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气相色谱-质谱联用法检测多聚物中多氯联苯

No.GCMS-026

摘要： 多氯联苯是一系列不同含氯量的同系物的混合物，被广泛应用于电力、电磁和液压设备以及被用于绝缘油、阻燃剂、导热剂、液压油、增塑剂和无碳复写纸。多氯联苯世界性污染主要来源于大量使用多氯联苯的工厂，如用多氯联苯作绝缘油的电机工厂，大量使用多氯联苯作热载体和润滑油的化学工厂,造纸厂特别是再生纸厂。船舶的耐腐蚀涂料中含有多氯联苯,被海水溶出也是相当大的污染源。这些污染源的多氯联苯以废油、渣浆、涂料剥皮等形式进入水系，沉积于水底，然后缓慢地向水中迁移，污染生态系统，多氯联苯导致癌症和免疫力低下的案例屡见不鲜。因此多氯联苯是首批被《斯德哥尔摩公约》列入全球控制的１２种持久性有机污染物（ＰＯＰｓ）之一。

虽然多氯联苯在商业上不再生产并被禁用，但在世界上许多电器系统中仍然有多氯联苯的存在，所以有必要严格管制此类物质的进出口并严格管理以多氯联苯为基质的电力电容器、变压器及其他有关装置和由此产生的含多氯联苯的废物，谨防随意拆卸废弃多氯联苯电容器造成的污染。

本文参照EPA3546、EPA8082A方法，对多聚物中的多氯联苯进行定性和定量分析，结果选择性，重现性且线性关系好。

关键词： GCMS 多聚物 多氯联苯

仪器

岛津GCMS-QP2010 Plus气相色谱-质谱联用仪，EI离子源，AOC-20i自动进样器，GCMSsolution工作站；

仪器分析条件

色谱柱：Rtx-5ms 30m x 0.25mmID x 0.25μm，

色谱柱温度: 120℃(0.5min)→10℃/min→

200℃(2min)→20℃/min→290℃(10min)

进样口温度:280℃

色谱-质谱接口温度:280℃

载气:氦气 流速:1.5mL/min

进样方式:不分流进样,

进样量: 1μL

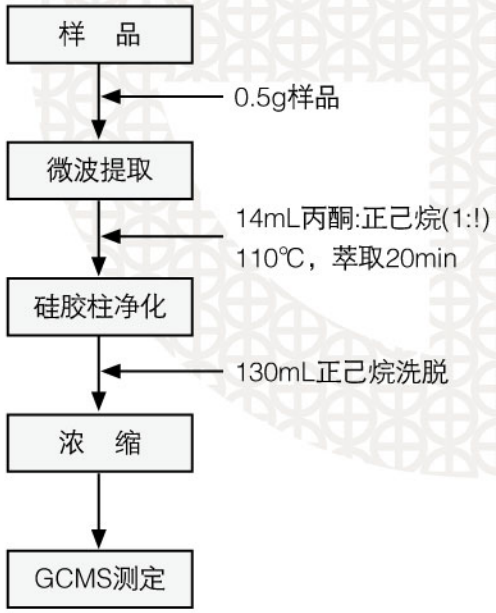
分流比：20:1

离子源温度:250℃

线速度：46.0cm/sec

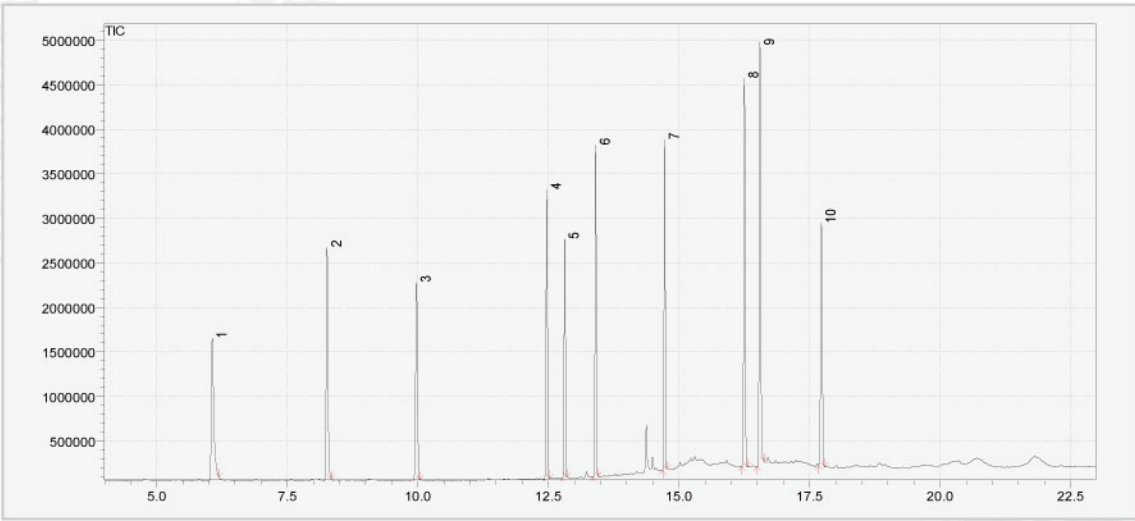
采用SCAN全扫描模式进行定性分析，采用SIM选择离子模式进行定量分析。

样品的制备



分析结果

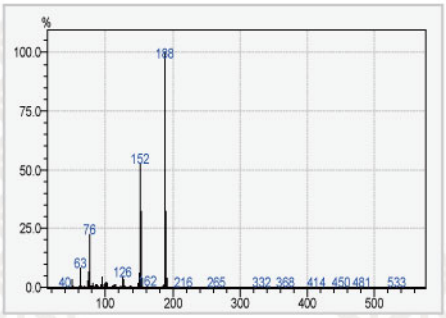
1、10种多氯联苯标准的TIC图



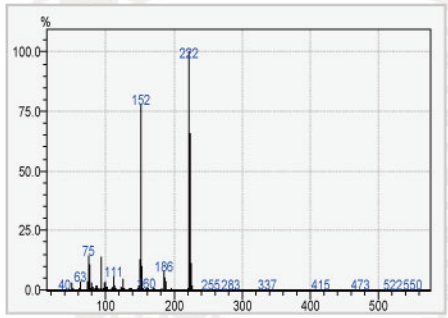
1. 2-Chlorobiphenyl,　2. 2,3-Dichlorobiphenyl,　3. 2,4,5-Trichlorobiphenyl,
4. 2,3,4,5-Terachlorobip-henyl,　5. 2,2`,4,4`,6,6`-Hexachlorobiphenyl,　6. 2,3,4,5,6-Pentachlorobiphenyl,
7. 2,2`,3,4,4`,5,6`-Heptachlorobiphenyl,　8. 2,2`,3,3`,4,5,5`,6,6`-Nonachlorobiphenyl,
9. 2,2`,3,3`4,4`,5,5`-Octachlorobiphenyl,　10. 2,2`,3,3`,4,4`,5,5`,6,6`-Decachlorobiphenyl

2、10种多氯联苯全扫描质谱图

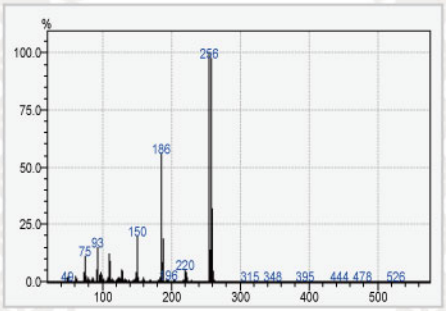
2-Chlorobiphenyl



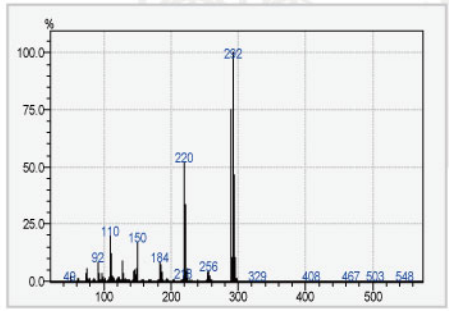
2,3-Dichlorobiphenyl



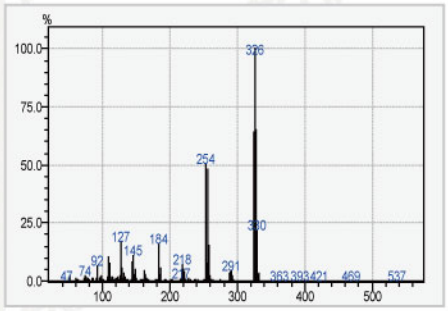
2,4,5-Trichlorobiphenyl



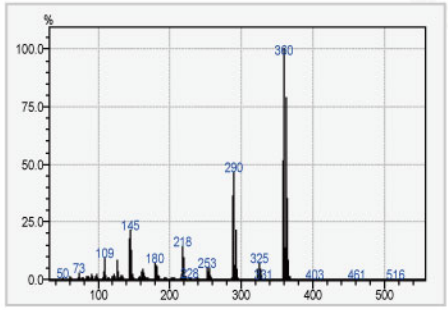
2,3,4,5-Terachlorobip-henyl



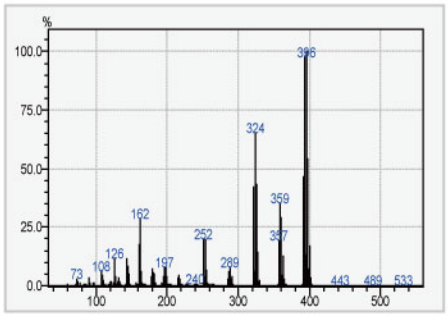
2,3,4,5,6–Pentachlorobiphenyl



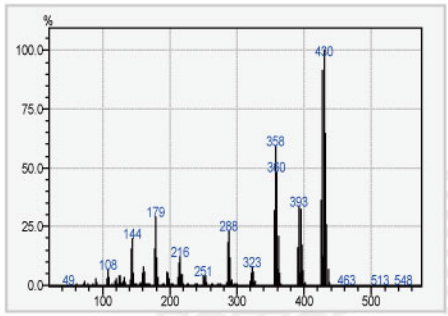
2,2`,4,4`,6,6`–Hexachlorobipheny



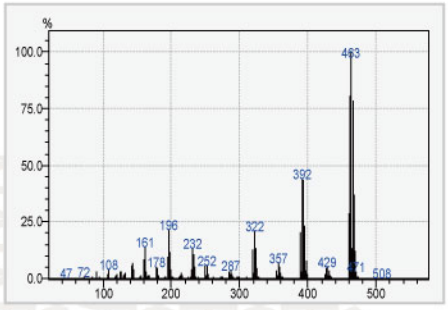
2,2`,3,4,4`,5,6`–Heptachlorobiphenyl



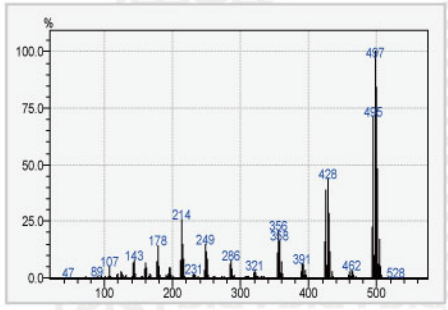
2,2`,3,3`4,4`,5,5`–Octachlorobiphenyl



2,2`,3,3`,4,5,5`,6,6`–Nonachlorobiphenyl



2,2`,3,3`,4,4`,5,5`,6,6`–Decachlorobiphenyl



3. 标准曲线

以5.0ppm，2.5ppm，1.0ppm，0.1ppm标准系列建立的线性回归方程见表1，线性关系良好。

表1 标准曲线方程和相关系数

化合物名称	保留时间	定量离子	线性方程	线性相关系数
2-Chlorobiphenyl	6.058min	187.95	Y = 349828.8X - 22789.89	0.9991972
2,3-Dichlorobiphenyl	8.258min	221.90	Y = 304542.1X - 13128.06	0.9994968
2,4,5-Trichlorobiphenyl	9.975min	255.85	Y = 237188.0X - 13282.75	0.9993418
2,3,4,5-Terachlorobiphenyl	12.467min	291.85	Y = 239958.1X - 3971.363	0.9997073
2,2`,4,4`,6,6`-Hexachlorobiphenyl	12.817min	359.70	Y = 175276.8X + 2766.581	0.9996244
2,3,4,5,6-Pentachlorobiphenyl	13.408min	325.75	Y = 229614.2X + 7097.413	0.99983
2,2`,3,4,4`,5,6`-Heptachlorobiphenyl	14.725min	395.65	Y = 119834.5X + 18692.88	0.9978227
2,2`,3,3`,4,5,5`,6,6`-Nonachlorobiphenyl	16.250min	463.55	Y = 235469.4X + 34453.75	0.9985562
2,2`,3,3`4,4`,5,5`-Octachlorobiphenyl	16.550min	429.60	Y = 215072.4X + 29297.09	0.9986996
2,2`,3,3`,4,4`,5,5`,6,6`-Decachlorobiphenyl	17.725min	497.50	Y = 177582.6X + 4908.973	0.9998875

4. 重复性测试：

以5ppm的标准溶液连续进样5次，进行重复性实验，保留时间和峰面积重现好。结果见表2、表3。

表2 保留时间重现性(n=5)

化合物名称	1	2	3	4	5	平均值	相对标准偏差
2-Chlorobiphenyl	6.062min	6.062min	6.063min	6.065min	6.063min	6.063min	0.02%
2,3-Dichlorobiphenyl	8.265min	8.265min	8.265min	8.266min	8.265min	8.265min	0.005%
2,4,5-Trichlorobiphenyl	9.975min	9.976min	9.977min	9.977min	9.976min	9.976min	0.008%
2,3,4,5-Terachlorobiphenyl	12.472min	12.472min	12.473min	12.471min	12.471min	12.472min	0.007%
2,2`,4,4`,6,6`-Hexachlorobiphenyl	12.817min	12.818min	12.818min	12.817min	12.817min	12.817min	0.004%
2,3,4,5,6-Pentachlorobiphenyl	13.410min	13.411min	13.410min	13.410min	13.410min	13.410min	0.003%
2,2`,3,4,4`,5,6`-Heptachlorobiphenyl	14.730min	14.732min	14.732min	14.730min	14.731min	14.731min	0.007%
2,2`,3,3`,4,5,5`,6,6`-Nonachlorobiphenyl	16.257min	16.256min	16.257min	16.255min	16.255min	16.256min	0.006%
2,2`,3,3`4,4`,5,5`-Octachlorobiphenyl	16.554min	16.553min	16.554min	16.553min	16.552min	16.553min	0.005%
2,2`,3,3`,4,4`,5,5`,6,6`-Decachlorobiphenyl	17.732min	17.733min	17.732min	17.731min	17.729min	17.731min	0.009%

表3 面积重现性(n=5)

化合物名称	1	2	3	4	5	平均值	相对标准偏差
2-Chlorobiphenyl	1809594	1752606	1742859	1746964	1739361	1758277	1.66%
2,3-Dichlorobiphenyl	1564066	1519110	1509280	1523472	1511661	1525518	1.46%
2,4,5-Trichlorobiphenyl	1220309	1184447	1172721	1185249	1177676	1188080	1.58%
2,3,4,5-Terachlorobiphenyl	1236471	1182526	1192632	1203433	1205431	1204099	1.69%
2,2`,4,4`,6,6`-Hexachlorobiphenyl	891628	864840	882234	883439	813127	867054	3.65%
2,3,4,5,6-Pentachlorobiphenyl	1171363	1160603	1145649	1156094	1084491	1143640	3.00%
2,2`,3,4,4`,5,6`-Heptachlorobiphenyl	672304	661146	606826	606701	602865	629968	5.37%
2,2`,3,3`,4,5,5`,6,6`-Nonachlorobiphenyl	1197849	1181976	1065974	1196562	1052116	1138895	6.44%
2,2`,3,3`4,4`,5,5`-Octachlorobiphenyl	1089130	1013166	967140	1091215	951676	1022465	6.44%
2,2`,3,3`,4,4`,5,5`,6,6`-Decachlorobiphenyl	852942	817565	795251	892336	895864	850792	5.24%

5. 样品测试

按本方法测定实际塑料样品，未检测出多氯联苯，得到的图谱见图1所示。

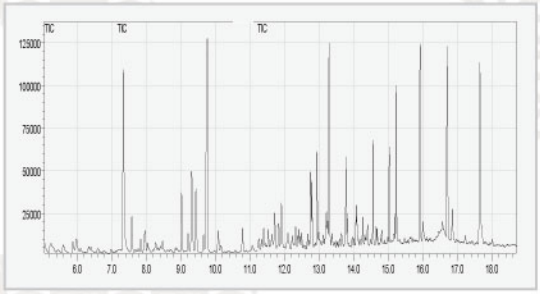


图1塑料样品TIC

讨论

采用岛津公司的GCMS-QP2010 Plus气相质谱联用仪对多氯联苯进行了分析，结果重现性和线性关系良好，定量准确，完全能满足企业及检测机构所要求的精确定性定量分析的要求。