

Gas Chromatography (GC) Combined with Coulometry
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The method is based on determining hydrocarbon types in gasoline containing olefines by coupling capillary GC with coulometry. The contents of saturants-olefines-

aromatics (SOA) and individual aromatic hydrocarbons in catalytic cracking gasoline boiling below 100°C and 205°C, were determined by the method. The information of the carbon number and the content of high-boiling-point aromatics was obtained by determining individual aromatic components.

杀虫脒溴化产物的气相色谱/质谱鉴定

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食品中杀虫脒 (Chlordimeform) 残留量早已引起世界各国的重视。Huns 等⁽¹⁾将杀虫脒水解为4-氯邻甲苯胺,须用特制的提取器提取,再经重氮化制备碘衍生物,最后用气相色谱电子俘获检测器检测。庄无忌等⁽²⁾用同样的方法提取,不用重氮化而将其制备成碘衍生物用 ECD 测定,但衍生化反应条件和稳定性还有待进一步研究。黄志强等⁽³⁾采用微量样品的提取技术,直接制备成溴衍生物,用电子俘获检测器检测,无须特殊设备,不但省试剂,检测结果准确,而且分析速度快。本文采用 GC-MS 联用技术鉴定了文献⁽³⁾中分析的杀虫脒溴化产物。

实验部分

(一) 仪器及操作条件

1. 气相色谱仪 Shimadzu GC-9AM 气相色谱仪, 配备 ECD, C-R3A 数据处理机及 SPL-G9 分流/不分流毛细管柱进样系统; 25m × 0.5mm i. d. OV-101 石英毛细管柱, 载气为高纯氮气, 尾吹 40ml/min, 柱入口压力 0.17MPa; 分流比 40:1; 进样口及检测器温度为 270°C; 柱温程序升温: 初温 150°C, 保持 2min, 升温速率 30°C/min, 终温 250°C, 保持 6min。

2. 气相色谱-质谱联用仪 Shimadzu QP-1000A; EI 电离, 能量 70eV; 质量扫描范围 20—300amu; 扫描速度 9 档; 载气为高纯氮气, 尾吹 40ml/min, 柱入口压力 0.17MPa; 分流比 40:1; 进样口及离子源温度为 250°C; 柱温程序升温: 初温 150°C, 保持 2min, 升温速率 30°C/min, 终温 250°C, 保持 6min。

(二) 试剂

1. 石油醚、氢氧化钠、亚硫酸钠、盐酸均为分析

纯。

2. 杀虫脒标准品由中国进出口商品检验技术研究所提供, 纯度为 99.5%; 用 1mol/L HCl 配成 0.2mg/ml 的标准溶液。

(三) 操作步骤

按文献⁽³⁾的操作步骤及衍生化条件制备相当于 0.2mg/ml 杀虫脒的溴化物及未溴化的杀虫脒的石油醚溶液, 分别进行 GC 及 GC-MS 分析。

结果与讨论

按前述的条件, 分别分析杀虫脒及其溴化产物, 总离子流色谱图如图 1, 碎片图见图 2 和图 3。

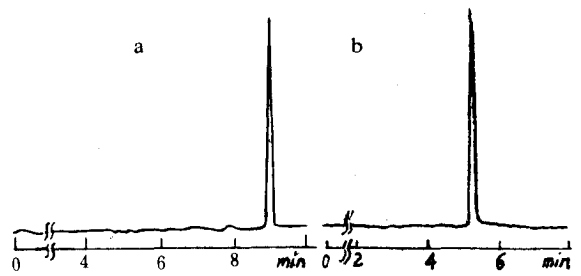


图 1 杀虫脒(a)及其溴化产物(b)的总离子流色谱图

GC 分析结果表明: 杀虫脒溴化产物的保留时间 (9.6min) 比杀虫脒的保留时间 (5.2min) 长 4.4min, 这符合化合物在 OV-101 柱上的保留规律。

GC-MS 分析, NBS 谱库计算机检索, 经人工核对各碎片峰, 结果表明: 未溴化的杀虫脒通过文献⁽³⁾的过程处理后, 其产物为氯苯脒而不是对氯邻甲苯胺。由此可见, 杀虫脒在 5mol/L NaOH 中, 短时间内仅转变为氯苯脒。



图2 杀虫脒的碎片图

溴化产物在 NBS 谱库中未能检索到,从碎片图2和图3可知,图2中所出现的碎片(包括氯苯脒的分子离子峰196m/z)在图3中都出现了,氯苯脒分子量为196,如一个溴加到氯苯脒的苯环上,图3中应当出现276 m/z的分子离子峰,在79m/z,80m/z有强度相当的碎片峰。从图3可以看到较强的276,80,79 m/z峰,因氯苯脒上含有3个甲基,所以还有(276-15)m/z碎片峰,且图2、图3中均有甲脒的特征峰44m/z。再根据苯环上基团定位规律确定,杀虫脒碱解后的溴化产物为 N'-(6-溴-4-氯-2-甲基苯基)-N,N-二甲基甲脒,分子式为 C₁₀H₁₂BrClN₂,分子量276。

参考文献

- [1] G. Huns et al., J. Agric. Food Chem., 19(2), 365 (1971).
- [2] 庄无忌等,环境科学,(4),38(1978).

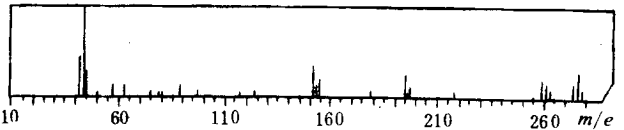


图3 杀虫脒溴化产物的碎片图

[3] 黄志强等,色谱,9(1),53(1991).

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Identification of Brominated Chlordimeform by Gas Chromatography (GC) and Gas Chromatography/Mass Spectrography (GC/MS) Huang Zhiqiang and Nie Hongyong, Hunan Import & Export Commodity Inspection Bureau, Changsha, 410007

By means of GC and GC/MS, two chlordimeform-related compounds have been identified in this work. The product from the decomposition of chlordimeform in 5 mol/L NaOH solution is N'-(4-chloro-2-methylphenyl)-N,N-dimethyl-methanimide.

The degradation product is brominated in 1 mol/L HCl solution with saturated bromine water. The brominated product is N'-(6-bromo-4-chloro-2-methylphenyl)-N,N-dimethyl-methanimide.

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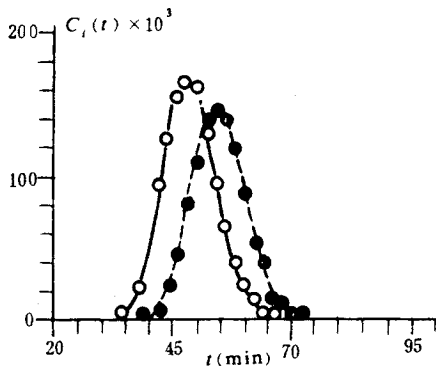


图3 色谱分离理论流出曲线与实验流出曲线比较

T = 50°C, u = 2.74cm/min, L = 93.8cm, D61 型树脂.

— 计算值,葡萄糖;○实验值,葡萄糖;---计算值,果糖;●实验值,果糖.

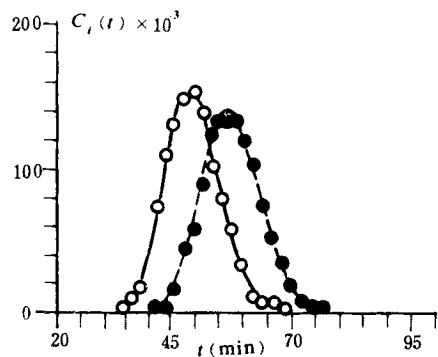


图4 色谱分离理论流出曲线与实验流出曲线比较

T = 50°C, u = 3.46cm/min, L = 93.8cm, 734 型树脂.

— 计算值,葡萄糖;○实验值,葡萄糖;---计算值,果糖;●实验值,果糖.

Determination of Phase Equilibrium and Lumped Mass Transfer Parameters of Glucose and Fructose on Ca Form Adsorbents by Liquid Chromatographic Technique Li Zhong and Ye Zhenhua, Chemical Engineering Research Institute, South China University of Technology, Guangzhou, 510641

Physical and mathematical models used to determine adsorption phase equilibrium and lumped mass transfer

parameters by liquid chromatographic technique were established, as axial dispersion being taken account. Adsorption phase equilibrium and lumped mass transfer parameters of glucose and fructose on Ca form adsorbents were determined. The effects of velocity and temperature on them were studied. Theoretical elution curves were in good agreement with those from experiments.