

水体中总有机卤化物的测定*

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摘要 研究一种测定水体中总有机卤化物(TOX)含量的方法。分别通过气提和乙醚萃取并使用高温热解分光光度法测定挥发性有机卤(POX)和非挥发有机卤(NPOX)。方法检测限为 $1 \mu\text{mol/L}$, 变异系数 $< 3\%$, 测得 10 种不同类型的模拟化合物的平均回收率为 81% 。自来水测定结果 TOX 为 $217-483 \mu\text{g/L}$ 。

关键词 总有机卤化物(TOX), 挥发性有机卤(POX), 非挥发有机卤(NPOX), 高温热解分光光度法。

总有机卤(TOX)包括挥发性有机卤(POX)和非挥发性有机卤(NPOX), 它是指水体中有有机卤化物的总量, 用相应氯离子的浓度($\mu\text{g/L}$ 或 $\mu\text{mol/L}$)表示。它是评价水质有机污染的一种综合指标, 1973 年德国 Kuhn & Sontheimer^[1] 首先应用 TOCl 这一参数评价饮用水的质量。

TOX 的测定是首先富集有机卤化物并与水中无机卤离子分离, 然后将有机卤高温热解成无机卤离子加以检测。常用的富集方法是活性炭(AC)吸附^[2]、XAD 树脂吸附^[3]和液液萃取法^[4], 卤离子的检测有微库仑(MC)技术^[3, 5]、电位滴定(PT)^[6]、离子选择电极(ISE)^[7]和分光光度^[8]等方法。国外对较经典的 AC/MC 和 XAD/PT 法研究较多^[9], 并根据上述原理设计制造了有机卤分析仪^[10]。国内仅见 AC/PT 法测定水体中 TOX^[11]。

1 实验部分

1.1 仪器与试剂

仪器: WK-2 型气路与温度控制器(江苏电分析仪器厂); 721 分光光度计(上海第三分析仪器厂); 超级恒温缸, K-D 浓缩装置等。

试剂: 三氯乙酸, 二氯乙酸, 氯乙酸, 2, 4, 6-三氯苯酚, 2, 4-二氯苯酚, 对-氯苯酚, 对-二氯苯, DDE, 六氯乙烷, 对-氯苯胺, 氯仿, 四氯甲烷(经处理后色谱归一化定量纯度均超过 98% , 用无水乙醇配制成 0.5 g/L 的储备液); 硝酸, 硫氰酸汞, 硫酸亚铁铵, 硫酸, 磷酸二氢钾(均为 A. R.); 甲醇, 乙醚(A. R. 重新蒸馏);

氯化钠, 氢氧化钠为 G. R.; 活性炭: 30 目(Calgoncarbon Corporation, USA), 100 目(American Norit Co. Inc)(用酸、蒸馏水洗涤, 通氮气高温活化); 树脂: XAD-2, XAD-4, GDX-502(预先用回流洗涤法处理); 实验用水为蒸馏水经离子交换树脂和 XAD-4 树脂净化处理后的处理水; 氯标准液: 准确称取在 500°C 烘 15 min, 于干燥器中冷却后的氯化钠 0.3296 g , 溶于水, 稀释至 500 ml , 此溶液(Cl^-)为 $400 \mu\text{g/ml}$ 。(储备液)准确吸取储备液 25 ml 置于 1000 ml 容量瓶中, 用水稀释至刻度, 摇匀。溶液(Cl^-)为 $10 \mu\text{g/ml}$ 。

1.2 实验方法

1.2.1 标准曲线的制作^[8]

分别取 $10 \mu\text{g/L}$ 氯的标准溶液 $0.2, 0.5, 1.0, 2.0, 4.0, 5.0 \text{ ml}$ 于一组 25 ml 容量瓶中, 准确加入 2.00 ml 1.0 mol/L NaOH, 1.00 ml 2.0 mol/L HNO_3 , 3.00 ml 0.0073 mol/L $\text{Hg}(\text{SCN})_2$ 无水乙醇溶液, 2.00 ml 0.62 mol/L $\text{FeNH}_4(\text{SO}_4)_2$, 用水稀释到刻度, 摇匀。显色 $5-10 \text{ min}$ 后用 2 cm 比色皿以试剂空白为参比, 在 460 nm 处测其吸光度。

1.2.2 仪器安装

仪器按示意图安装, 系统检漏, 吸收管内装好 NaOH 吸收液。

1.2.3 水样的采集与保存

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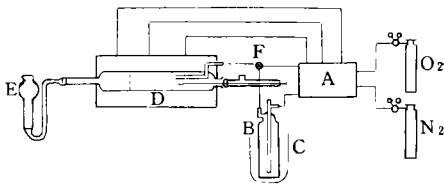


图 1 TOX 测定仪器示意图

A. 气路与温度控制器 B. 洗气瓶 C. 恒温水浴
D. 高温燃烧炉 E. 吸收管 F. 三通活塞

水样采集于定体积洗气玻璃瓶中，加入硫代硫酸钠溶液，用玻璃塞密封(无气泡)，置于冰箱避光保存，或尽快按下述方法处理测定。

1.2.4 TOX 的测定

(1) POX 的测定 燃烧炉达各区设置温度，水浴恒温后，开启氮气、氧气，设定流量。吸收管装入 2.0 ml 1mol/LNaOH 溶液，用水稀释至 10 ml。待气流平稳后，小心换上如图 1 洗气瓶塞，置于 50℃水中，以 $N_2 : O_2 = 150 : 150$ ml/min 的流速吹出可挥发性卤化物，经高温炉热解和 NaOH 溶液吸收 30 min 后，分光光度法测定 POX 的含量。

(2) NPOX 的测定 将上述吹出 POX 后的水样取 50 ml，加入 1—2 g 硫酸钠，用硫酸调节 pH=0.5，用 30 ml 乙醚分 3 次萃取(碱性模拟化合物调节 pH 为 8)，合并萃取液，无水硫酸钠干燥，K-D 浓缩到约 2 ml，再用氮气流吹至小体积，用注射器全部慢慢注入石英小舟中，置于远离炉区位 10 min、近炉区约 5 min，待乙醚挥发完，再推进燃烧炉汽化区约 10 min，最后推至燃烧区反应 5 min 后，卸下吸收管，吸收液分光光度法测定。

2 结果与讨论

2.1 富集方法的选择

本实验使用活性炭吸附^[2]、树脂吸附^[3]、液液萃取进行模拟水样的富集，经反复实验与论证，发现液液萃取是最简单、有效的方法。

2.1.1 系统空白实验

用处理水 500 ml 代替水样，分别测得各方法的系统空白值如表 1。

表 1 系统空白的测定(μmol/L)

项 目	萃 取	活性炭吸附		树脂吸附		
		100 目	30 目	XAD-2	XAD-4	GDX-502
系统空白	0.461	38.5	5.87	4.79	7.60	6.74
变异系数	1.8	4.1	4.6	6.3	4.5	3.2

从表 1 中可见萃取富集测定的系统空白值和变异系数都较吸附法小，故从减少系统空白及降低检测限的角度考虑选用液液萃取较好。

2.1.2 回收率的比较

活性炭吸附(过柱法，搅拌过滤法)，树脂吸附，液液萃取 3 种富集方法回收率实验结果见表 2，3，4

由表 2，3，4 可见对所选的各种代表化合物，液液萃取富集的平均回收率均高于树脂吸附和活性炭吸附富集，且变异系数较小，对树脂吸附很差的占 NPOX 比例较大的卤代酸类也有较满意的富集效果。

活性炭搅拌过滤法一般 500 ml 水加入 80 mg 活性炭，在过滤和转移过程中会有损失(粉末状活性炭有时浮于水面，粘附于烧杯壁或漏斗壁，这部分活性炭吸附容量大，转移易损失)；另外，活性炭活化后放置时间长会影响吸

表 2 活性炭吸附回收率(%)

卤 化 物	水样 浓度 (μmol/L)	过柱法(30 目)		搅拌过滤法(100 目)	
		回收率	变异系数	回收率	变异系数
DDE	5.63	73.6	6.0	79.0	4.6
对-二氯苯	5.63	17.5	4.3	22.5	3.5
对-氯苯胺	5.63	21.6	4.7	34.5	3.8
六氯乙烷	5.63	28.8	3.6	35.4	4.2

附。而过柱法，考虑到过柱的速度，选用 30 目活性炭，比表面小，且直接将石英小柱置于燃烧区，小柱内流速小，燃烧时间长而不完全，这都会影响回收率。

由表 3 可看出极性较大、粒度小的树脂，极性较小的氯化物有较好的回收率，但对三氯

表 3 树脂吸附回收率(%)

卤化物	水样 浓度 (μmol/L)	XAD-2(20—60 目)		XAD-4(20—60 目)		GDX-502(80—100 目)	
		回收率	变异系数	回收率	变异系数	回收率	变异系数
DDE	5.63	70	5.0	79	3.8	94	4.0
六氯乙烷	5.63	93	6.5	105	5.5	47	6.0
对-氯苯胺	5.63	34	8.0	29	4.5	75	3.7
对-二氯苯	5.63	27	6.0	54	3.4	83	5.5
五氯苯酚	5.63					72	5.0
二氯乙酸	5.63					3.0	0.34
三氯乙酸	5.63					3.8	0.6
2, 4-二氯苯酚	5.63	29	3.6	29	5.0	33	2.8

表 4 液液萃取回收率(%)

卤化物	水样浓度 (μmol/L)	回收率 (%)	变异系数 (%)
三氯乙酸	5.63	108	1.8
二氯乙酸	5.63	107	2.4
一氯乙酸	5.63	57	1.6
对-氯苯酚	5.63	88	2.2
邻-二氯苯	5.63	55	1.1
DDE	5.63	98	2.3
六氯乙烷	5.63	60	1.5
对-氯苯胺	5.63	83	1.2
2, 4, 6-三 氯苯酚	5.63	81	2.5
2, 4-二 氯苯酚	5.63	75	2.2

乙酸、二氯乙酸、氯代酚等在 TOX 中比例较大的酸性卤代物富集较差，回收率很低。因为 3 种树脂均吸附分子状态的样品，而中性或弱酸性条件下，氯乙酸多呈离子状态，难于吸附。而强酸性条件会使树脂分解。

2.1.3 操作方法比较

活性炭和树脂吸附富集耗时长，操作复杂(活性炭和树脂均需要预处理)。且活性炭高温燃烧时常会发生喷爆，使实验失败。液液萃取与它们比较，所用仪器和试剂少，操作简单，引进误差小，空白低，对各种卤代物都有较好回收率，因此是较为理想的富集方法。

2.2 燃烧条件的选择

汽化区、燃烧区、稳定区的温度，氮、氧的流量，反应时间 6 个因素都会影响燃烧效率，且各因素间有交互影响。其中燃烧区、稳定区温度的影响相对独立，即温度越高回收率越高(但温度太高会缩短石英管寿命)，所以均选为 850℃，它们属次要因子；其余 4 个因素有交互影响，为主要因子，所以用浓度为 0.5 g/L 的 DDE，2, 4, 6-三氯苯酚，对-氯苯胺的无水乙醇溶液，选 L₉(3⁴) 的正交试验设计表安排实验。其结果如表 5。

经过正交分析，燃烧的最优条件为：汽化区温度 300℃，氮气流量 150 ml/min，氧气流量 150 ml/min，燃烧时间 30 min。

2.3 NaOH 溶液吸收效果

本法用 NaOH 溶液吸收有机结合氯热解后的无机氯，经二级串联吸收试验结果与一次吸收相同，证明一次吸收已完全。燃烧机理有争论，有人认为本实验通入湿润氮气和氧气高温裂解，可能按 Cl₂ + H₂O = HCl + HClO = 2HCl + 1/2O₂ 方程热解，HClO 仅作为中间体，在 H₂O 存在下迅速转化为 HCl，经实验证实湿氧燃烧效率高于干燥氧气。

2.4 POX 回收率测定

以占 POX 大多数的三氯甲烷作标样进行 POX 回收率的测定。实验分别多次测定 0.563, 1.69, 2.82 μmol/L 氯离子浓度的氯仿模拟水

表 5 正交实验表

	汽化温度 (C)	氮气流量 (ml/min)	氧气流量 (ml/min)	反应时间 (min)	回收率 (%)	变异系数
1	300	150	200	20	100	1.1
2	300	100	150	30	97	1.4
3	300	50	100	40	86	2.7
4	400	150	150	40	100	1.2
5	400	100	100	20	91	1.9
6	400	50	200	30	96	2.2
7	500	150	100	30	92	2.6
8	500	100	200	40	80	2.1
9	500	50	150	20	61	2.7

样，得平均回收率分别为 82%，89%，97%。

2.5 TOX 的计算

水体中总有机卤表示成： $TOX = POX + NPOX$ 。本法测得的水样中的 TOCl 包括其它有机卤化合物(溴、碘)，因此用 TOX 表示水体中有机卤的总浓度而不用 TOCl 表示^[12]，单位为 $\mu\text{mol/L}$ 或 $\mu\text{g/L}$ 。

2.6 方法检测限

用去离子水 500 ml 代替水样测定，测得系统空白为 $0.461 \mu\text{mol/L}$ 。按系统空白的 2 倍计算，本方法的检出限约为 $1 \mu\text{mol/L}$ 。分光光度线性范围是 $0-112.68 \mu\text{mol/L}$ (2 cm 比色皿)^[8]。

2.7 方法干扰

饮用水中残存的游离氯及 HOCl 对本法有干扰，采样时加 3 倍余氯量的硫代硫酸钠^[12]将 Cl_2 还原为 Cl^- 。乙醚萃取液中可能会含有少量的 Cl^- (乙醚中少量水带入)，将乙醚萃取液用无水硫酸钠干燥，以除去 Cl^- 的干扰^[12]。

2.8 水样的测定结果

采用本方法测定了南京 BHK 水厂、YZ 水厂；无锡市 QY 水厂、MY 水厂以及常州 XJH

水厂的饮用水中的 NPOX，POX，TOX 含量(见表 6)。

这几个水厂中 TOX 浓度与 Amy 等测得美国某 2 个水厂 TOX 值相近 ($POX = 20-290$ ； $NPOX = 200-600$ ； $TOX = 220-900 \mu\text{g/L}$)^[13]，另外，Reckhow 等测得末稍水的 TOX 值为 $153-550 \mu\text{g/L}$ ^[14]，也与 本法测定的江苏这几个水厂的 TOX 值相近。

参考文献

1 Kuhn W & Sontheimer H. Vom Wasser. 1973, **41**: 65

2 Jekel M R et al. Environ. Sci. & Technol.. 1980, **14**(8): 970

3 Glaze W H et al.. Environ. Sci. & Technol.. 1977, **11**(7): 685

4 Barth R C et al. J. AWWA.. 1992, **84**(11): 94

5 Solomon J and Uthe J F. Analytica Chimica Acta. 1974, **73**: 149

6 Coulson D M and Cavanagh L A. Analytical Chemistry. 1960, **32**(10): 1247

7 Florence T M. J. Electroanal. Chem.. 1971, **31**: 77

8 都恒华等, 南京大学学报(自然科学版). 1979, **2**: 65

9 Lars Sjostrom et al.. Chemosphere. 1985, **14**(8): 1107

10 相尺贵子等, 水质汚染研究. 1984, **7**(2): 36

11 陈锡均等. 环境科学与技术. 1993, **2**: 1

12 张曼平等译. 水质分析. 北京: 北京大学出版社, 1991: 279

13 Amy G L et al.. Jolley R L et al.. (ed.). Water Chlorination Chemistry. Environmental Impact and Health Effects. Michigan: Lewis Publishers INC. 1990, **6**: 605

14 Reckhow D A and Singer P C. J. AWWA. 1990, **82**(4): 173

表 6 饮用水中 NPOX, POX, TOX 浓度 ($\mu\text{g/L}$)

卤化物	BHK	YZ	MY	QY	XJH
NPOX	385	361	184	162	192
POX	98	62	63	55	59
TOX	483	423	247	217	251

pp. 46—48

Lignin extracted from an alkaline wheat straw pulping black liquor was modified by sulfonation to study the feasibility of its use as a concrete water-reducing agent. This has resulted in the development of ZS-3 water-reducing admixture. In addition, a liquor containing sulfonated lignin and polysaccharides from the conversion process of wheat straw pulping black liquor was found to have a function of concrete water reduction and was turned into a superplasticizer ZS-2. Both ZS-3 and ZS-2 had a water reduction by 10%. The compressive strength of concrete was increased by 18% (7 days) or 5% (28 days) when ZS-3 was added, and by 73% (7 days) or 2% (28 days) when ZS-2 was added.

Key words: concrete water-reducing admixture, wheat straw lignin, sulfonation.

Small-Sized Non-Sludge-Discharged Sewage Treatment and Reuse System. Chen Xueyi et al. (Weifang Bestec Environmental Protection Engineering Development Co., Ltd., Weifang 261011); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 49—50

A small-sized sewage treatment and reuse system without sludge discharge has been developed, based on a process consisting of two stages of contact anaerobic filters, two stages of contact aerobic filters, a slow sand filter and a fast sand filter. Generally, a domestic sewage can be treated through this system to give a satisfactory effluent, with a BOD removal of 91.7%, a COD removal of 88.9%, a SS removal of 91.1%, and a total P removal of up to 43.5%.

Key words: excess sludge, anaerobic treatment, aerobic treatment.

Determination of Chlordimeform Residues in Rice by Enzyme Immunoassay Using Monoclonal Antibody. Yu Wanjun et al. (West China University of Medical Sciences, Chengdu 610041); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 51—53

Three sensitive enzyme-linked immunosorbent assays (ELISAs)—indirect competitive ELISA, direct competitive ELISA, and reverse direct competitive ELISA—with immobilized antibody were developed for the determination of chlordimeform residues in rice. Their IC_{50} are of 1.3, 1.7 and 5.3 ng/ml, respectively. Samples were homogenized with methanol in a blender or in an ultrasonic disintegrator. The extracts could be measured directly after dilution, or underwent

a simple clean up procedure, which could improve the accuracy of the ELISAs. Effects of pH in the reaction medium, the incubation temperature, the extracting agent and the sample matrix on the detection sensitivities were also studied and discussed.

Key words: chlordimeform, pesticide residue analysis, enzyme-linked immunosorbent assay (ELISA).

Synchronous Scanning Derivative Spectrofluorimetry for the Determination of Selenium with 2, 3-Diaminophthalene. Zhao Zhenhua et al. (Beijing Municipal Research Academy of Environmental Protection, Beijing 100037); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 54—56

The synchronous fluorescence spectra of fluorescent chelate of selenium with 2, 3-diaminophthalene (DAN) and its synchronous scanning derivative spectra were studied. The specific $\Delta\lambda$ of the synchronous spectra was found to be 140 nm. The first derivative spectrofluorimetry for the determination of selenium with DAN was described. The limits of detection were 1.5, 1.9 and 3.0 for the first derivative, second derivative and normal spectrofluorimetric technique, respectively. Coefficient of variation was 6.7 for the first derivative spectrofluorimetry, and 9.2 for the normal spectrofluorimetry.

Key words: selenium, synchronous spectrofluorimetry, derivative spectrofluorimetry.

Determination of Total Organic Halogen (TOX) in Water. Zou Huixian et al. (Dept. of Environ. Sci. and Eng., Nanjing Univ., Nanjing 210093); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 57—60

A modified determination method for TOX was described, whereby purgeable and nonpurgeable fractions were measured respectively. Purgeable organic halogen (POX) was stripped with a mixture of N_2 and O_2 ; and nonpurgeable organic halogen (NPOX) was enriched with a Liquid-liquid Extraction (LLE) method. Both were introduced into a combustion system to change them into X^- , which were then determined with spectrophotometry. There was a detection limit of about 1 $\mu\text{mol/L}$, a variation coefficient of less than 3%, with an average recovery of 81% for 10 model compounds. The TOX concentration in the tap water from Jiangsu province was from about 217 to 483 $\mu\text{g/L}$.

Key words: purgeable organic halogen, non-purgeable organic halogen, total organic halogen,

spectrophotometry.

Speciation of Arsenic in the Surface Microlayers of Natural Lakes. Yu Jianshuan (Xiamen Environmental Monitoring Station, Xiamen 361004); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 61—63

Water samples were collected both from the surface microlayers of natural lakes by using a glass plate surface microlayer water sampler and from the surface layers in a depth of 0.5 m under water surface by using a conventional water sampler, and analyzed for arsenite, arsenate, monomethylarsonate (MMA) and dimethylarsinate (DMA) by using a high performance liquid chromatography/hydride generation/atomic absorption spectrometry technique. The concentrations of arsenic species in surface microlayer water were compared to those in surface layer water. The results show that the arsenic species in surface microlayer water had a significantly different distribution from these in surface layer water and had their concentrations usually higher than these in surface layer water, indicating that they were richer in surface microlayer water with an enrichment factor of 1.66, 1.35, 1.58 and 1.09 for As(III), As(V), MMA and DMA, respectively. As(V) is a dominant arsenic species present in both surface microlayer and surface layer of lake water, and DMA is a major organic arsenic species present in both layers. The distribution of arsenic species was dependent on sampling sites.

Key words: lake, surface microlayer water, surface layer water, arsenic species, speciation, sampler.

Spectrophotometric Determination of Trace Chromium in Water Samples with Sym-Diphenylcarbazone. Li Huizhi et al. (Dept. of Chemistry, Shandong Institute of Building Material, Jinan 250022); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 64—66

Chromium(VI) was reacted with sym-diphenylcarbazone to form a red complex in the presence of sodium dodecylbenzenesulfonate and 0.15 mol/L of H_2SO_4 . The complex had a maximum absorbance at 560 nm with a molar absorptivity of 9.74×10^4 L/(mol · cm). Beer's law was obeyed in the range of 0—10 μ g of Cr(VI) in 25 ml solution. The common metal ions were able to be separated and concentrated by amberlite 717, giving a better selectivity. The method has been applied to determining chromium in water samples with satisfactory results.

Key words: chromium, spectrophotometric, sym-diphenylcarbazone.

Study on a General ICP-AES Method for Simultaneous Multielement Analysis of Water or Wastewater. Sha Weinan et al. (Dept. of Chemistry, Nankai Univ., Tianjin 300070); *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 67—71

A general ICP-AES method for simultaneous multielement analysis of water or wastewater was studied and samples pretreatment process, experimental condition optimizing, interference judging, correction and the aspects needed for paying attention during the analysis were discussed. The results showed that analytical data were accurate, reliable, and coincident with the standard values of certified reference samples with a recovery of 90%—110%. The overall relative standard deviation is within 5%. The detection limits were 0.1—100 μ g/L. The calibration curve has a wide linearity range of 4—6 orders of magnitude.

Key words: water, wastewater, ICP-AES.

Pretreatment for the Test of DEHP in Crops and Soil. Pang Jinmei et al. (Soil and Fertilizer Institute, Shanxi Academy of Agri. Sci., Taiyuan 030031); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 72—74

This paper deals with the pretreatment method for testing DEHP from farm soil and crops with $CHCl_3$ as a solvent and with the absorbent. Compared with those from Beijing, Denmark and United States of America, this method took a short extracting time of 0.5—0.7 h, 2—11 h shorter than others, and the solvent of 75—90 ml, 110—1200 ml less than others. This method is easy to use and has a high effective separation. There was a DEHP recovery rate of about 90%, except for cotton seeds. The coefficient of variability was less than $\pm 3\%$. It's very suitable to test phthalic acid esters.

Key words: DEHP, extraction, $CHCl_3$, absorbent.

Methodological Study of the Operating-Mode Sampling Method Applied to Collecting PAH Compounds in Exhausts from Diesel Engines. Sun Chen et al. (Beijing Municipal Environmental Monitoring Center, Beijing 100044); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 75—77

A new method, operomode sampling method was presented for the first time for collecting polycyclic aromatic hydrocarbons (PAHs) in the exhaust from diesel engines. With benzo-a-pyrene (BaP) as a main index, the efficiency, precision