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环境水中灭多威的固相萃取和气相色谱测定*

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摘要　用活性炭固相萃取环境水中微量灭多威，然后用气相色谱法直接测定，方法简便、灵敏、准确。灭多威的检测限为 0.2 ng。水样中的最低检出浓度为 0.2 μg/L，平均加标回收率为 95.8%－100.7%，高、中、低 3 种浓度的变异系数均小于 5%。

关键词　灭多威，固相萃取法，活性炭，气相色谱法。

灭多威(Methomyl)是一种具有触杀、胃毒作用的新型氨基甲酸酯类杀虫剂，现已广泛用于我国的农林业生产。在灭多威的生产和使用过程中，对环境造成一定程度的污染，有关水中灭多威的固相萃取富集法，近年来国外有报道，是用 C_{18} 柱、online 等作为固相萃取剂[1-3]，这些吸附剂价格昂贵且不易得。国内未见报道。本文采用廉价易得的普通吸附剂活性炭，固相萃取富集环境水中微量灭多威，气相色谱法直接测定其含量，收到了满意的效果。该方法简便、灵敏、快速、准确，适用于环境水中微量灭多威的测定。

1　实验部分

1.1　仪器与试剂

SP-502 气相色谱仪，火焰光度检测器(带有 394 nm 硫滤光片)，腾州化工仪器厂；CDM-C-2A 色谱处理仪，上海计算机技术研究所；玻璃层析柱(7.0×1.4 cm i.d.)；B70-30 型真空抽气泵。

灭多威标准品：≥99%，青岛海洋大学提供；灭多威储备液：1.0 mg/ml 甲醇溶液；抗坏血酸溶液：10 g/L(用盐酸酸化，pH＝2)；活性炭：将粉状活性炭(北京光华木材厂生产，分析纯)筛分，取 120－180 目部分，比表面积为 712 m^2/g[4]；其它试剂均为分析纯。

1.2　实验步骤

(1) 吸附柱的装填与预洗　将 250 mg 活性炭装填于 7.0×1.4 cm i.d. 的玻璃层析柱中，玻璃棉塞于上下，以免活性炭被冲散、冲下，层析柱下接真空抽气装置，用 5.0 ml 氯仿/甲醇(80∶20)混合液，2.0 ml 甲醇、15 ml 10 g/L 抗坏血酸溶液(pH＝2)依次流经吸附柱，调节压力，使上述预洗液以约 5 ml/min 的速度流出。

(2) 水样的固相萃取　水样先经抽滤，以除去悬浮物，然后准确量取 2.0 L，加入亚硫酸钠，使浓度为 0.4 g/L，将水样倒入安装在吸附柱上方的滴液漏斗中，调节滴液速度和压力，使水样以 10 ml/min 的速度流经吸附柱，待水样流完后，用 5 ml 蒸馏水充满柱子，减压，让其流尽，然后用 1.0 ml 甲醇，9.0 ml 氯仿/甲醇(60∶40)混合液依次洗脱，控制洗脱液流速，使其一滴滴流出吸附柱，洗脱液接收于刻度试管中，减压，使洗脱液流尽。将刻度试管置于 50℃恒温水浴中，缓缓吹氮，使溶剂挥发至 1.0 ml以下，用甲醇定容至 1.0 ml。

(3) 色谱分析　色谱柱为 1.5 m 不锈钢柱，

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内装涂有 5% OV-101 的 Chromosorb W-AWDMCS 担体；检测器为装有 394 nm 硫滤光片的火焰光度检测器；操作温度：柱温：110℃，汽化室及检测器 180℃；气体流速：氮气 15 ml/min，氢气 136 ml/min，空气 60 ml/min；仪器灵敏度 10^2，衰减 8，记录仪衰减 4，纸速 5 mm/min，灭多威保留时间 1.30±0.2 min，色谱峰经色谱处理机处理给出峰面积，用峰面积经外标法定量，样品中灭多威含量按下式计算：

$$R = \frac{M\,V_f}{V_i\,V_m}$$

式中，R 为水中灭多威含量(mg/L)；M 为由回归方程求得的灭多威进样量(ng)；V_f 为样品定容体积(ml)；V_i 为进样量(μl)；V_m 为水样体积(ml)。

2　结果与讨论

2.1　工作曲线的绘制

按上述方法装 5 个活性炭吸附柱，预洗，用灭多威储备液配成 0.040、0.10、0.20、0.30、0.40 μg/ml 的标准应用液(其中亚硫酸钠浓度为 0.4 μg/ml)，分别取 10 ml 倒于各吸附柱中，减压，让其流过吸附剂，按照实验方法洗脱、挥发浓缩、定容和进行气相色谱测定，得标准曲线(图 1)和气相色谱图(图 2)，回归方程为 $Y=-2438.5+1084.5X$，$r=0.9988$。

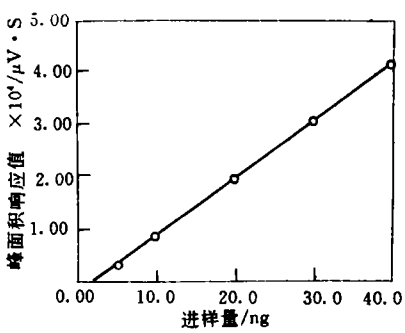

图 1　水中灭多威测定的工作曲线

2.2　吸附剂的选择

分别称取若干份 250 mg 活性炭、硅镁吸附剂和碱性氧化铝装柱，按照实验方法预洗各吸附柱，然后，配制一系列不同浓度的灭多威标准溶液，分别取 10 ml 流经各吸附柱，测定流出液中灭多威含量，求出各种吸附剂对不同浓度灭多威溶液的吸附效率，硅镁吸附剂和碱性氧化铝的平均吸附效率分别小于 30%和 50%，活性炭的吸附效率(见表 1)大大高于上述 2 种吸附剂，平均为 97.4%。

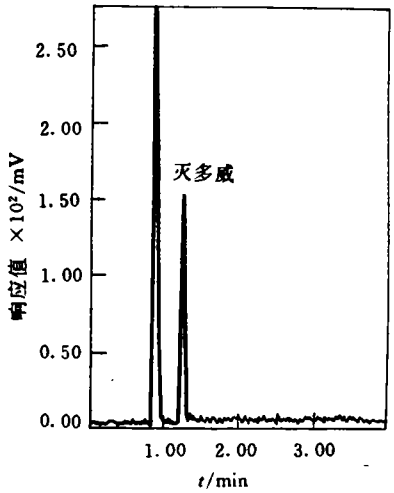

图 2　灭多威标准色谱图(进样量 10 ng)

表 1　活性炭对灭多威的吸附效率(%)

灭多威浓度(μg/ml)	50	200	500	1000
吸附效率(%)	96.7	98.2	98.9	95.6

在室温(25℃)下做吸附性能实验。称取若干份 250 mg 上述吸附剂分别加到 10 ml 不同浓度的灭多威标准溶液中，在恒温 25℃下振荡 20 min，离心分离，取上清液测定灭多威含量，用灭多威加入量扣除平衡溶液中灭多威含量，可

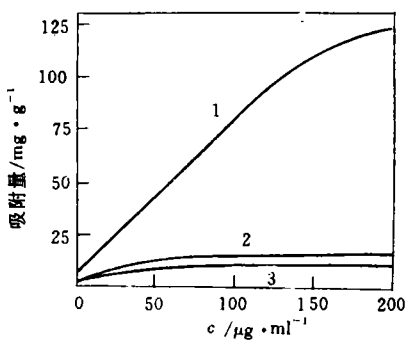

图 3　几种吸附剂对灭多威的吸附等温线

1. 活性炭　2. 硅镁吸附剂　3. 碱性氧化铝

求出吸附剂对灭多威的吸附量，以吸附量对平衡浓度作图，得吸附等温线(图3)。由图3可见，活性炭对灭多威的吸附性能远好于其它2种吸附剂。吸附液中灭多威的起始浓度为100 μg/ml—4000 μg/ml，实验结果表明，活性炭对灭多威的饱和吸附量为112 mg/g，硅镁吸附剂和氧化铝分别为6 mg/g和10 mg/g。故选活性炭作为固相萃取灭多威的吸附剂。

2.3 吸附柱预洗方法的选择

通过实验比较吸附柱不经预洗和经不同溶剂预洗的吸附与洗脱效率，实验结果表明，吸附柱不经预洗，吸附与洗脱效率均不理想，这是由于活性炭表面吸附的脂溶性物质的影响造成的；吸附柱只经氯仿/甲醇混合液和甲醇预洗，不经抗坏血酸溶液预洗，吸附效率高，但洗脱效率仍不理想，是因活性炭表面的氧化性物质与灭多威反应，造成了不可逆吸附；吸附柱经氯仿/甲醇混合液、甲醇、抗坏血酸溶液依次预洗，吸附与洗脱效率均明显提高，是因抗坏血酸还原了活性炭表面的氧化性物质，避免了不可逆吸附。故预洗方法确定用氯仿/甲醇(80∶20)混合液、甲醇、抗坏血酸溶液依次预洗。

2.4 洗脱剂的选择

用各种极性的溶剂或混合溶剂做平行实验，并改变配比，结果表明，先用1.0 ml甲醇洗脱，将活性炭表面吸附的水分顶替下来，然后再用9.0 ml氯仿/甲醇(体积比为60∶40)混合液依次淋洗，其洗脱效率最佳，故实验选用1.0 ml甲醇、9.0 ml氯仿/甲醇(60∶40)混合液依次淋洗。

2.5 方法的准确度与精密度

用加标回收率检验方法的准确度，在线性范围内按表1的高、中、低3种浓度往水样中加灭多威标准溶液，按照实验方法进行固相萃取富集、气相色谱分析，得水样的灭多威加标回收率(见表1)，平均加标回收率为96.8%—100.7%。

方法的精密度用同一浓度重复分析所得值的变异系数来表示，由表1可见，各种浓度水样的变异系数均小于5%，符合水质分析的要求。

表2 灭多威在水样中的加标回收率

试样	样本(个)	加标量(μg/ml)	平均回收率(%)	CV(%)
1	4	1.00	98.2	3.27
2	4	5.00	95.8	3.95
3	4	10.00	100.7	2.76

2.6 方法的检测限及最低检测浓度

以产生二倍噪声信号时的最小进样量测得该法的检测限为0.2 ng，测定水样中灭多威的最低检出浓度为0.2 μg/L。

2.7 试样分析

田间喷施灭多威后，在受污染的田头水渠中采集水样，采集距水面10 cm深处的水，抽滤除去悬浮物后，取2 L，按照实验方法富集并测定水样中灭多威含量，色谱图见图3，4份污染水样的平均灭多威含量为0.65 μg/L，变异系数为3.1%。

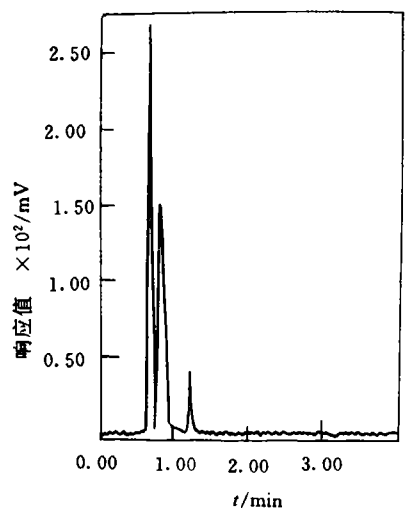

图4 实测水样灭多威色谱图

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tor. Zhou Lu et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084): *Chin. J. Environ. Sci.*, **17** (2), 1996, pp. 54—56

This paper indicated a new way to speed up granulation in UASB reactor by adding GAC. The results of experiment on UASB reactor with and without GAC treating effluence from petrochemical plant showed that the time of sludge granulation in the reactors with and without GAC were 39 days and 63 days respectively. The sludge pellet in the reactor with GAC had larger diameter than one in the reactor without GAC, and maximum COD removal rate was above 86%. Organic load of reactor with GAC was 2 times larger than the reactor without GAC. The reactor with GAC became more steady in process.

Key words: UASB reactor, granular active carbon, sludge pellet, granulation.

A Study on New Purification of High Concentration Sulphur Dyeing Sewege. Sun Jianhui et al. (Research Institute of Environ. Sci., Henan Normal Univ., Xinxiang 453002): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 57—59

The combined technology of coagulative precipitation-iron chippings filtering-alkaline separation was used to purify the high concentration sulphur dyeing sewage. The results in the mode of production showed that the removel rates of sulphide, COD, BOD_5 and colority were 97.0%, 87.4%, 85.7% and 98.9% respectively. Every pollution index is up to the National Water Emission Standard. This technology system has the advantage in run stable, operation and management easy, engineering invest low, and treatment cost cheap.

Key words: coagulative precipitation, iron chippings filtering, alkaline separation, sulphur dyeing sewage.

Ecological Restoration of Coal Mining field in Loess Plain. Xue Ling et al. (Inner Mongolia Environmental Research Institute, Huhhot 010010): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 60—63

This paper reports the results of an ecological restoration project in the Zhunger open-cut coal mining field in Inner Mongolia. The design, technique and effectiveness of the project are described. The results showed that the key points for ecological restoraton in the Loess Plain condition include: selection of suitable plant species, proper soil treatments plus necessary construction work, adapt suitable ecological planting patterns based on site conditions. More than sixty plant species and eight ecological planting patterns were evaluted. Over 70% plant coverage and high yields of the crops (compared with the same crops in the nearby area) were obtained. A good ecological and economical return was achieved from the project.

Key words: ecological resteration, demanstrative project, Zhunger, open-cut coal mine in inner mongolia, land reclaim.

Determination of Atmospheric Methyl Bromide by Photoionization Detector. Zhong Jinxian and Liu Ye (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 64—65

Atmospheric CH_3Br was trapped by Tenax adsorbent and was determined by gas chromatography with photoionization detector. The CH_3Br concentrations in indoor and outdoor are $24\times10^{-12}(V/V)$ and $77.4\times10^{-12}(V/V)$. The standard deviation and detection limit for the method are 0.0521, 10 pg respectively. The level of CH_3Br pollutions is $10^{-11}(V/V)$.

Key words: methyl bromide, GC, photoionization detector.

Indirect Spectrophotometric Determination of Trace Cyanide by Means of the Colour Reaction of Silver with Cadion in Presence of Triton X-100. Gong Churu et al. (Dept. of Chemistry, Hubei Normal University, Huangshi 435002): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 66—67

Silver gives a colour reaction with Cadion in the presence of Triton X-100, and suppression of the colour competitive complex ion of the silver can be used for the indirect spectrophotometric determination of trace cyanide. Cyanide in waste water can be separated by distillation from other ions that also interfere, and then determinated. The determination range of this method is 0—10 μg/25 ml. The recoveries of standard cyanide added to waste water samples are in the range of 91.0—100%, and its relative standard deviation is less than 9%.

Key words: cyanide, cadion, indirect spectrophotometry.

The Liquid-Solid Extraction of Methomyl in Environmental Water and Gas Chromatographic Analysis. Chen Yanjun et al. (Dept. of Chemistry, Jining Medical College, 272113): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 68—70

A solid-phase extraction procedure of methomyl from environmental water with active carbon cartridge for gas chromatographic analysis is presented. The detection limit and the minimum detectable concentration of methomyl in water were 0.2 ng and 0.2 μg/L, respectively. The average recoveries of methomyl as added to water were in the range of 95.8—100.7%. The relative standard deviations were lower than 5%.

Key words: methomyl, solid-phase extraction, active carbon, gas chromatography.

Determination of Trace Levels of Nitrophenols in Water by Polyvinylpyrrolidone Modified Carbon Paste Electrode. Wang Kaixiong et al. (Dept. of Environ. Protection, Zhejiang Agricultural University, Hangzhou 310029): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 71—73

In this paper, a method to determine simultaneously p-nitrophenol and 2,4-dinitrophenol in water by differential pulse voltammetry (DPV) with a carbon paste electrode modified with 10% (*W/W*) polyvinylpyrrolidone (PVPr) was described. The electrode showed a strong response to the nitrophenols, and the sensitivity and selectivity were much higher than ordinary carbon paste electrode. The nitrophenols were preconcentrated in 0.1 mg/L KCl solution during open circuit period, then the preconcentrated nitrophenols at the electrode were determined in phosphate buffer solution (pH7.0). The oxidation peak potentials were +0.88 V and +1.23 V (VS Ag-AgCl) respectively and two current peaks were completely separated. The detection limits were 0.50 μg/L (p-nitrophenol) and 1.80 μg/L (2,4-dinitrophenol). This method had been applied to the determination of nitrophenols in pol-