technology, 150006); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 78—79

The new wastewater monitoring system by use of reversed flow injection spectrophotometry has been developed with injection of different reagents to produce similar color compounds by chemical reactions. The system has been used to simultaneous determination of nickel and copper in wastewater. The detection frequency of the method is 60 samples h⁻¹, the minimum detection limits are 0.03 µg Ni ml⁻¹ and 0.04 µg Cu ml⁻¹ respectively.

Key words: environmental monitoring, flow injection analysis, nickel, copper.

Acidification Models and Their Application to the Determination of Critical Load for Acid Deposition. Xie Shadong et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 80—84

This paper briefly discusses different models developed abroad in the study of precipitation effects to predict the long-term effects of acid deposition on soil, surface water, ground water and lakes in the past ten years. The basic methods to establish these models and the principles to apply them to the determination of critical load for acid deposition are presented based on through comparisons and analyses.

Key words: acidification model, critical load, acid deposition, acid rain.

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