

水中阴离子表面活性剂的测定

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摘要 偶氮红两相滴定法在 pH=7.5 的条件下, 能测定水和废水中的各种阴离子表面活性剂的摩尔浓度。本文通过对硫酸盐、磺酸盐、苯磺酸盐、肥皂和磷酸盐等各类阴离子表面活性剂的测定, 以及干扰试验和实际水样测定, 表明此法优于亚甲基蓝分光光度法。方法的变异系数为 1.0% ($n=11$), 最小检出浓度 0.052 mg/L ($n=21$), 加标回收率 92.1%—110.2%, 平均 100.6% ($n=14$)。建议水中阴离子表面活性剂用摩尔浓度或 PSAA 表示。

关键词 偶氮红, 两相滴定法, 阴离子表面活性剂, 废水。

一般地说, 测定阴离子表面活性剂(以下表面活性剂用 SAA 表示, 阴离子表面活性剂用 ASAA 表示)溶液, 可用指示剂两相滴定法, 如国际标准方法混合指示剂两相滴定法^[1], 包括亚甲基蓝^[2]、二甲基黄^[3]、溴酚蓝-酸性铬深蓝^[4]等。对于稀溶液和废水中的 ASAA, 可用萃取分光光度法, 如最常用的亚甲基蓝分光光度法^[5], 甲基紫^[6]、乙基紫^[7]和溴甲酚红紫^[8]等。两相滴定法精度高、简单、方便、可测定 ASAA 的摩尔浓度, 但灵敏度低, 因此不能测定水和废水中的 ASAA, 萃取分光光度法正好相反。偶氮红两相滴定法灵敏度高, 测定水和废水中的 ASAA 兼有两类方法的优点^[1]。

1 实验部分

1.1 试剂

(1) 偶氮红指示剂 0.4% 水溶液。

(2) 十二烷基硫酸钠(DS)标准深液 准确称取 0.0500 g DS(上海牙膏厂精制品, 分子量 288.4)于 100 ml 烧杯中, 用水溶解, 定量转移到 100 ml 容量瓶中, 用水稀释至刻度。溶液浓度为 173 $\mu\text{mol/L}$ (50.0 mg/L)。

(3) 海明 1622 滴定液 称取 0.08 g 海明 1622(苜基苯氧基氯化铵, 分子量 448, 含量大于 98%, AR), 用水溶解, 转移到 1000 ml 容量瓶中, 稀释到刻度。待标度。

(4) pH7.5 缓冲溶液 用称量纸称取

13.613 g 磷酸二氢钾, 转入 1000 ml 烧杯中, 加 500 ml 水, 以 0.2 mol/L 氢氧化钠溶液调节 pH 至 7.5, 转移到 1000 ml 容量瓶中, 稀释至刻度。

(5) 试验用水均为重蒸水。

1.2 实验步骤

1.2.1 海明 1622 的标定

用 2 ml 移液管移取 2.00 ml DS 标准溶液于 100 ml 具塞量筒中, 加入 48 ml 水, 10 ml 缓冲溶液, 2 ml 指示剂和 5 ml 苯, 用 5 ml 微量滴定管以海明 1622 滴定。每次加液后均需摇振、静置、分层。当有机相出现红色即达终点。根据 $c_1V_1=c_2V_2$ 计算海明 1622 浓度。

1.2.2 水样测定

如水样为均匀液体, 摇匀水样, 用 50 ml 移液管移取 50.00 ml 水样滴定。如果水样含有悬浮固体杂质, 混匀水样, 移取 50.00 ml, 用大孔径滤纸过滤, 收取滤液于 100 ml 具塞量筒中, 用 2 次(每次 5 ml)缓冲溶液淋洗固体杂质, 合并滤液于量筒中滴定。

2 结果与讨论

2.1 原理

在 pH7.5 的条件下, 用偶氮红作指示剂, 苯作萃取剂, 以阳离子 SAA 海明 1622 作滴定

剂滴定阴离子 SAA。开始时偶氮红溶于水相而不溶于有机相，随着滴定的进行，阴、阳离子 SAA 化合而沉淀，到达化学计量点时反应完全，过量一滴，海明 1622 与偶氮红生成海明 1622-偶氮红络合物、能溶于苯而不溶于水相，所以当有机相一出现红色即为滴定终点。

2.2 偶氮红两相滴定法与亚甲基蓝分光光度法测定含硫 SAA 比较

亚甲基蓝法主要测定水和废水中的硫酸盐、磺酸盐和苯磺酸盐 SAA。表 1 列出 2 种方法测定 3 种典型含硫 SAA：DS、ABS(十二烷基苯磺酸钠)和 SLS(十二烷基磺酸钠)的结果比较。

表 1 2 种方法测定含硫 SAA 结果

样品名称	分子量	亚 甲 基 蓝 法		偶 氮 红 法			
		重量吸光系数 [(L/(g·cm))]	摩尔吸光系数 [L/(mol·cm)]	实验浓度 (mg/L)	测得浓度 (μmol/L)	出厂指标含量 (%)	计算含量 (%)
DS	288.4	1.26×10 ³	3.63×10 ⁵	2.00	6.93	99.9	99.9
ABS ¹⁾	348.48	0.863×10 ³	3.01×10 ⁵	2.00	5.68	98 ¹⁾	99.0
SLS	272.38	0.862×10 ³	2.35×10 ⁵	2.00	7.17	97	97.6

1) 按参考文献[5]提纯

由表 1 可以看出，用亚甲基蓝法测得的 3 种含硫 SAA 的重量吸光系数和摩尔吸光系数均无规律。而偶氮红两相滴定法，则根据实验配制浓度和测得的摩尔浓度计算所得的试剂含量与生产厂的出厂指标相符，也就是说，它可以统一到摩尔浓度，因此更科学。

2.3 肥皂的测定

肥皂的主要成分是硬脂酸钠：羧酸型 SAA，C₁₇H₃₅COONa，M=306.52。分别用硬脂酸钠(CP，上海试剂二厂生产，无含量指标，干燥失重 5.0%，游离酸 1.0%)和碱肥皂(粉碎后 105℃烘干 2 h)试验，结果见表 2。

表 2 肥皂测定结果比较

样品名称	亚 甲 基 蓝 法			偶 氮 红 法			
	实验浓度 (mg/L)	吸光度	相当于 DS (mg/L)	实验浓度 (mg/L)	测得浓度 (μmol/L)	PSAA	计算含量 (%)
硬脂酸钠	2.00	0.017	0.014	2.00	5.82	5.24	89.2
	100	0.767	0.609				
碱肥皂	5.00	0.024	0.019	5.00	8.42	5.07	51.6
	100	0.444	0.353				

由表 2 可以看出，偶氮红法可测定肥皂 ASAA 的摩尔浓度，而亚甲基蓝法测定 100 mg/L 的肥皂相当的 DS 还不到 1 mg/L，即用亚甲基蓝法测定的 ASAA 中不包括肥皂，和文献[2, 10]的报道相符。原因是亚甲基蓝法在强酸性条件下测定，此时肥皂水解成脂肪酸(已不是 SAA)溶解在氯仿中，不能被测出。而偶氮红法在 pH7.5 条件下测定，肥皂在微碱性条件下不水解，故能测出肥皂的 ASAA。

2.4 含磷 SAA 的测定比较

用 PK(十二烷基磷酸酯钾盐，上海牙膏厂生产，工业产品)进行试验，亚甲基蓝法测定

PK 和 DS 的校正曲线比较见图 1，偶氮红法测定结果见表 3。

表 3 偶氮红法测定结果

试验浓度 (mg/L)	测得浓度 (μmol/L)	PSAA	表观摩尔质量 (g/mol)	平均表观摩尔质量 (g/mol)
0.80	2.043	5.69	391.6	393.9
1.60	4.038	5.39	396.2	

由图 1 可以得出：亚甲基蓝法测定 PK 的灵敏度较低。由表 3 可见，偶氮红法可测定含磷 SAA 的摩尔浓度，其换算的表观摩尔质量的平均值为 393.9 g/mol，与笔者曾研究的混合指示

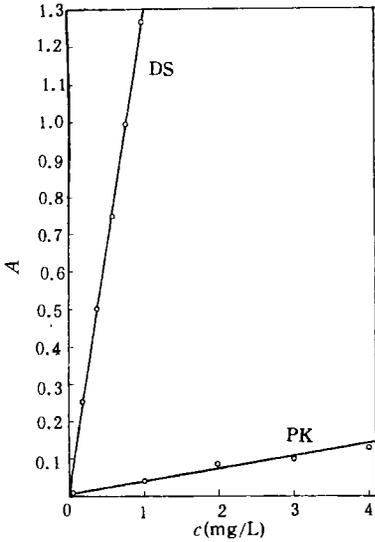


图1 亚甲基蓝法测定PK和DS比较

剂单相滴定法 355.1 g/mol 及非水电位滴定法测得的单、双酯值(单酯 20.7%、双酯 66.5%)的换算值 381.8 g/mol 比较接近。

目前测定水中 ASAA 的标准物质主要有 2 种, ABS 和 DS, 其浓度都是用重量浓度(mg/L)表示。排放标准: 美国: ABS 0.5 mg/L^[11]; 日本: ABS 0.5 mg/L, DS 0.5 mg/L^[11]; 前苏联: ABS 0.5 mg/L, DS 0.5 mg/L, SLS 0.5 mg/L^[11]。废水中有各种 ASAA, 成分相当复杂, 如果用亚甲基蓝法, 用 ABS 和 DS 作标准, 结果

是不同的。另外, 如果废水中 ABS、DS 和 SLS 都是 0.3 mg/L, 那么用 ABS=0.5 mg/L 作为排放标准是否超标, 这些都很易引起混乱。如果用偶氮红法, 则可统一用 ASAA 的摩尔浓度, 就不会引起混乱。为此建议 ASAA 的浓度用更科学的摩尔浓度(mol/L、 $\mu\text{mol/L}$)或 PSAA (ASAA 摩尔浓度的负对数, 即 $-\lg[\text{SAA}]$) 表示。

因环境中 ASAA 的浓度比较低, 用摩尔浓度表示不方便, 用 PSAA 可使数据简单, 一般为 10 以内的正数。如表 1 中 3 种 SAA 的 PSAA 分别是 5.16, 5.25 和 5.14。而作为 0.5 mg/L 排放标准的 DS 和 ABS 的 PSAA 分别是 5.76 和 5.84, 这样 ASAA 的排放标准可定为其平均值 $\text{PSAA}=5.8(1.58 \mu\text{mol/L})$, PSAA 大于 5.8 不超标, 小于 5.8 则超标。

2.5 干扰试验

用 1.00 mg/L 的 DS 试验, 干扰物质分别为蛋白质(牛肉浸膏)、非离子 SAA(T600, 即聚氧乙烯醚月桂酸酯), 氯化钠、氯化钙、硝酸镁、淀粉均为分析纯。2 种方法结果比较见表 4, 表 4 中干扰程度计算为:

$$\text{干扰程度} = \frac{\text{测得浓度} - \text{标准浓度}}{\text{标准浓度}} \times 100\%$$

表 4 2 种方法干扰试验结果比较

干扰物含量 (%)	测定方法	干扰程度 (%)					
		氯化钠	氯化钙	硝酸镁	淀粉	蛋白质	非离子 SAA
10	亚	+0.32	+0.49	+0.49	+0.09	+2.46	+0.08
50	甲	+1.61	+2.05	+1.97	+5.55	+3.18	+0.32
100	基	+5.67	+2.95	+2.87	+6.92	+4.64	0.00
200	蓝	+10.03	+3.93	+3.77	+9.74	+5.55	-0.08
10	偶	0.00	+0.74	-1.58	-1.08	-0.18	-0.36
50	氮	+0.52	-0.17	+0.35	+0.71	+0.35	-0.36
100	红	+0.87	+1.05	+1.75	+0.54	-0.35	+0.18
200		+1.74	+0.00	+0.00	-1.08	-0.52	-0.89

由表 4 可以看出, 氯化钠的含量对偶氮红法的干扰程度呈正相关, 但当其含量达到 200% 时, 只产生 1.74% 的正干扰, 说明干扰甚小。其他干扰物质的含量与干扰程度不呈相关性, 实验所得百分误差, 可视为实验误差, 即其他物质对该法无干扰。对亚甲基蓝法, 除非离子

SAA 不干扰外, 其他物质都对其有一定程度的正干扰。

2.6 实际水样测定

对本公司各分厂排放废水分别进行 2 次测定, 结果见表 5, 为了便于比较, 偶氮红法也列出重量浓度结果。

表 5 实际水样测定结果比较

采 样 点	亚甲基蓝法 ¹⁾ (mg/L)	偶 氮 红 法		
		重量浓度 ¹⁾ (mg/L)	摩尔浓度 ($\mu\text{mol/L}$)	加标回收率 (%)
涤纶二厂气浮后排放	0.001	0.228	0.79	104.3
涤纶厂生化出水	0.025	0.383	1.33	100.3
维纶厂总排	0.480	0.625	2.27	99.8
腈纶厂 B 阴阱	0.057	0.516	1.79	98.7
实验厂 B 阴阱	0.001	0.329	1.14	99.5
水质净化厂进水	0.101	1.224	4.24	110.2
水质净化厂出水	0.035	1.138	3.95	100.7
涤纶二厂气浮后排放	0.002	0.230	0.80	92.1
涤纶厂生化出水	0.010	0.041	0.14	99.4
维纶厂总排	0.367	1.271	4.41	97.1
腈纶厂 B 阴阱	0.034	0.099	0.34	100.0
实验厂 B 阴阱	0.062	1.265	4.39	100.9
水质净化厂进水	0.144	1.677	5.81	105.1
水质净化厂出水	0.050	0.298	1.03	99.6

1) 结果用 DS 表示

由于涤纶二厂、涤纶厂、维纶厂、腈纶厂和实验厂的水样都是化纤上油排放,与其他废水混合,再经过混凝或生化处理的水,而化纤上油油剂的主要成分是各种 SAA,尤以含磷 SAA 为最多,如 PK、E502A(十六至十八碳的烷基磷酸酯钾盐)、棉型 101(十六烷基聚氧乙烯醚磷酸酯钾盐)等,亚甲基蓝法对含磷 SAA 灵敏度低(参见 2.4),所以结果低于偶氮红法,即亚甲基蓝法结果偏低。水质净化厂的水除了工业废水外,还有大量未经处理的生活污水,生活污水中含有亚甲基蓝法不能测出的肥皂,所以结果更加偏低。实际上,在水质净化厂氧化塘取样时,可见到氧化塘进水口水面上有许多泡沫,但亚甲基蓝法的测定值仅 0.003—0.15 mg/L 范围内,远不到美国、日本和前苏联的排放标准 0.5 mg/L^[11],用其值来代表 ASAA 浓度,不符合实际情况。偶氮红法在 1—2 mg/L 范围内,较符合实际情况。我国的排放标准是 10 mg/L^[12],也就是说,即使加上肥皂和含磷 SAA,水质净化厂的 ASAA 也不会超过国家标准。

3 结语

偶氮红两相滴定法可以测定水和废水中的各种 ASAA 的摩尔浓度,其中包括亚甲基蓝分光光度法不能测定的肥皂和含磷 SAA。这样,就可用更科学的废水中的 ASAA 浓度表示方法——摩尔浓度或 PSAA 代替重量浓度。

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for 3 hours at a temperature of 90°C. The coagulant thus prepared was used to treat various kinds of industrial wastewaters, giving a COD removal of 53%—83%, a colourness removal of 89%—98%, a higher rate of settlement, a smaller volume of sludge, and a lower cost of treatment.

Key words: fly ash, coagulant, pyrite slag, wastewater treatment.

Concentration Levels, Change Records and Enrichment Patterns of Heavy Metals in Waters and Sediments in Both Lake Dianchi and Lake Erhai, Yunnan Province.

Li Bingmin et al. (National Laboratory of Environ. Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 50—52

The heavy metals in waters of Lake Erhai, Yunnan Province, were found not at higher levels, with the following mean values calculated in ppb: Cu 1.6, Pb 0.59, Zn 9.8, Cd 0.009, and Cr 0.24, so that the water quality was assessed as a better one. The same elements in each sample of the sediments from Lake Erhai generally had a value approximate to their respective average levels as calculated in ppm as follows: Cu 111, Pb 60, Zn 127, Cd 0.591 and Cr 130, so that so far Lake Erhai has been still a cleaner lake. Lake Dianchi in the Yunnan Province was found to have a rather worse water quality, particularly in its section of Inner Caohai where there were significantly increased levels of heavy metals in water as calculated in ppb as follows: Cu 5.8, Pb 0.55, Zn 32, Cd 1.611 and Cr 0.24, which are well below the national standards for drinking water. The sediments in different sections of the lake have been found to be polluted with some heavy metals, to a more significant extent in the section of Outer Caohai and to a more serious extent in the section of Inner Caohai. The heavy metals in the top layer of sediment were calculated in ppm at the following levels: Cu 920, Pb 647, Zn 2208, Cd 164.85 and Cr 55.

Key words: Dianchi, Erhai, Sediment, heavy metals.

Effects of Environmental Change on the Corrosion of Historical Bronze Relics.

Cheng Derun et al. (College of Culture and Museology, Northwest Univ. Xi'an 710069); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 53—55

Affected by the change in environmental factors, the ancient bronze relics in several famous cultural relics sites in Shaanxi Province were found being

subject to a serious rusting corrosion, especially by forming a powdery copper rust, the development of which may lead the historical relics to being destroyed in a moment. Based the environmental monitoring carried out in the above relics sites, the reports on the environmental monitoring in Xi'an area, and the analysis for the chemical compositions of the main body and surface rust of the ancient bronze relics, a corrosion mechanism of cultural bronze relics was suggested, which was a combination of chemical and electrochemical corrosions. The conditions under which the historical bronze relics were being rustingly corroded were identified as a chloride ion contained, humid and acidic environment. Thus, it was pointed out that the environmental control would be a key to the protection of the historical bronze relics. In order to maximize the life time of the historical bronze relics, it was necessary to improve the environmental conditions that were a radical measure for conserving the relics.

Key words: historical bronze relics, chemical corrosion, electrochemical corrosion, environmental factors.

Environmental Impact Assessment of Electromagnetic Radiation by a Doppler Very High Frequency Omnidirectional/Distance Measuring Equipment (DVOR/DME). Yao Gengdong et al. (School of Public Health, Zhejiang Medical Univ., Hangzhou 310006); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 56—58

Based on an analogic survey and a theoretical calculation, an environmental assessment impact of the electromagnetic fields (EMF) of a Doppler very high frequency omnidirectional/distance measuring equipment (DVOR/DME) to be extensively applied in China has been conducted. The results show that the field intensities were below 8.5×10^{-2} V/m at an altitude of 1.7—20 m above the ground within an area of a 1000 m radius centred on the antenna of a DVOR/DME, indicating that the low level of EMF from a DVOR/DME used in the guide station of civil aviation would not cause a health hazard among the local residents.

Key words: DVOR/DME, electromagnetic radiation, environmental impact assessment.

Determination of Anionic Surfactants in Water.

Liu Weiguo, Zhu Herong (Environ. Protection Research Institute, Shanghai Petrochemical Company Ltd., Shanghai 200540); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 59—62

The molar concentration of various kinds of

anionic surfactants in water and wastewater were determined at pH = 7.5 with azophloxine two-phase titration. The results of determination of anionic surfactants such as sulfates, sulfonates, benzenesulfonates, soap and phosphates etc, with azophloxine titration and methylene blue photometry, respectively, were compared and the interference tests and actual samples analysis were performed. All results show that the azophloxine titration was superior to the methylene blue photometry. The coefficient of variation was 1.0% ($n = 11$); minimum detectable concentration, 0.052 mg/L ($n = 21$); recovery of standard addition, 92.1%—110.2% on average 100.6% ($n = 14$). It was suggested that the concentration of anionic surfactants in water should be expressed in molar concentration or PSAA, instead of mg/L.

Key words: azophloxine, two-phase titration, anionic surfactants, wastewater.

Determination of Aniline in Polluted Water by Tridimensional Fluorescent Spectrometry. Wang Lun et al. (Dept. of Chemistry, Anhui Normal Univ., Wuhu 241000); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 63—64

The diagram of the tridimensional fluorescent spectrum (TDFS) of aniline was given by using an authors-developed program SIMS (surface image maker system) on a computer. The characteristic peak of aniline was defined. A new method for the determination of aniline by TDFS was suggested. When the concentration was in the range of 2.0×10^{-7} — 5.6×10^{-6} mol/L, a fine linear relationship between aniline concentration and relative fluorescence intensity was shown. The R. D. S. was 2.5%. The detection limit was 1.0×10^{-7} mol/L. With the method, aniline in polluted water from industry was determined satisfactorily.

Key words: aniline, fluorescence, polluted water.

Passive Integrating Measurement of Indoor and Outdoor Radon Concentrations. Zhai Pengji (Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100080); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 65—66

Both indoor and outdoor ^{222}Rn concentrations of an office building in Zhongguancun, Beijing, were determined by using a CR-39 detector and passive integrating radon monitor in different seasons of spring, summer, autumn and winter, with a total sampling time of 2—6 months. The

results show that the radon level found in the basement was higher than that in the office rooms above the basement and the indoor radon levels were higher than the outdoor radon levels. The error sources, including the effects of CR-39 random scanning and reading ways on the results of determination, were also discussed. It was found that, except in some individual cases, the extent of influence caused by different scanning ways was within the range of statistical variation.

Key words: radon, concentration, α tracks, CR-39 detector.

Total Radioactivity in Drinking Water for the Residents Living in Cities and Towns in Liaoning Province. Ma Junjie et al. (Liaoning Provincial Institute of Labour Hygiene, Shenyang 110005);

Chin. J. Environ. Sci., **16**(2), 1995, pp. 67—68

The detection of total α and β radioactivities in the water samples collected from 50 waterworks companies and 40 self-supported water supply systems for factories or mines in the Liaoning Province was carried out in 1990 to 1994 and the results were reported. It was found that the total α radioactivity was in the ranges of 0.9×10^{-2} — 16.3×10^{-2} and 0.3×10^{-2} — 21.6×10^{-2} Bq \cdot L $^{-1}$, with the averages of 0.046 and 0.065 Bq \cdot L $^{-1}$ which were 8% and 15% over the national standards, respectively in the above two corresponding cases. The total β radioactivity was found in the range of 0.08—1.07 Bq \cdot L $^{-1}$, with less water samples which were exceeding the national standards. The results show that the natural radioactive nuclides were the major contributors to the total α radioactivity in the drinking water and the natural uranium compounds made the largest contribution by about 43% of the total α radioactivity.

Key words: uranium, α radioactivity, β radioactivity, drinking water, Liaoning Province.

Investigation on the Organic Pollutants in Suspended Solid Particles and Sediments in the Great Canal. Chen Jianlin et al. (Dept. of Environ. Sci. and Eng., Nanjing Univ., Nanjing 210093);

Chin. J. Environ. Sci., **16**(2), 1995, pp. 69—72

A simple and effective pretreatment procedure was developed to generally analyze the organic pollutants in suspended solid particles and sediment in the Great Canal (Changzhou part) by using a GC/MS/DS system and a method of retention time index. The results show there were relatively high concentrations of carcinogens and