

流动注射-催化褪色光度法测定痕量亚硝酸根的研究

王建华 何荣桓

(烟台师范学院化学系,烟台 264025)

摘要 依据亚硝酸根对溴酸钾氧化罗丹明 B 褪色反应体系的催化作用,建立了测定痕量亚硝酸根的停流-催化褪色光度法,确定了最佳测定条件: $[\text{KBrO}_3]=5.0 \times 10^{-2} \text{mol} \cdot \text{L}^{-1}$, $[\text{罗丹明 B}]=4.8 \times 10^{-5} \text{mol} \cdot \text{L}^{-1}$, $[\text{H}_2\text{SO}_4]=0.75 \text{mol} \cdot \text{L}^{-1}$, 50°C 。线性测定范围为 $0-0.6 \mu\text{g} \cdot \text{ml}^{-1}$,方法检出限为 $2 \text{ng} \cdot \text{ml}^{-1}$ 。本法操作方便、快速、重现性好,且选择性较一般催化光度法显著提高。测定了不同样品中的亚硝酸根含量,结果满意。加标回收率为 $96.1\%-103.0\%$,相对标准偏差 $\text{RSD}(n=6)$ 为 $2.1\%-4.0\%$ 。

关键词 亚硝酸根,催化褪色光度法,停流流动注射。

常用于测定亚硝酸根的 Griess 比色法^[1]及改进 Griess 法^[2],其缺点是耗时且灵敏度不够高。近年来,动力学法测定 NO_2^- 的报道渐多^[3-5],此类方法灵敏度高,所需设备简单。已报道的多为依据亚硝酸根催化溴酸钾氧化有机试剂的指示反应建立的方法,其不足之处是一般动力学反应体系影响因素较多,重现性差,且有干扰。

本文依据亚硝酸根对溴酸钾氧化罗丹明 B 褪色的催化作用,建立了测定痕量亚硝酸根的停流-动力学光度法,本法既保持了动力学法的高灵敏度,显著改善了测定的重现性;又由于大大缩短了反应时间,有效地消除了干扰离子的影响,从而显著提高了方法的选择性。

1 实验部分

1.1 主要仪器和试剂

FIA-2400 流动注射分析仪(中科院信通公司);

721 型分光光度计(配 7521 型恒温比色架);

JY-501B 超级恒温槽(上海仪器商店);

XWT-264 台式记录仪(上海大华仪表厂)。

亚硝酸根标准溶液($25 \mu\text{g} \cdot \text{ml}^{-1}$):准确称取分析纯 NaNO_2 0.150g 溶于适量水并定容至

100ml ;取此溶液 5.0ml 稀释至 200ml 即得 $25 \mu\text{g} \cdot \text{ml}^{-1}$ 的贮备液。不同浓度的工作液由此标准溶液适当稀释得到。

溴酸钾贮备液($5.0 \times 10^{-2} \text{mol} \cdot \text{L}^{-1}$):称取 KBrO_3 8.35g 溶于适量水中,转入 1000ml 容量瓶并定容至刻度。

罗丹明 B 溶液($4.8 \times 10^{-5} \text{mol} \cdot \text{L}^{-1}$):称取 0.0478g 罗丹明 B 溶于水中定容至 100ml ,得 $1.0 \times 10^{-3} \text{mol} \cdot \text{L}^{-1}$ 的贮备液;适当稀释后得 $4.8 \times 10^{-5} \text{mol} \cdot \text{L}^{-1}$ 的工作液。

H_2SO_4 水溶液(载液): $0.75 \text{mol} \cdot \text{L}^{-1}$ 。

本实验中所用试剂均为分析纯。

1.2 实验方法

按图 1 所示联接好实验流路。

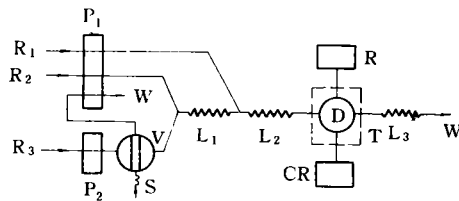


图 1 实验流程图

P_1, P_2 为蠕动泵 V 为进样阀 L_1, L_2 为混合盘管 L_3 为反压圈 R 为记录仪 CR 为微机控制及数据处理系统 D 为检测器 T 为恒温装置 R_1 为溴酸钾溶液 R_2 为罗丹明 B 溶液 R_3 为载液 S 为样品 W 为废液

收稿日期:1994-06-15

本文所用为双泵可调速流动注射分析仪,微机控制采样、进样;选择采样时间为 10s,样品混合后在恒温流通池中停流 25s;以试剂空白为参比在 552nm 波长处测定体系的吸光度降低值(以记录纸的格数-相对峰高 H 表示)。

2 结果与讨论

2.1 流路参数的选择

本实验流路选用内径为 0.8mm 的聚四氟乙烯管;反压圈由内径为 0.25mm 的聚四氟乙烯管绕成,并选择混合盘管长度分别为 $L_1=100\text{mm}$, $L_2=250\text{mm}$, 反压圈长度为 $L_3=2000\text{mm}$ 。

实验表明,主、副泵流速对测定的灵敏度影响不大,本文选择 KBrO_3 和罗丹明 B 溶液的流速均为 $2.8\text{ml} \cdot \text{min}^{-1}$,载液流速为 $2.4\text{ml} \cdot \text{min}^{-1}$,采样环体积为 $40\mu\text{l}$ 。

2.2 介质酸度的影响

实验表明,酸度对反应的影响很大。在一定浓度范围内,体系的吸光度降低值即相对峰高 H 随 H_2SO_4 浓度的增加而增大;当最后溶液中 H_2SO_4 的浓度大于 $0.80\text{mol} \cdot \text{L}^{-1}$ 时,在本文选定的停流时间内(25s),罗丹明 B 的颜色已完全消失,继续增大酸度已无意义;且酸度增大时,非催化反应加快,重现性降低;故本文选择体系酸度为 $0.75\text{mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ 。

2.3 试剂浓度的影响

罗丹明 B 和溴酸钾浓度的影响示于图 2 和图 3 中。由图 2 可见,随体系中罗丹明 B 浓度增大,相对峰高 H 增加,测定灵敏度提高。当罗丹明 B 浓度为 $6.0 \times 10^{-5} \text{mol} \cdot \text{L}^{-1}$ 时,若体系中 NO_2^- 含量为 $0.5\mu\text{g} \cdot \text{ml}^{-1}$,则记录仪已达满量程,此时测定的灵敏度已足够高,继续增加罗丹明 B 的浓度,空白增大,重现性降低;故本文选择罗丹明 B 浓度为 $4.8 \times 10^{-5} \text{mol} \cdot \text{L}^{-1}$ 。从图 3 可知,相对峰高 H 随着 KBrO_3 浓度增加而增大,但当 KBrO_3 浓度超过 $7.0 \times 10^{-2} \text{mol} \cdot \text{L}^{-1}$ 时,罗丹明 B 全部氧化,相对峰高 H 不再随 KBrO_3 浓度变化,而是趋于恒定;本文选择 KBrO_3 浓度为 $5.0 \times 10^{-2} \text{mol} \cdot \text{L}^{-1}$ 。

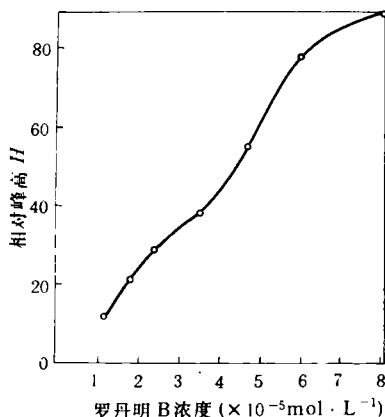


图 2 罗丹明 B 浓度的影响

$[\text{KBrO}_3] = 5.0 \times 10^{-2} \text{mol} \cdot \text{L}^{-1}$ $[\text{H}_2\text{SO}_4] = 0.75 \text{mol} \cdot \text{L}^{-1}$
 $[\text{NO}_2^-] = 0.5\mu\text{g} \cdot \text{ml}^{-1}$ $t = 5^\circ\text{C}$

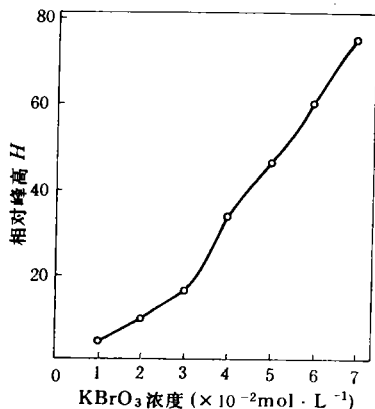


图 3 KBrO_3 浓度的影响

$[\text{罗丹明 B}] = 4.8 \times 10^{-5} \text{mol} \cdot \text{L}^{-1}$ $[\text{H}_2\text{SO}_4] = 0.75 \text{mol} \cdot \text{L}^{-1}$
 $[\text{NO}_2^-] = 0.5\mu\text{g} \cdot \text{ml}^{-1}$ $t = 5^\circ\text{C}$

2.4 反应时间和温度的影响

温度对反应的影响如图 4 所示,显而易见,本文反应在室温(25°C)下即可进行,但随温度升高,催化反应速度加快,而非催化反应速度变化很小;当反应温度超过 50°C 时,这种变化略趋于缓慢;为缩短反应进程,并尽量减小反压力,本文选择反应在 50°C 下进行。另外,实验表明,相对峰高 H 随停流时间延长而增大;仅从缩短分析周期,提高进样频率的观点出发,选择停流时间为 25s,此时测定灵敏度已足够高完全满足痕量亚硝酸根分析的要求,进样频率为 102 样/h。

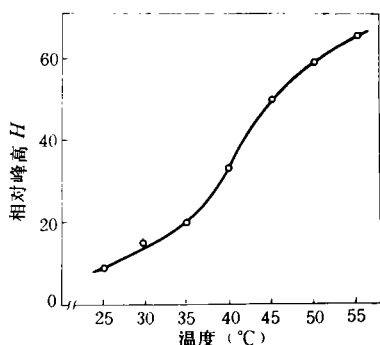


图 4 温度的影响

$[\text{KBrO}_3] = 5.0 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ $[\text{H}_2\text{SO}_4] = 0.75 \text{ mol} \cdot \text{L}^{-1}$
 $[\text{罗丹明 B}] = 4.8 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ $[\text{NO}_2^-] = 0.5 \mu\text{g} \cdot \text{ml}^{-1}$
 停流时间 $t = 25\text{s}$

2.5 线性范围及检测限

在上述确定的实验条件下,考察了相对峰高 H 与亚硝酸根浓度之间的线性关系,得到了下列线性回归方程:

$$H = 102.046c_{\text{NO}_2^-} (\mu\text{g} \cdot \text{ml}^{-1}) - 0.208$$

线性测定范围为 $0-0.6 \mu\text{g} \cdot \text{ml}^{-1}$; 若以吸光度变化 0.004 单位时仪器所能检测出的浓度为检出限,则本方法的检出限为 $2 \text{ ng} \cdot \text{ml}^{-1}$ 。对 $0.40 \mu\text{g} \cdot \text{ml}^{-1} \text{ NO}_2^-$ 溶液平行测定了 11 次,平均回收率为 97.5%; 另外, $0.40 \mu\text{g} \cdot \text{ml}^{-1} \text{ NO}_2^-$ 的加标回收率大于 97%。

2.6 干扰试验

当最后溶液中的 NO_2^- 含量为 $0.5 \mu\text{g} \cdot \text{ml}^{-1}$ 时,考察了部分常见共存离子对亚硝酸根测定的影响。实验结果表明,在 $\pm 5\%$ 的误差允许范围内,以本文所拟实验条件,除 10 倍量的 I^- , 20 倍量的 Br^- 和 SCN^- 对测定略有影响外,其余离子诸如 F^- 、 SO_3^{2-} 、 $\text{C}_2\text{O}_4^{2-}$ 、 NO_3^- 、 Cl^- 、 Fe^{2+} 、 Zn^{2+} 、 Cd^{2+} 、 Co^{2+} 、 Ni^{2+} 、 Mn^{2+} 、 Cu^{2+} 、 NH_4^+ 及碱金属和碱土金属离子等均具有较大允许共存量而不影响测定。这说明本法测定亚硝酸根的选择性较一般动力学方法得以显著提高; 且一般样品中 I^- 、 Br^- 及 SCN^- 含量均低于上述允许限量,故在多数情况下可不经分离而直接测定样品中的亚硝酸根。

3 样品测定结果

为评价方法的可行性,测定了土壤,蔬菜,雨水,生活及工业废水中的亚硝酸根含量。

土壤:称取研细过筛的土样 2.5g 置于 50ml 烧杯中,加入 20ml 水,充分搅拌浸取 60min,过滤,滤液定容至 25ml 待测。

菜花:称取切成碎片的菜样 2.5g 于研钵中充分研细后,转入 50ml 烧杯,加 20ml 水并充分搅拌浸取 60min,过滤,滤液定容至 25ml 待测。

雨水,生活污水及工业废水均经澄清处理后直接测定。

测定结果列于表 1 中,表 1 中同时列出了用改进 Griess 法^[2]测得的土壤及蔬菜中的亚硝酸根含量。

表 1 样品中亚硝酸根含量的测定结果

样品	测得量 ($\mu\text{g} \cdot \text{ml}^{-1}$)		加入量 ($\mu\text{g} \cdot \text{ml}^{-1}$)	回收率 (%)	相对标准偏差 (%) (n=6)
	本法	改进 Griess 法			
土壤	0.416	0.397	0.100	103.0	3.1
菜花	0.118	0.122	0.100	97.0	4.0
雨水 ¹⁾	0.047		0.100	96.1	3.4
生活污水	0.105		0.100	102.8	2.1
工业废水	0.153		0.100	97.4	2.9

1) 雨水中的含量是先加入 $0.100 \mu\text{g} \cdot \text{ml}^{-1} \text{ NO}_2^-$, 测得总量后差减得到 2) 工业废水取自市区总排污管道

4 小结

依据 NO_2^- 对 KBrO_3 -罗丹明 B 氧化褪色反应的催化作用建立了测定痕量亚硝酸根的停流-催化褪色光度法; 本法操作方便, 快速, 选择性较一般动力学方法明显提高。

测定了土壤, 蔬菜, 雨水, 生活污水及工业废水中的亚硝酸根含量, 结果满意。

参考文献

- 1 刘志民. 现代实用毒物分析. 北京: 人民卫生出版社, 1984: 466
- 2 吴乾丰, 刘鹏飞. 分析化学. 1982, 10(3): 262
- 3 郑肇生, 吴和舟, 彭敏利, 林东辉. 分析化学. 1992, 20(1): 91
- 4 张振辉. 分析化学. 1989, 17(2): 122
- 5 高甲友, 赵金龙. 分析化学. 1991, 19(11): 1329

Abstracts

Chinese Journal of Environmental Science

sands, measurements should be made also on the concentration of yellow sand aerosol, the distribution of its particle sizes, the chemical compositions in the particles of different sizes, and the changes in rain-borne soils, rainfall, dust deposition, and air temperature.

Key words: surface dust storm, yellow sand, TSP, Haboob phenomenon, The Hexi (Gansu) Corridor.

Study on Acrylic Wastewater Treatment Using an Internal Circulating Bio-Fluidised Bed. Zhou Ping and Qian Yi (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 58—61

A pilot study on acrylic wastewater treatment by using an internal circulating three phase bio-fluidised bed was conducted. There were N_v of 4.0 and 6.8 kgCOD/(m³ · d) and N_s of 1.6 and 2.8 kgCOD/(kgVSS · d) when the influent had COD of 710 to 992 mg/L and 1277 to 2276 mg/L, respectively. Oxygen utilization rate was about 17%. Post-treatment experiment of the effluent from fluidised bed was also carried out and an acrylic wastewater treatment process was suggested.

Key words: acrylic wastewater, internal circulating three phase bio-fluidised bed, wastewater treatment.

Determination of Iron (I) and (II) in water by Ion Chromatography Combined with Atomic Absorption Spectrometry. Wang Xiaoqin et al. (Dept. of Chemistry, Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 62—64

A method for determination of Fe(I) and Fe(II), which combines ion chromatography and atomic absorption spectroscopy, is described. Fe(I) and Fe(II) were first separated on a Shima Pack column packed cation-exchange resin, and then determined by a graphite furnace atomic absorption spectrometry. The detection limits of Fe(II) and Fe(I) were at the 7.7 ng · ml⁻¹ and 3.8 mg · ml⁻¹, respectively. The method has been successfully used in iron species of tap water and river water.

Key words: ion chromatography, atomic absorption spectrometry, iron, species analysis.

Analysis of Atmospheric Particulates and Organic Pollutants in Datong. Liu Ruilian et al. (Datong Municipal Institute of Environmental Protection, Datong 037006), Zhao Zhenhua (Beijing Municipal Research Academy of Environmental protection, Beijing 100037); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 65—67

This paper reports the determination of atmospheric

particulates from different functional districts in Datong. The inhalatable particulates (< 10μm) concentration accounts for about 50% of the total suspended particulates (TSP). The extracts in methylene chloride representing the total polluted organic materials account for about 20% of TSP. The compounds in the total polluted organic materials identified with GC, GC/MS and HPLC included 38 compounds of benene series and other aromatic hydrocarbons, 31 compounds of paraffins, and 14 compounds of phenols, ketones, nitrogen-containing organic and phthalates.

Key words: air pollution, particulate, organic pollutants.

Sequential Determination of Trace Chromium(VI), Nickel and Zinc in Electroplating Waste Waters by Flow-injection Spectrophotometry. Wang Peng et al. (Dept. of Applied Chemistry Harbin Institute of Technology, Harbin 150006); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 68—70

An automated flow-injection system is described for the sequential spectrophotometric determination of trace Cr(VI), Zn and Ni in waste waters. The sample analysis frequency is 60h⁻¹ and the detection limit is 0.1 mg/L(Cr), 0.2mg/L(Zn), and 0.3mg/L(Ni), respectively. The relative standard deviation is around 1%. Results obtained with the proposed method are in a good agreement with the standard manual spectrophotometric methods.

Key words: environmental monitoring, flow-injection analysis, chromium(VI), nickel, zinc, wastewater.

Studies on the Determination of Nitrite with a Stopped Flow-Catalytic Spectrophotometric Procedure. Wang Jianhua and He Ronghuan (Chemistry Dept. of Yantai Teachers College, Yantai 264025); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 71—73

A stopped flow-catalytic spectrophotometric procedure for the determination of nitrite was established based on its catalytic effect on the bromate-rhodamine B oxidation decolouring reaction. The optimal conditions for the determination were established as: [KBrO₃] = 5.0 × 10⁻² mol · L⁻¹, [rhodamine B] = 4.8 × 10⁻⁵ mol · L⁻¹, [H₂SO₄] = 0.75 mol · L⁻¹, and 50°C. The calibration graph was linear for 0—0.6 μg · L⁻¹ NO₂⁻, and the detection limit was 2 ng · L⁻¹. The reproducibility of the method was good, and the selectivity was improved significantly, with respect to conventional procedures. Nitrite contents in soil, vegetable, rain water and wastewater had been determined, and the results were satisfactory, the

Abstracts

Chinese Journal of Environmental Science

recoveries were 96.1%—103.3%, and RSD ($n=6$)=2.1%—4.0%.

Key words: nitrite, catalytic decolouring spectrophotometry, determination procedure.

Study on the Spectrophotometric p-Dimethylaminobenzaldehyde in water. Sun Hong et al. (Benxi Municipal station of Environ. Monitoring, Benxi 117021); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 74—77

The condition for reaction of hydrazine with dimethylaminobenzaldehyde and the composition of complex formed in the presence of acid have been studied. The concentration of the complex is in proportion to the colour in a range of 1.00—0.002mg/L. The maximum absorbance is at 458nm. The relative standard deviations with in the labs are 3.7%, 0.9% and 0.6% at 0.100, 0.500 and 0.800mg/L, respectively; and those among different labs are 4.4%, 1.3% and 0.9%, respectively. The recoveries are 88% to 110%.

Key words: hydrazine, dimethylaminoben, spectrophotometric.

Analysis of the environmental pollution sources in the oil and gas fields in China. Chen Changxing et al. (Environ. Monitoring Centre, China National Petroleum Corporation, Langfang, Hebei 102801); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 78—82

The paper focuses on the macroscopic analysis and study of the characteristics of distribution, emission and pollution of pollution sources and also on the environmental impact, based on a general study on the overall constitution of oil and gas pollution sources. It described the differences between the environment pollution sources of oil and gas fields

and other industries.

Key words: oil and gas fields, environmental effect, review.

Evaluation and Discussion on the Test Method for the Catalytic Converter of Automobile Exhaust. Li Beilu and Li Shiyao (Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 83—86

By measuring the initial ignition temperatures at a 50% conversion of CO and HC and studying the effect of oxygen content in exhaust on the initial ignition temperature over many of practical catalysts available from home and abroad, an initial ignition temperature in the range of 210—230°C was considered generally normal. It was found that under the condition of an idling speed the exhaust temperature and oxygen content in exhaust were both at the lowest levels, leading to a conclusion that the use of an idling speed condition at present to evaluate a catalytic converter for vehicle exhaust in this country is unreasonable.

Key words: vehicle exhaust, evaluation, measure, initial ignition temperature.

Chemistry in Space Environment. Hu Dingxi (Sichuan Education College, Chengdu 610041), Zhou Tianze (Capital Normal University, Beijing 100037); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 87—90

In this paper, a review has been made based on a survey of chemistry in the space environment, particularly, environmental chemistry in space flights and the adaptability of astronauts to the space environment.

Key words: space environment, chemistry, review.