无汞盐化学需氧量测定方法研究

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摘要　本法基于可定量测定 $K_2Cr_2O_7$ 和 Cl^- 的反应产物 Cl_2 这一原理，在用吸收装置吸收 Cl_2 后，用碘量法测定余氯．试验结果表明，本法有较高的准确度和精密度．

关键词：化学需氧量；余氯；重铬酸钾氧化．

化学需氧量（COD）是测定水样中易受强氧化剂氧化的有机物在氧化时所需的氧当量，普遍采用重铬酸钾回流法．大部分废水中，氯化物的浓度很高，常用硫酸汞消除氯离子的干扰，而且用量较大，硫酸汞与氯离子浓度比不少于 10:1，严重污染环境，因此国内外学者一直在研究无汞盐测定化学需氧量的方法．

1982 年，Ballinger 等人提出加硝酸银消除氯离子干扰的方法[1]．同年，A. Lloyd 提出以密封烧瓶测定化学需氧量的方法[2]，也是通过大剂量加银盐来抑制氯离子的干扰．1984 年，K. E. DE. Casseres 等人提出用加大硫酸银用量来抑制氯离子干扰的开管化学需氧量测定法[3]．国内亦有用硝酸银的报道[4]．以上方法均要消耗大量昂贵的银化合物，且不能完全抑制氯离子的干扰[4]，故一直未被普遍采用．

我们所研究的无汞盐化学需氧量测定法是基于可定量测定被重铬酸钾氧化出的氯气（水溶液中表现为余氯）来完成的（如果存在氧化产物 ClO_2，亦可定量测定[5]）．重铬酸钾氧化氯离子为氯气，消耗了重铬酸钾，使化学需氧量测定结果偏高，但是，如果测得了氯气的当量数，自消耗掉的重铬酸钾的当量数中减去氯气的当量数便可准确测得化学需氧量．

一、试验部分

1. 主要设备和方法

250ml 全玻璃回流装置；加热装置为电热板或变阻电炉；多孔玻板吸收管．

我们在全玻璃回流装置上端接上多孔玻板吸收管，不加硫酸汞，加入与“标准方法”相同量的硫酸银作为催化剂，以多孔玻板吸收管吸收被重铬酸钾氧化出的氯气[6]，以碘量法定量测定氯气（余氯）[7]．试验装置如图 1 所示．

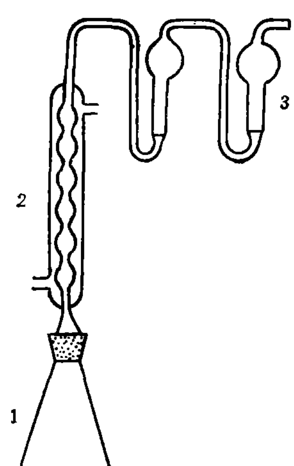

图 1　试验装置图
1. 锥形瓶 2. 回流管 3. 多孔玻板吸收管

2. 化学试剂

0.2500N 重铬酸钾标准溶液；试亚铁灵

指示剂溶液; 0.1N 硫酸亚铁铵标准溶液;硫酸-硫酸银溶液;10g Ag_2SO_4/L; 化学纯硫酸汞;浓(冰)醋酸;结晶碘化钾 (KI);苯二甲酸氢钾(分析纯); 0.025N 硫代硫酸钠标准溶液;淀粉指示剂

3. 分析步骤

取 20.0ml 混合均匀的废水样(或适量废水样稀至 20.0ml)于 250ml 磨口回流锥形瓶中,加数粒玻璃珠,慢慢加入 30ml 硫酸-硫酸银溶液,轻轻摇动锥形瓶使溶液均匀,放置稍冷,准确加入 10.00ml 0.2500N 重铬酸钾标准溶液. 用乳胶管将装有 45ml 左右蒸馏水的多孔玻板吸收管与回流管联接起来(氯离子浓度高时可加两个吸收管),加热回流 2h. 至 115min 时,停止回流水,以锥形瓶内产生的水蒸气将回流装置内的残余氯气带出,至第一个多孔玻板吸收管稍热时停止加热(此过程约用 3—5min),迅速取下多孔玻板吸收管,以碘量法测定多孔玻板吸收管中的余氯,以硫酸亚铁铵标准溶液滴定锥形瓶中的重铬酸钾.

(1) 碘量法测定余氯

将多孔玻板吸收管中的吸收液转入 250 ml 碘量瓶中,用蒸馏水洗涤几次吸收管,用醋酸调节吸收液的 pH 至 3—4. 加入 1g 结晶碘化钾,盖塞后摇匀,放于暗处 5min. 用 0.025N 的硫代硫酸钠标准溶液滴定至黄色几乎消失,加入 1ml 淀粉溶液,并滴定至蓝色消失为止. 记录硫代硫酸钠标准溶液的用量.

(2) 重铬酸钾的回滴

回流装置冷却后,用适量水冲洗冷凝管壁,取下锥形瓶,再用水稀至 140ml 左右. 溶液再度冷却后,加 3 滴试亚铁灵指示液,用硫酸亚铁铵标准溶液滴定至红褐色即为终点,记录硫酸亚铁铵标准溶液的用量. 测定废水样的同时,以 20.0ml 重蒸馏水按同样操作步骤作空白. 记录空白滴定时,硫酸亚铁铵标准溶液的用量.

(3) 计算

$$COD_{Cr}(mg/L) = \frac{[(V_0 - V_1)N_1 - V_2N_2] \times 8000}{V}$$

式中, N_1 为硫酸亚铁铵标准溶液的当量浓度;

V_0 为空白滴定时硫酸亚铁铵标准溶液的用量 (ml);

V_1 为废水样滴定时硫酸亚铁铵标准溶液的用量 (ml);

V 为废水样体积 (ml);

V_2 为硫代硫酸钠标准溶液用量(ml);

N_2 为硫代硫酸钠标准溶液的当量浓度.

4. 氯离子的干扰实验

我们配制了 COD 浓度为 508mg/L 的苯二甲酸氢钾标准溶液,通过加入不同量的氯离子,进行无汞盐法的 COD 回收试验,其结果如表 1 所示. 由表 1 可见,在氯离子浓度高至 4000mg/L、Cl^-/COD 高至 20:1 时,COD 回收率尚好. 而标准方法最大允许氯

表 1 不同 Cl^-浓度下的 COD 测定值及回收率

Cl^-浓度 (mg/L)	1000	1500	2000	3000	4000
Cl^-/COD	4	6	8	12	20
COD 测定值 (mg/L)	498 502 511 523	492 505 513 521	492 498 518 526	490 507 516 519	507 513 536 542
COD 回收率(%)	98.0—103.0	96.9—102.6	96.9—103.5	96.5—102.2	99.8—106.7

离子浓度为 2000mg/L，国外研究者报告的无汞盐法最大允许 Cl^-/COD 为 5:1. 可见本法明显优于其它方法.

5. 准确度与精密度试验

在无氯离子的情况下，本法与标准法无甚差别. 为突出本法特点，在氯离子浓度为 2000 mg/L 条件下，用本法对 COD 值为 508mg/L 的标准苯二甲酸氢钾溶液进行了 15 次测定，其结果如表 2 所示. 根据表 2 数据，求得其平均值为 509mg/L，标准偏差为 ±15.18mg/L，变异系数为 2.99%. 在如此高的氯离子浓度下，其准确度与精密度已经很理想了.

表 2 用本法测定标准苯二甲酸氢钾溶液的结果

批号	COD 测定值 (mg/L)		
1	492	518	526
2	488	498	521
3	492	530	527
4	511	523	490
5	519	497	507

表 3 本法与标准方法 COD 测定值对照（双分均值）

废水种类	标准方法 COD 测定值 (mg/L) A_1	本法 COD 测定值 (mg/L) A_2	$\frac{A_1 - A_2}{\bar{A}}$ (%)
生活污水	249	249	0.0
医院污水	88.8	89.0	−0.2
煤气站废水	191	201	−5.1
生物制品废水	79.4	74.1	+6.9
豆制品废水	1037	1016	+1.1
酿造废水	1121	1122	−0.1
油漆废水	1240	1248	−0.6
中药废水	2056	2045	+0.5

6. 与标准方法的对比试验

用一种生活污水和七种废水，进行了本法与“标准方法”的对比试验，其结果如表 3 所示. 由表 3 中数据可见，两种方法的测定结果吻合.

二、结 论

与“标准方法”相比，本法不用硫酸汞来消除氯离子的干扰，避免了硫酸汞对环境的污染.

与国外其它无汞盐测定化学需氧量的方法相比，本法克服了银盐用量过大及高银盐浓度下仍有氯离子被氧化，从而使化学需氧量测定结果偏高的缺点.

本法在氯离子高至 4000mg/L，Cl^-/COD 高至 20:1 时，仍可准确测定化学需氧量.

本法具有较高的准确度和精密度.

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In this study a polot upflow anaerobic sludge blanket reactor of capacity of 6.7 m^3 was used at ambient temperature (about 20°C) to treat brewery wastewater (the influent COD concentration was about 2400 mg/L). Seed sludge was obtained from an Imhoff tank. By controlling the operation conditions granular sludge was well formed. A volumetric COD loading up to 10—13 kg/ m^3·d was achieved with more than 85% removal of COD.
Key Words: upflow anaerobic sludge blanket reactor, ambient digestion, sludge granulation, brewery wastewater.

An Experimental Study on Desulfurization of Pulverized Coal Firing by Magnetic Separation.

Wu Shibing, Zhang Hengjian, Zhang Sijing (Xuzhou Municipal Institute of Environmental Protection, Jiangsu Province): *Chin. J. Environ. Sci.*, 11(6), 1990, pp. 25—28

Desulfurization of pulverized coal firing by magnetic separation is one of important methods that remove SO_2 from firing coal. The key technology of desulfurization is to apply appropriately a high-gradient magnetic separator. The authors first completed the experiments in China during 1987—1989. The paper introduces briefly the technogical process and results.
Key Words: desulfurization, pulverized coal firing, magnetic separation.

Investigation of Organic Pollutants in the Songhuajiang River Basin.

Xu Zhiyi, Gao Yifei, Cao Shuying, He Zunshi, Jia Yiqun (Changchun Institute of Applied Chemistry, Academia Sinica): *Chin, J. Environ. Sci.*, 11(6), 1990, pp. 29—31.

The organic pollutants in the Songhuajiang River basin have been analyzed with GC, GC/MS, HPLC and TIC methods, water samples were treated in situ for GC/MS and HPLC and treated in the laboratories for GC and TIC. The samples were collected in winter and summer. 152 organic compounds were detected out. Among them, 19% were PAHs, 14% were chlorocompounds, 13% aromatic compounds and 54% others. Most of the organic counpounds polluting some sections of the River haver been found from the analytical results.
Key Words: organic pollutants, the Songhuajiang River basin.

Determination of Chemical Oxygen Demand without Using Mercury Salts.

Han Xiangkui, Yao Xiuqin, Liu Ying (Jilin College of Architectural and Civil Engineering, Jilin): *Chin. J. Environ. Sci.*, 11(6), 1990, pp. 32—34

This method is based on the principle that potassium dichomate and chlorine (Cl_2) can be quantitatively determined. An absorber was used to absorb Cl_2 that was the product of what dichromate oxidated. Then iodimetry was used to determined the residual chlorine, of which the equivalent numbers were subtracted from the equivalent numbers of the dichromate consumed. Thus the interference of chloride was eliminated. The result showed that the method was of higher accuracy and precision and reproducibility of results covered a wide range of chloride concentrations.
Key Words: Chemical Oxygen Demand, determination, without mercury salts.

Conservation of Soil Resources in the Scenic Regions of the Huanshan Mountain, Jiuhuashan Mountain and the Tianzhushan Mountain.

Chen Conghong (The Agriculture-Animal Husbandry-Fishery Department of Anhui Province, Hefei): *Chin. J. Environ. Sci.*, 11(6), 1990, pp. 35—40.

The author has made a survey of soil resources in the three famous scenic mountains, and found that soil resources are getting deteriorative there, facing a potential crisis. Its anthropocentric causes are mainly due to soil erosion aggravated by over-cultivation, construction of highway and tourist facilities as well as excessive numbers of tourists so that soil and the environment in the lanscape regions burden with heavy pressure. The article presents some measurements to preserve the landscape soil, such as speeding up greening barren hills, moderate utilization of landscape resources, development of soil amelioration in the regions, development of local special products, strengthening eco-environmental protection around the regions etc.
Key Words: conservation, soil erosion, scenic mountain.

Aluminum in Acidic Soils and Its Phytotoxicity.

Tian Rensheng, Liu Houtian (Chinese Research academy of Environmental Sciences, Beijing): *Chin. J. Environ. Sci.*, 11(6), 1990, pp. 41—46.

Madè in this paper is a general review on following topics: (1) factors of soil acidification and process of aluminum activation; (2) the symptoms of Al-injured plants, the resistance of palnts to aluminum and the relationship between aluminum speciation and phytotoxicity; (3) the external factors affecting aluminum toxicity expression, such as P, Ca and organic matter; and (4) some mechanism of Al phytotoxicity relating to biomembrane,