硫化物标准溶液的配制及其稳定性研究

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摘要　采用在碱性条件下加入乙酸锌-乙酸钠溶液形成硫化锌沉淀的形式配制硫化物标准溶液，可使其稳定保存。溶液酸度、水中溶解氧、痕量重金属离子存在、乙酸锌-乙酸钠纯度及光照射等因素，对硫化物标准溶液的稳定性有较大影响。实验结果表明：采用去离子除氧水、控制 pH＝10—12、对乙酸锌-乙酸钠进行提纯等方法配制的硫化物标准使用液，室温下至少可稳定保存2个月，浓度基本不变。

关键词　硫化物，标准溶液，配制方法，稳定性。

关于亚甲基蓝光度法测定微量硫化物的标准分析方法，长期以来由于硫化物在溶液中易形成硫化氢而逸失、容易被空气及水中的溶解氧所氧化、受光照射易分解等，使硫化物标准溶液不能长期稳定保存，因此每次分析测定均需重新配制、标定和稀释成标准使用液，仅此一项工作既费时又消耗药品，给实际工作带来诸多不便。硫化物的测定，一般采用硫化钠溶液作标准，为提高硫化钠溶液的稳定性，常加入乙酸锌或乙酸锌-乙酸钠溶液，使硫化钠转化成硫化锌沉淀的形式保存。在实际工作中笔者发现，采用《水和废水监测分析方法》[1]中介绍的配制方法，即使加乙酸锌溶液固定，硫化物标准使用液实际只能稳定1—2d。为了解决硫化物标准溶液的稳定性，本文讨论了硫化物沉淀形式、痕量重金属离子存在、水中溶解氧、溶液酸度、乙酸锌-乙酸钠纯度及光照射等因素对硫化物标准溶液稳定性的影响，提出了硫化物标准溶液的配制方法。

1　影响硫化物标准溶液稳定性的因素

1.1　硫化物沉淀形式的影响

硫化物沉淀形式一般为硫化锌（白色）或硫化镉（淡黄色）。由于镉盐的毒性较大，且硫化镉比硫化锌更易被氧化，实际工作中大都采用硫化锌沉淀形式固定。溶液中若同时加入适当的保护剂如甘油[2]或聚乙烯醇[3,4]等，可防止硫化锌进一步被氧化。

1.2　溶液酸度的影响

硫化物沉淀的完全程度与溶液的酸度有很大关系。硫化锌开始沉淀的 pH≥6，沉淀完全的 pH≥9；而氢氧化锌开始沉淀的 pH≥6，沉淀完全的 pH≥8，沉淀开始溶解的 pH≥10。为使溶液中的硫离子以硫化锌的形式沉淀完全，同时又避免出现氢氧化锌沉淀，溶液的酸度应控制在较强碱性。

为确定溶液的最佳酸度，采用不同酸度的水配制硫化物标准使用液（5.0μg S^{2-}/ml），以亚甲基蓝光度法对其吸光度逐日进行了测定，其结果见表1。

表1　不同酸度下硫化物标准溶液的稳定性

溶液酸度 (pH)	不同时间内溶液的吸光度(d)			
	1	3	5	7
6.0	0.471	0.453	0.441	0.412
7.0	0.514	0.500	0.479	0.470
8.0	0.517	0.510	0.506	0.485
9.0	0.547	0.485	0.485	0.475
10.0	0.555	0.553	0.552	0.550
12.0	0.554	0.552	0.550	0.550

从表1结果看出：溶液的 pH＜10 时，硫化物标准溶液的吸光度较低，且一周内下降约6%—13%；溶液的 pH≥10 时，硫化物标准溶液的吸光度较高且稳定，一周内仅下降约0.7%—0.9%。因此，配制硫化物标准溶液时，溶液的酸度应控制在 pH＝10—12 左右。

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1.3 水中溶解氧的影响

水中溶解氧的存在，容易使溶液中的硫离子被氧化，所以配制硫化物标准溶液所用水必须除去其中的溶解氧，除氧方法一般采用通入氮气至饱和或加热煮沸后迅速冷却。在实验中发现，通高纯氮比加热煮沸除氧效果好，且节省时间。

1.4 痕量重金属离子存在的影响

痕量重金属离子如 Cu^{2+}、Hg^{2+} 等的存在，因形成酸难溶性金属硫化物，往往会使硫化物的测定结果偏低，同时某些金属离子对硫离子的氧化反应还具有一定程度的催化作用[5]。因此，为消除重金属离子对测定的干扰，配制硫化物标准溶液所用水还必须经离子交换柱去除残存于水中的重金属离子，最好使用当天处理的去离子除氧水。

市售的乙酸锌、乙酸钠即使是分析纯试剂，其中仍可能残存痕量的重金属离子，为消除试剂中痕量的重金属离子对硫化物标准溶液稳定性的影响及测定的干扰，必要时可对乙酸锌-乙酸钠溶液进行提纯。提纯方法为：称取 25g 乙酸锌和 12.5g 乙酸钠溶于 1000ml 去离子除氧水中，摇匀后边搅拌边一滴一滴地加入 2ml 新鲜配制的 0.05mol/L 硫化钠溶液，转移至 1000ml 容量瓶内，摇匀后静置过夜，然后以双层中速定量滤纸过滤上述溶液，开始的过滤液应弃去。

1.5 光照射的影响

光照射对硫离子的氧化反应具有催化作用，为防止硫离子被氧化，配制好的硫化物标准溶液应盛于棕色瓶内保存。

2 硫化物标准溶液的配制方法

2.1 硫化物标准贮备液

取一定量结晶状的硫化钠[$Na_2S \cdot 9H_2O$]置于布氏漏斗或小烧杯中，加水淋洗除去表面杂质，用于滤纸吸去水分后称取约 0.75g 溶于少量水中，转移至 100ml 棕色容量瓶内，以水稀至刻度，摇匀后标定其准确浓度，标定方法参见文献[1]。

2.2 硫化物标准使用液

配制硫化物标准使用液所用水，先以新鲜配制的 1mol/L NaOH 溶液调节 pH＝10—12，取约 400ml 盛于 500ml 棕色容量瓶内，加 1—5ml 乙酸锌-乙酸钠溶液，混匀。吸取一定量刚标定过的硫化物标准贮备液，移入上述棕色瓶内，注意边振荡溶液边加入，然后加已调 pH＝10—12 的去离子除氧水稀至刻度，充分混匀，使成均匀的含硫离子浓度为 0.1μg/ml 至 100μg/ml 的硫化锌混悬液每次取用时，应充分摇匀。

3 硫化物标准溶液的稳定性

3.1 硫化物标准贮备液

按不同方法配制硫化钠标准贮备液，逐日以碘量法对其硫离子含量进行标定，其结果见表 2。

表 2 硫化物标准贮备液的稳定性

标准贮备液[1)]	不同时间(d)的碘量法标定值(mg/L)					
	1	3	5	7	14	30
贮 1	1.22	0.92	0.82	0.71	0.51	0.43
贮 2	1.29	1.29	1.29	1.22	1.18	1.04
贮 3	1.25	1.25	1.24	1.24	1.21	1.18

1) 贮 1 以去离子除氧水直接配制，贮 2 以 pH＝10—12 的去离子除氧水配制，贮 3 以 pH＝10—12 的去离子除氧水并加 10ml $ZnAc_2$-NaAc 溶液配制

从表 2 结果看出：直接配制的硫化物标准贮备液仅能稳定 1d；pH＝10—12 介质下配制的硫化物标准贮备液可稳定 2 周；pH＝10—12 介质且加入乙酸锌-乙酸钠溶液时，硫化物标准贮备液可稳定保存 1 个月。

3.2 硫化物标准使用液

按上述方法配制了不同硫离子浓度的标准使用液，盛于棕色瓶内并在室温下保存。以亚甲基蓝光度法对溶液的吸光度逐日进行测定，其结果见表 3。

从表 3 结果可知：按本文方法配制的硫化物标准使用液，其允许保存的硫离子浓度范围为 1.0—50.0μg/ml，保存时间 2 个月；硫离子浓度太低或太高时，其稳定性下降。（下转第 91 页）

固化处理法的处理费用较低，能够在短时间内简单、迅速地固化各种废泥浆，固化物可作为回填土再次利用，可防止环境污染。

3 环境对岩土工程活动的制约

随着人类进步和社会发展，环境问题成为人类不容忽视的问题。我们知道，岩土工程活动可能对周围环境产生一些不良的影响。因此，当今的岩土工程设计师不可能只对所设计工程本身负责，而不考虑在实施建设时对周围环境的影响。从保护环境的角度出发进行岩土工程的设计与施工，是今天的岩土工程师面临的新课题。

以往的岩土工程师在选择最优方案时，总是以经济指标作为衡量标准。但今天的岩土工程师必须将经济效益和社会效益综合起来考虑。有时还必须将社会效益放在首要地位，而将经济问题放在次要地位。

例如，在建筑物和人口密集的市区，打设预制桩一般是不可取的，不仅会损坏邻近建筑物或挤土引起煤气管道爆炸，而且振动和噪音会对居民产生严重的不良影响，再例如，若施工现场小或无法处理泥浆污染时，则钻孔、振动水冲等方法不应作为优选方案。在进行大的工程，如大坝工程的方案论证时，不得不考虑生态环境破坏、水库诱发地震等各种次生效应对社会产生的不良影响。环境因素制约着岩土工程活动。因此今天的岩土工程师们在设计与施工过程中，必须首先考虑到振动、噪音和化学污染等环境因素的影响，必须注意到环境问题的重要性。如何选择最佳经济效益和社会效益的方案是广大岩土工程的专家、学者和工程师们必须努力的方向。

参考文献

1 唐业清. 岩土工程学报. 1990,12(4):73
2 侯学渊. 第六届全国土力学及基础工程学术会议论文集. 上海：同济大学出版社，1991:63

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表3 硫化物标准使用液的稳定性

标准使用液浓度[1] (μg/ml)	不同时间(d)溶液的吸光度								
	1	3	5	10	15	20	25	30	60
0.1	0.031	0.027	0.018	0.011	0.008				
0.5	0.070	0.063	0.055	0.052	0.036	0.031	0.020		
1.0	0.129	0.119	0.118	0.111	0.103	0.100	0.098	0.100	0.095
5.0	0.555	0.553	0.552	0.550	0.550	0.549	0.548	0.543	0.540
10.0	0.552	0.552	0.550	0.550	0.548	0.548	0.549	0.548	0.549
50.0	0.556	0.551	0.548	0.546	0.543	0.536	0.532	0.532	0.530
100.0	0.560	0.550	0.532	0.511	0.507	0.497	0.418	0.409	0.372

1) 10.0—100.0μg/ml的标准使用液均稀至5.0μg/ml后测定

4 结论

硫化物标准溶液应在碱性介质中乙酸锌-乙酸钠存在下配制。按本文方法配制的硫化物标准贮备液及标准使用液分别可稳定存放1—2个月。

参考文献

1 国家环保局编. 水和废水监测分析方法. 第3版. 北京：中国环境科学出版社，1989:326
2 孙瑞林，罗军. 化学通报. 1990,2:47
3 中国预防医学中心卫生研究所编. 大气污染监测方法. 北京：化学工业出版社，1984:841
4 王丽文等. 中国环境监测. 1988,4(3):20
5 Gustafsson L. Talanta. 1960,4:227

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Study on a Dose - Response Relationship of *Tradescantia* Micronucleus to Atmospheric SO_2 and NO_x. Luo Buyun, Liu Wenxia et al. (Baoji Station of Environmental Protection and Monitoring, Baoji 721006): *Chin. J. Environ. Sci*., **15**(2), 1994, pp. 62—64

A study has been carried out on monitoring atmospheric SO_2 and NO_x by using *Tradescantia* micronucleus technique. The results showed that *Tradescantia* was sensitive to a variation in the atmospheric concentration of SO_2 and NO_x. A *Tradescantia* micronucleus response (frequency) was closely related to the domain doses (concentrations) of SO_2 and NO_x in the air. A linear regression equation of the *Tradescantia* micronucleus frequency as a function of SO_2 and NO_x doses had been deduced. It was found that the response to SO_2 was inferior and opposite to a response to NO_x. This can be used to properly estimate the concentrations of SO_2 and NO_x in the air and to assess the level of air pollution.

Key words: *tradescantia* micronucleus frequency, dose-response relationship, sulfur dioxide, nitrogen oxides.

Study on an Express Determination method of Lead in Stream Sediment by Spectrofluorimetry. Huang Chengzhi, Chi Xizeng (Department of Chemistry, Beijing Normal University, Beijing 100875): *Chin. J. Environ. Sci*., **15**(2), 1994, pp. 65—68

A simple and express determination method of lead was established by spectrofluorimetry. The complex of Pb^{2+} with Cl^{-1}, at a concentration ranging from 1.4 to 2.0 mol/L, fluoresced at 485.0nm, which could be applied to the determination of trace Pb^{2+} when the pH was lower than 6.8 and the complex was excited by 262.5 nm ultraviolet light. Under the conditions of excitation bandpass 10.0nm, emission bandpass 20.0 nm and at the temperature of 23±3℃, the equation of $\triangle F = 1.01\times10^5 c + 0.020$ ($n = 13$, $r = 0.9998$) was followed for 1.0×10^{-7}—1.0×10^{-5} mol/L Pb^{2+}, the determination limit was 5.3×10^{-8}mol/L ($K = 3$). The analitical results of lead in reference stream sediment were compatible with the reference values with the recovery ratios going from 95.9 to 104.9% ($n = 10$), RSD=2.1%.

Key words: stream sediment, spectrofluorimetry, lead.

Determination of Acetonitrile, Acrylonitrile, Aniline and Nitrobenzene in Water and Discharged Industrial Water by Direct Aqueous Injection Gas Chromatography. Hou Ding' yuan, Tang Jianfei (Institute of Suzhou Enviromental Science, Suzhou 215004): *Chin. J. Environ. Sci*., **15**(2), 1994, pp. 69—70

Direct aqueous injection (DAI) gas chromatography is a rapid, simple and accurate method for the determination of nitrogenous organic pollutant at μg/L levels in water and discharged industrial water. In this method a 0.53 mm id. fused silica capillary column was used in order to enhance resolution. Bacause of the high sensitivity of nitrogen phosphorous detector a 1μl sample injection is enough for the determination with satisfactory accuracy, precision and sensitivity.

Key words: direct aqueous injection gas chromatography, nitrogenous organic pollutant, nitrogen phosphorous detector.

Study on Simulating the Biodegradation of Mixed Organic Pollutants in Songhuajing River. Yuan Xing, Ding Yunzheng et al. (Dept. of Environmental Science, Northeast Normal University, Changchun 130024): *Chin. J. Environ. Sci*., **15**(2), 1994, pp. 71—74

A study was made to simulate the biodegradation process of a mixed system of 21 organic pollutants which were detectable in the songhuajiang River, by using the water samples and sediments collected from different sites of the River as the sources of microorganism. The results showed that the main factors affecting the biodegradation included the structures of compounds, the sources of microorganism, and the period of acclimation. Under the conditions of acclimation, the rate of the biodegradation of mixed organic pollutants at a low concentration was found to fit the equation of first order reaction kinetics.

Key words: mixed organic pollutants, biodegradation, simulation.

Method for Preparing a Standard Sulfide Solution and Its Stability. Wen Zhiming, Qi Min et al. (Dept. of Environmental Protection, Fushun Research Institute of Petroleum and Petrochemicals, Fushun 113001): *Chin. J. Environ. Sci*., **15**(2), 1994, pp. 75—76

A method for preparing a standard sulfide solution has been established by examining the following variables: form of sulfide precipitation, effects of trace heavy metals, dissolved oxygen level in water, acidity of solution, purity of zinc acetate- sodium acetate, and effect of irradiation. The stability of such a standard sulfide solution was also discussed. A standard sulfide solution prepared by this method can be kept stable for at least 2 months in the range of

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1. 0—50μg S^{2-}/ml.

Key words: sulfide, standard solution, solution preparation method, solution stability.

Persistence and Biodegradation of Polyolefine Plastic Films and Phthalate Esters in the Environment. Wu Jiemin (Dept. of Environmental Science, Zhejiang Agricultural University, Hangzhou 310029): *Chin. J. Environ. Sci.*, **15**(2), 1994, pp. 77—80

The persistence and damage to crops of polyolefine plastic films and phthalate esters used as a plasticizer in farm lands were described. The characteristics of biodegradation of these organic compounds and the corresponding informations were summarized, and some effective measures which may be taken to reduce and eliminate the load of these pollutants also were proposed.

Key words: polyolefine plastic films, phthalate esters, characteristics of biodegradation.

Biodegradation of Surfactants in the Environment. Guan Jingqu and Li Jisheng (Dept. of Chemistry, Shandong Normal University, Jinan 250014): *Chin. J. Environ. Sci.*, **15**(2), 1994, pp. 81—85

The influence of surfactants on the environment was reviewed and the testing methods and kinetics for surfactant biodegradation were discussed. It was found that the microbial activity and exposure condition would affect the biodegradability of surfactants. Type, extent of branching, and number of carbon atom of the hydrophobes and the number of EO and PO units would also affect the biodegradation of surfactant. A complex system of different surfactants could be easily degraded.

Key words: biodegradation, surfactants, environment.

Data Processing and Application of the Automatic Air Quality Monitoring System. Fan Shaojia et al. (Dept of Atmospheric Sciences, Zhongshan University, Guangzhou 150275): *Chin. J. Environ. Sci.*, **15**(2), 1994, pp. 86—88

This study deals with data process and applications of the Automatic Air Quality Monitoring System. An assessment of the models which goodness- of- fit among lognormal, exponetial, gamma and Weibull distribution is presented. A concluding survey of data applications in representative analysis and prediction of air pollution is made.

Key words: the Automatic Air Quality Monitoring System, distribution models, data processing and application.

Geotechnical Engineering and the Environment. Zheng Junjie et al. (Wuhan Foundation Engineering Center, Wuhan 430071): *Chin. J. Environ. Sci.*, **15**(2), 1994, pp. 89—91

The relationship between geotechnical engineering and the environment was discussed. At first the problem how to protect the environment using geotechnical processes was discussed in three aspects: (1) making the use of waste materials; (2) landfilling solid wastes and ; (3) preventing natural calamities. Then the bad effects that geotechnical enginering imposes on the envirenment were reviewed in the following four aspects: (1) deformation of surrounding buildings; (2) vibration; (3) noise and; (4) chemical pollution. At the same time, some ways of reducing these bad effects were put forward. Finally, the restrictions that the environment exerted on geotechnical engineering were also discussed.

Key words: geotechnical engineering, environment.