Cu-T(4-MOP)PS_4光度法间接测定水中可溶性硫化物*

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摘要 利用Cu^{2+}与水中的S^{2-}形成难溶的CuS，剩余Cu^{2+}的含量用T(4-MOP)PS_4光度法测定，间接求得S^{2-}的含量. 研究了沉淀和显色的最佳条件. 在pH8.5左右，形成难溶的CuS，过量的铜在pH4.0用T(4-MOP)PS_4显色，然后用稀HCl酸化至pH2.3左右测定，以提高方法的选择性，并探讨了共存离子的干扰情况. S^{2-}的含量在0—0.20 μg/ml范围内符合比尔定律，相关系数$r=0.9995$，回收率为94.02%—100.8%. 建立的方法用于废水中可溶性硫化物的测定，结果与标准方法一致.

关键词 铜，T(4-MOP)PS_4，硫化物，分光光度法.

剩余的Cu^{2+}用T(4-MOP)PS_4光度法测定，间接测得S^{2-}的研究鲜见报道. 本研究废水中的S^{2-}在弱碱性条件下与铜形成难溶的CuS，过量的铜用超高灵敏度的卟啉试剂在pH4.0显色，当Cu-T(4-MOP)PS_4络合物形成后，以稀盐酸酸化至pH2.3左右测定，提高了方法的选择性，所建立的方法可用于实验室废水和工业废水中可溶性硫化物的测定，也可用于有色废水样品的测定，结果满意.

1 实验部分

1.1 试剂和仪器

铜标准溶液：称取光谱纯CuO 0.3130 g溶于少量硝酸中，移入250 ml容量瓶，用水稀释至刻度，此液每毫升含Cu^{2+} 1.0000 mg，临用时稀释至所需浓度；四(4-甲氧基-3-磺酸苯基)卟啉[T(4-MOP)PS_4]：3.0×10^{-4} mol/L水溶液；S^{2-}标准溶液：称取6 g分析纯$Na_2S\cdot9H_2O$溶于水，定容至500 ml，此液含S^{2-}约1.6 mg/ml，临用时经碘量法标定后，稀释至所需浓度；盐酸羟胺：0.2%；缓冲溶液：pH4.0为邻苯二甲酸氢钾体系，pH8.5为5%六次甲基四胺体系；盐酸：0.02 mol/L和0.1 mol/L；吸收液：1.0 ml三乙醇胺加水至100 ml，滴加氢氧化钠溶液至pH10左右.

722型光栅分光光度计(上海第三分析仪器厂)；UV265型紫外可见分光光度计(日本岛津)；pHS-4酸度计(杭州亚美电子仪器厂).

1.2 实验方法

于25 ml比色管中，依次加入20.00 μg铜标准溶液，2.0 ml 5%六次甲基四胺溶液，加一定量S^{2-}标准溶液或含硫水样，稀释至一定体积，振摇1 min，放置片刻，加入0.02 mol/L盐酸3 ml酸化，此时pH约5—6，用蒸馏水稀释至25 ml，充分摇动1 min.

移取上述溶液2.00 ml于25 ml比色管中，加入0.2%盐酸羟胺1.0 ml，pH4.0缓冲溶液2.0 ml，3.0×10^{-4} mol/L T(4-MOP)PS_4溶液1.00 ml，稀释至约10 ml，于沸水浴中加热2 min，流水冷却至室温，再加入0.1 mol/L盐酸3 ml，稀释至刻度，此时溶液的pH约2.3. 以试剂空白作参比，1 cm比色皿，于416.2 nm处测定吸光度，间接求出S^{2-}的含量.

2 结果与讨论

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2.1 吸收光谱

在不同量的 S^{2-} 存在下，按实验方法绘制吸收光谱，如图 1 所示. 由图 1 可知，络合物形成后酸化至 pH2.3 时，T(4-MOP)PS_4 的最大吸收波长位于 444.4 nm 处，Cu-T(4-MOP)PS_4 络合物的最大吸收波长位于 416.2 nm，当有适量 S^{2-} 存在时，络合物吸收光谱的峰形相似，最大吸收峰一致，吸光度随 S^{2-} 浓度增加而降低，且呈线性关系.

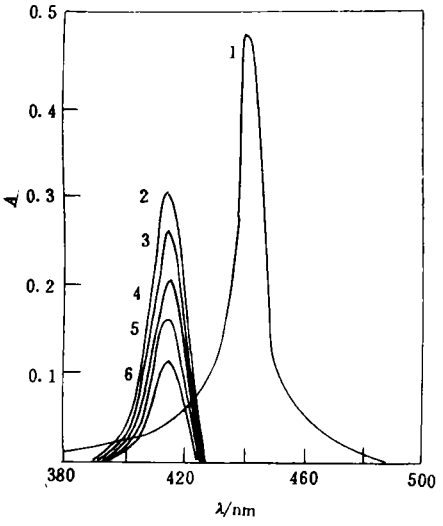

图 1　吸收光谱

(1) T(4-MOP)PS_4，[T(4-MOP)PS_4]=3.6×10^{-6} mol/L 以水为参比；(2)－(6) Cu-T(4-MOP)PS_4 络合物，[T(4-MOP)PS_4]=1.2×10^{-5} mol/L，[S^{2-}]：(2) 0；(3) 1.33×10^{-6}；(4) 2.65×10^{-6}；(5) 3.98×10^{-6}；(6) 5.30×10^{-6} mol/L，以试剂空白为参比

2.2 Cu^{2+} 用量的影响

Cu^{2+} 与 S^{2-} 形成 CuS 的原子量之比约为 2∶1，因此，Cu^{2+} 的用量与 S^{2-} 的测定范围密切相关. 按实验方法，加入适量 S^{2-}，分别考察了 10，20，25 μg Cu^{2+} 的情况，结果见图 2. 由图 2 可见，随着 Cu^{2+} 用量的降低，线性范围变窄. 本试验加入 Cu^{2+} 20 μg.

2.3 CH_2Cl_2 的影响

文献[1]利用 AAS 测定溶液中剩余的 Cu^{2+}，需加入 CH_2Cl_2 保护 CuS，并离心分离. 本法试验表明，CuS 极微小的胶粒存在于溶液中，用卟啉光度法测定 Cu^{2+} 时，对分析结果没有影响，而用 AAS 测定时，Cu^{2+} 的含量明显偏高，故本实验不加 CH_2Cl_2，这也说明了文献[1]是正确的.

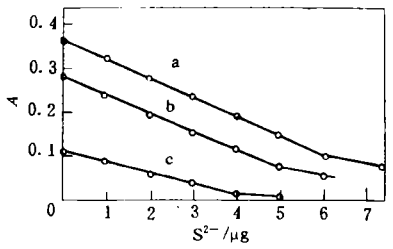

图 2　Cu^{2+} 用量的影响

a. 25 μg　b. 20 μg　c. 10 μg

2.4 酸度及缓冲体系对 CuS 形成的影响

用于 CuS 形成的缓冲体系有 pH8.5 的 NH_4OH-NH_4Cl 体系[1]和 pH4.5 的 NaAC-HAC 体系[2]，实验表明 2 者的再现性均不理想. 于是按实验方法，加入 S^{2-} 5.0 μg，考察了不同 pH 的六次甲基四胺缓冲体系对 CuS 形成的影响，结果表明，在 pH8.2－8.8 区间吸光度达最低值，且趋于恒定. 本文采用加入 5%六次甲基四胺 2.0 ml，此时 pH8.5 左右.

2.5 CuS 形成后溶液酸化的影响

实验表明在 pH8.5 形成 CuS 之后，直接测定过量的 Cu^{2+}，结果偏低约 25%，这可能是由于一部分 Cu^{2+} 水解形成 $Cu(OH)_2$ 所致，若用 0.02 mol/L HCl 2－4 ml 酸化，吸光度达最大且恒定，本工作选用加入 3.0 ml.

2.6 Cu-T(4-MOP)PS_4 形成后酸度的影响

为提高方法的选择性，参照文献[3]，在 Cu-T(4-MOP)PS_4 形成后，用 0.1 mol/L HCl 1－4 ml 酸化，吸光度仍保持恒定，本工作采用加入 3.0 ml，此时，pH 为 2.3.

2.7 共存离子的影响

共存离子对显色反应的影响文献已有报道[3]，本文主要考察共存离子对 CuS 形成的影响. 实验时，共存离子与 Cu^{2+} 同时加入，按实验方法考察了 17 种离子的干扰情况，对于 3 μg S^{2-}，误差≤±5%视为不干扰，其允许含量

(μg)为：Ca^{2+} 80，Cr^{3+} 48，Cd^{2+} 40，Zn^{2+} 20，Mg^{2+}、Ni^{2+}、Pb^{2+}、Al^{3+} 10，三乙醇胺 500(未做上限)，苯酚 50，苯胺 20，SDS 5，SO_4^{2-} 2000(未做上限)，PO_4^{3-} 1000(未做上限)，F^- 5000，SO_3^{2-} 200.

2.8 工作曲线的线性范围

按实验方法(与 S^{2-} 的测定一样)绘制工作曲线，S^{2-} 的含量在 0—0.20 μg/ml 范围内符合比尔定律，工作曲线的回归方程 $y=0.2896-4.472\times10^{-2}x$($x$ 的单位为：μg/25 ml)，相关系数 $r=0.9995$.

2.9 样品的测定

按常规取水样若干 ml 装于具塞塑料容器中(水需装满，不能留有空隙)，在采样现场，按每 L 水样加入 10 mol/L NaOH 0.5 ml，保持 pH10 左右，盖紧塞子，摇匀，带回实验室.

将上述水样过滤，取适量过滤的水样按实验方法进行分析，所得结果与亚甲基蓝法比较，结果较满意，见表 1. 若水样有色或含硫量较低，则水样过滤后，用酸化吹气法将 H_2S 吹出，以 10 ml TEA-NaOH 吸收液吸收，所得结果见表 2.

表 1 水样含硫量的分析结果

样品	本法测得值 /mg·L⁻¹	亚甲基蓝法测得值 /mg·L⁻¹	标准加入法 S^{2-}样品加入量 /μg	S^{2-}标准加入量 /μg	S^{2-}总量 /μg	回收率 /%
实验室废水Ⅰ	0.36	0.35	1.44	2.34	3.75	98.72
				2.34	3.70	96.58
				2.34	3.90	105.1
				2.34	3.80	100.8
实验室废水Ⅱ	0.39	0.40	1.56	2.34	3.78	94.87
				2.34	3.85	97.86
				2.34	3.80	95.73
				2.34	3.76	94.02
工业废水Ⅰ	0.48	0.46	1.92	2.34	4.28	100.8
				2.34	4.20	97.44
				2.34	4.34	103.4
				2.34	4.21	97.86

表 2 酸化吹气法测定水样中的 S^{2-}

样品	取样量 /ml	本法测得值 /mg·L⁻¹	亚甲基蓝法测得值 /mg·L⁻¹
工业废水Ⅰ	20.0	0.46	0.45
工业废水Ⅱ	100	0.069	0.065

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例子突出.

5 小结

(1) 引起秋季光化学污染的过程，除具有同冬夏两季类似的局地 O_3 污染特点外，还具有和春季某些情况下外来源造成的高浓度 O_3 污染一样的特点.

(2) 秋季地面风速大，垂直向湍流有利于从高空将高浓度 O_3(外来源)输向地面，这与冬夏季小风速下主要靠局地源产生和积累高浓度 O_3 的情况不同.

(3) O_3 浓度在秋季增值的诸多原因中，前体物 NO_x 是其中一个重要因素，而 O_3 背景浓度的季节变化及其他天气气象条件也是不容忽视的原因.

(4) 通过相关系数的比较可知，秋季的非 NO_x 影响因子，如气象因素，外来源要比冬夏为强.

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ferent phenol wastewaters is better than their separate treatment result. The immobilized enzyme prepared has fair repeating usage performance.

Key words: immobilized enzyme, enzyme catalyzed oxidation, horseradish peroxidase, phenol.

Determination of Trace Copper, Lead and Cadmium in Seawater by Graphite Furnace Atomic Absorption Spectrometry with Dithizone-n-Butyl Acetate Extraction. Jin Xuegen (Zhejiang Environmental monitoring Centre Station, Hangzhou 310012): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 61—63

This paper studied the optimum conditions for the determination of trace copper, lead and cadmium in seawater by graphite furnace atomic absorption spectrometry with dithizone-n-butyl acetate extraction. The results showed that copper, lead and cadmium in the weakly alkaline medium (pH8—10) can be quantitatively extracted simultaneously. The relative standard deviation is less than 3% and the recoveries for the added standard are between 92%—102%. The detection limit (μg/L) for copper, lead and cadmium are 0.06, 0.14 and 0.002, respectively. This method is simple and rapid. The method has been successfully applied to the determination of trace copper, lead and cadmium in seawater with satisfactory results.

Key words: dithizone, extraction, graphite furnace, seawater, copper, lead, cadmium.

Determination of Lead from Automobile Exhaust Using Anodie Stripping Voltammetry at Carbon Fiber Beam Mercury Film Electrodes. Shao Mengxin et al. (Dept. of Environ. Eng., Tianjin Professional College, Tianjin 300402): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 64—66

In this paper, the preparation for carbon fiber beam mercury film microelectrodes was described. The electrode voltammetric properties were investigated. Lead content from automobile exhaust was determined using anodic stripping voltammetry. The suitable experimental conditions were assigned. This technique is simple, quick, with high sensitivity and fine reproducibility. The detection limit is about 0.1 ng • ml^{-1}, the linear range is 1.0 ng • ml^{-1}—20 ng • ml^{-1}. The relative standard deviation is 9.4%.

Key words: carbon fiber microelectrodes, anodic stripping voltammetry, automobile exhaust, lead.

Determination of Phenol in Wastewater by Alternating-current Oscilloscopic Polarography Titration. Qiu Zhiguo (Dept. of Chemistry Northeast Forestry University, Harbin 150040): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 67—68

A method to use a mixed solution of hydrochloric acid and potassium bromide as base solution to titrate phenol in water sample directly was indicated. The method is simple and rapid. The measuring range is 11.07—2113.2 mg/L, variation coefficient is bellow 0.9%, recovery rate is 95%—102%.

Key words: phenol, alternating-current oscillopolarographyic titration, wastewater determination.

Analysis on the Typical Photochemical Processes of Pollution in Autumn. Zhu Yuxiu et al. (Dept. of Environ. Eng., Shanghai Institute of Urban Construction, Shanghai 200092): *Chin. J. En-viron. Sci.*, **17**(3), 1996, pp. 69—71

Synchronous observations of O_3-NO_x concentrations and relative meteorological meterial have been lasted for one month, in order to study the characteristics of photochemical pollution and their relations with meteorology. Photochemical pollution processes in the autumn have been found. It not only includes the mechanisms of producing and accumulating of local sources as in summer and winter, but also includes the feature of high ozone pollution from outer sources as in spring. The highest and mean maximum concentrations of O_3 reaches 168.7 μg/m^3 and 114.8 μg/m^3, respectively.

Key words: autumn, processes of ozone pollution, photochemical pollution.

Study on the Indirect Determination of the Soluble Sulfide in Water by Spectrophotometry. Wang Lihong et al. (Dept. of Environ. Sci., Hangzhou University, Hangzhou 310029): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 72—74

In this paper, a new method for indirect determination of trace sulfide ion was developed. The optimum conditions of precipitate reaction of copper with sulfide and color reaction of copper with T(4-MOP) PS_4 were discussed. At about pH 8.5, CuS was formed, and at pH4.0 the surplus

copper in the solution reacted with T(4-MOP) PS_4 to form Cu-T(4-MOP)PS_4. Acidifing about pH2. 3 by dilute hydrochloric acid, the solution was determined by spectrophotometry. The content of S^{2-} in the sample was calculated. The effect of interference ions was studied. The Beer's law is obeyed in the range of 0 — 0. 20 μg/ml. The correlation coefficient is 0. 9995 and the recoveries of sulfide are in range of 94. 02% — 100. 8%. The proposed method was used to determine the soluble sulfide in waste water and the results are agreed with the standard method.

Key words: copper, T(4-MOP)PS_4, sulfide, spectrophotometry.

Simultaneous Determination of Zinc and Copper With Derivative Spectrophotometry. Liu Guangdong et al. (Dept. of Chem. Eng., University of Petroleum, Dongying 257062): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 75—76

In this paper the simultaneous determination of zinc and copper with 5-Br-PADAP at pH8. 5 by using derivative spectrophotometry has been studied. The malar derivative absorption coefficients of zinc and copper are 3.0×10^5 and 1.0×10^5 respectively. The interference of overlapped spectra was overcome. Satisfactory results were obtained in the determination of zinc and copper in hair.

Key words: 5-Br-PADAP, derivative spectrophotometry, zinc, copper, determination, hair.

Principles and Methods to Assess the Relative Sensitivity of Ecosystems to Acidic Deposition. Hao Jiming et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 77—80

The conceptions of sensitivity, the absolute sensitivity and the relative sensitivity of ecosystems to acidic deposition have been described. Also an approach to assess the absolute sensitivity of water and soil to acidic deposition has been developed. According to the comparison of each ecological factor's buffering ability to acidic deposition, a basic principle to establish a method to assess the relative sensitivity of ecosystems to acidic deposition has been provided. Besides, the article had an introduction to the established assessment methods and their recent development.

Key words: acidic deposition, ecosystems, sensitivity.

Dissertation on Environmental Immigration. Xu Jiang, Ouyang Ziyuan et al. (State Key Laboratory of Environ. Geochemistry, Chinese Academy of Sciences, Guiyang, 550002): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 81—86

Because of environmental degradation, some areas have arisen a kind of new special type of immigration—— environmental immigration. Environmental immigration is the inevitable outcome of the contradiction between population growth and environmental capacity. The concept, factors and essence of environmental immigraiton initially were studied in this article, and an example of environmental immigration in Guangxi Province, China, was given.

Key words: environmental immigration, population, environmental capacity.

Technique and Application of Biological Treatment of Gaseous Emissions. Qiang Ning (School of Environ. Eng., Tongji University, Shanghai 200092): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 87—90

Three biological processes to treat waste gases are the bioscrubber, the biofilter and the biotrickling. Selecting the best biological processes suited for one paticular application depends on the contaminant concentration, stream composition etc. The biological treatment of gaseous emissions offers an inexpensive and environmentally safe alternative to conventional air treatment technologies such as absorption, adsorption and incineration. At first, the biological treatment of gaseous emissions are used to deodorize, and more recently, to remove volatile organic compounds from waste gases emited from chemical processe of industries. In Germany, Netherlands and Japan, there are nearly 1000 biological gaseous treatment systems in service.

Key words: biological treatment, gaseous emissions, biofilter, bioscrubber, biotrickling.