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顶空–GCMS测定土壤中挥发性有机物含量

No.GCMS-039

摘要： 土壤样品加入基质修正液，经顶空处理后，用气相色谱质谱法进行定性和定量分析。

关键词： 土壤 基质修正液 顶空 气相色谱质谱法

挥发性有机物（VOCs）的主要成分包括烃类、氧烃类、含卤烃类、氮烃类、硫烃类及低沸点多环芳烃类等有机物。近些年来土壤中挥发性有机物污染现象越来越严重。有机溶剂泄露、工厂废液处理不当等均会导致土壤和地下水的污染。而VOCs普遍具有迁移性、持久性和毒性，对人体具有致畸变、致癌等作用，对环境存在严重污染。

环境样品中残留的各种挥发性有机物的含量都比较低，国外环境监测中VOCs现行检测方法主要有直接进样法、顶空–气相色谱/质谱法、吹扫捕集–气相色谱/质谱法。国内标准HJ 350–2007展览会用地土壤环境质量评价标准对土壤中VOCs测试是采用吹扫捕集–气相色谱/质谱法，而顶空分析土壤中54种VOCs国家标准及相关文献报导甚少。

本文参照EPA5021，在土壤样品中加入基质修正液，经顶空处理后，用气相色谱质谱法对54种VOCs进行定性和定量分析。方法操作简便、分析快捷、准确灵敏、干扰少，重现性好。

实验部分

1、仪器与试剂

GCMS–QP2010 Plus气相色谱–质谱联用仪，

AOC–5000自动进样器，

GCMS–Solution工作站，54种VOCs混合标液购于安谱公司，氯化钠为优级纯、水为超纯水。

2、 分析条件

2.1 色谱条件

色谱柱：Rtx–624，60m × 0.32mm × 1.8 μ m

柱温程序：40℃(1min)–4℃/min–120℃(1min)
–5℃/min–220℃(3min)

恒线速度：31.1cm/sec　　进样模式：分流进样

进样量：1mL　　分流比：10

进样口温度：200℃　　接口温度：220℃

离子源温度：200℃　　扫描范围：40~300amu

2.2 顶空条件

平衡温度：50℃　　平衡时间：40min

注射器温度：60℃　　震荡速度：250rpm

冲洗时间：1 min

结果与讨论

1、54种挥发性有机物的色谱图

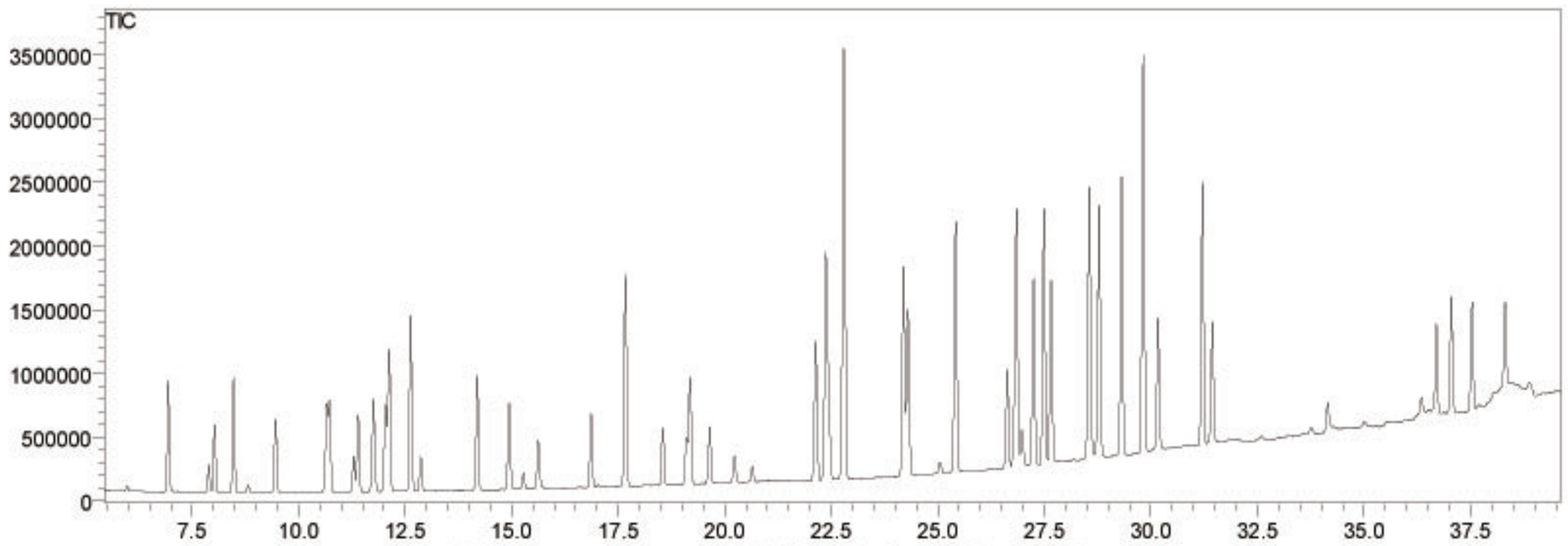


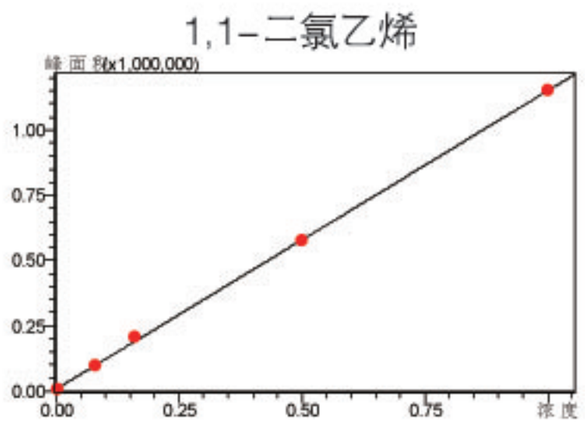
图1 0.1ppm54种挥发性有机物的TIC图

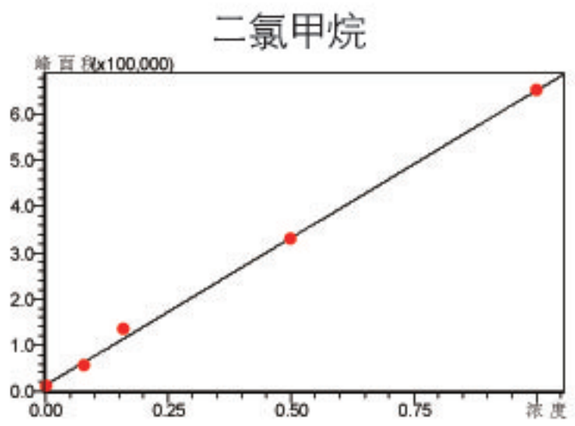
表1 54种挥发性有机物名称及保留时间

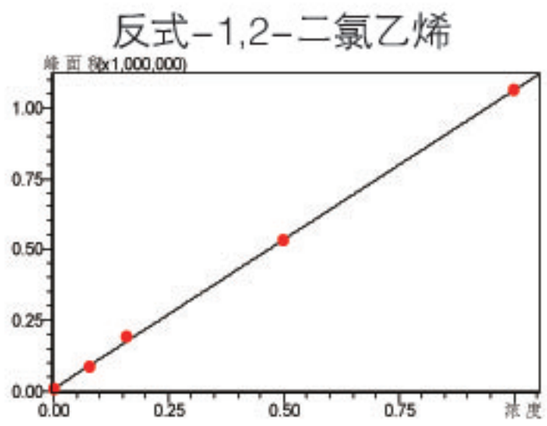
化合物名称	保留时间	化合物名称	保留时间	化合物名称	保留时间
1,1-二氯乙烯	6.942min	甲苯	17.667min	1,2,3-三氯丙烷	26.967mi
二氯甲烷	8.025min	顺式-1,3-二氯丙烯	18.542min	2-氯甲苯	27.242mi
反式-1,2-二氯乙烯	8.475min	1,1,2-三氯乙烷	19.100min	1,2,4-三甲苯	27.483mi
1,1-二氯乙烷	9.458min	四氯乙烯	19.183min	4-氯甲苯	27.658mi
2,2-二氯丙烷	10.658min	1,3-二氯丙烷	19.642min	叔丁苯	28.550mi
顺式-1,2-二氯乙烯	10.725min	二溴氯甲烷	20.225min	1,3,5-三甲苯	28.783mi
溴氯甲烷	11.292min	1,2-二溴乙烷	20.650min	仲丁苯	29.308mi
氯仿	11.400min	氯苯	22.133min	4-异丙基甲苯	29.817mi
1,1,1-三氯乙烷	11.758min	乙苯	22.375min	1,4-二氯苯	29.825mi
四氯化碳	12.042min	1,1,1,2-四氯乙烷	22.433min	1,3 二氯苯	30.158mi
1,1-二氯丙烯	12.125min	对+间-二甲苯	22.792min	正丁苯	31.200mi
苯	12.625min	邻二甲苯	24.192min	1,2-二氯苯	31.433mi
1,2-二氯乙烷	12.867min	苯乙烯	24.300min	1,2-二溴-3-氯丙烷	34.142mi
三氯乙烯	14.192min	溴仿	25.050min	1,2,4-三氯苯	36.692mi
1,2-二氯丙烷	14.942min	异丙苯	25.408min	六氯丁二烯	37.042mi
二溴甲烷	15.275min	溴苯	26.625min	萘	37.533mi
溴二氯甲烷	15.625min	1,1,2,2-四氯乙烷	26.750min	1,2,3-三氯苯	38.308mi
反式-1,3-二氯丙烯	16.867min	正丙苯	26.842min		

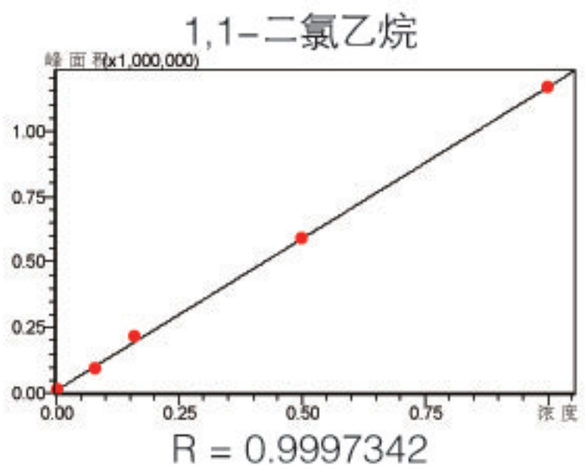
2、线性范围

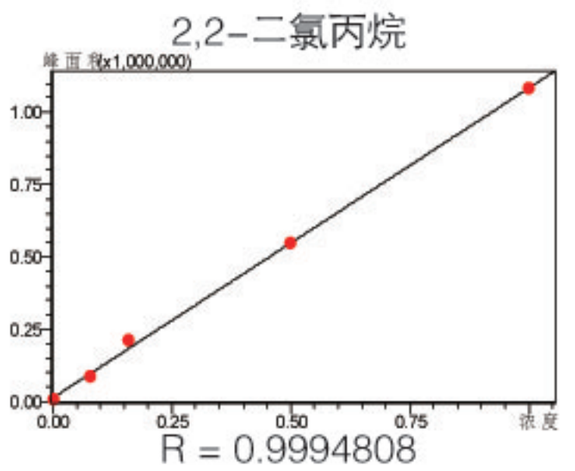
54种VOCs混合标液用甲醇配制成一标准储备液，依此标准储备液配制出系列浓度，工作曲线则是将标准样加入到含10mL基质修正液（基质修正液是用500mL纯水用磷酸调成pH为2，再加入180gNaCl溶解。）的顶空瓶中。得系列浓度为0.004、0.08、0.16、0.5、1.0ppm。以SIM方式采集，各组分定量离子见表2，各组分标准曲线及线性相关系数如下所示：

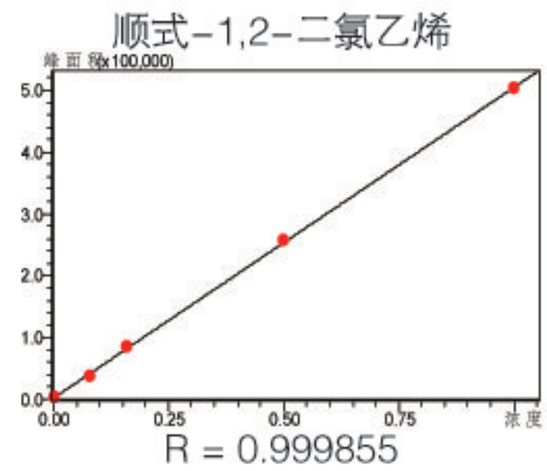


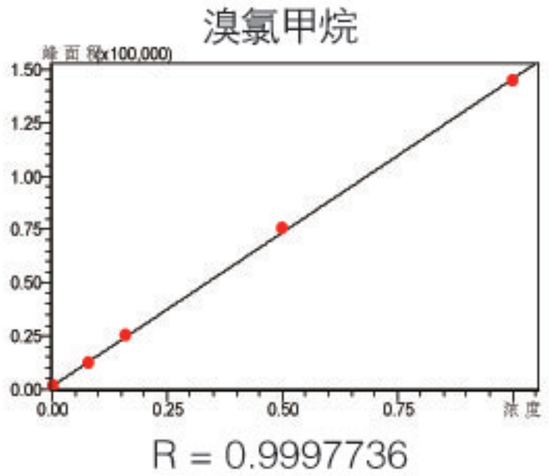


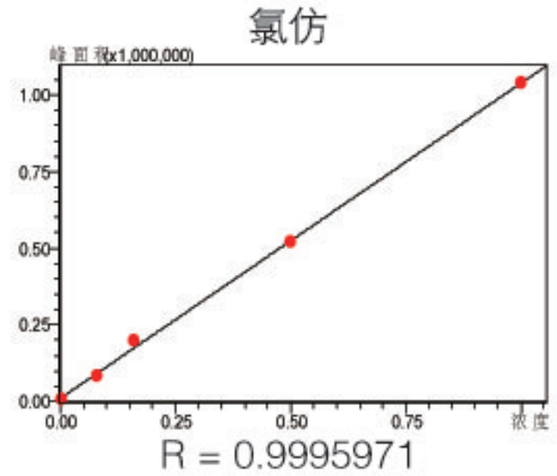


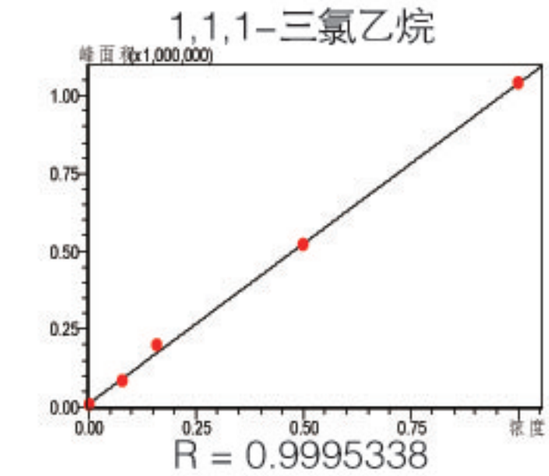




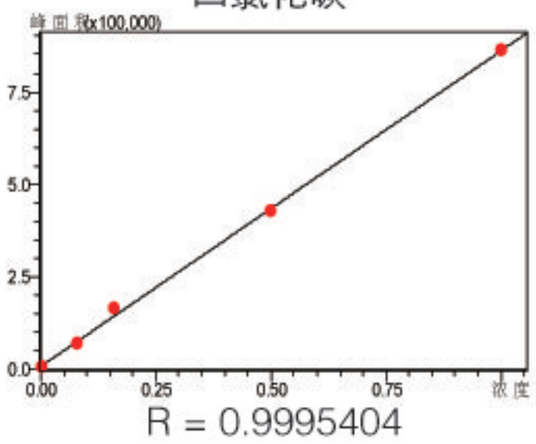








四氯化碳



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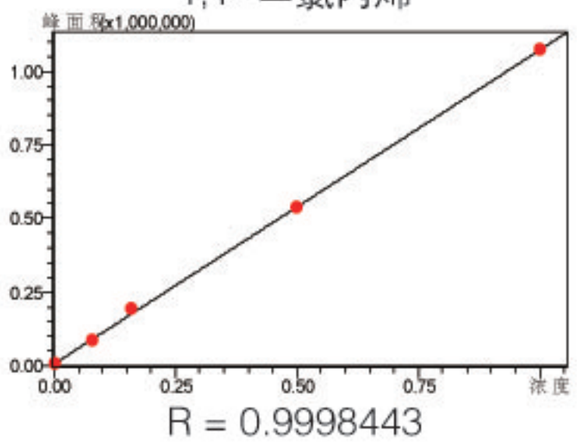
1,1-二氯丙烯



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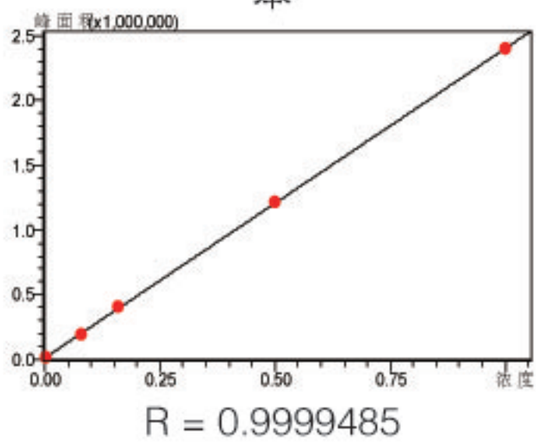
苯



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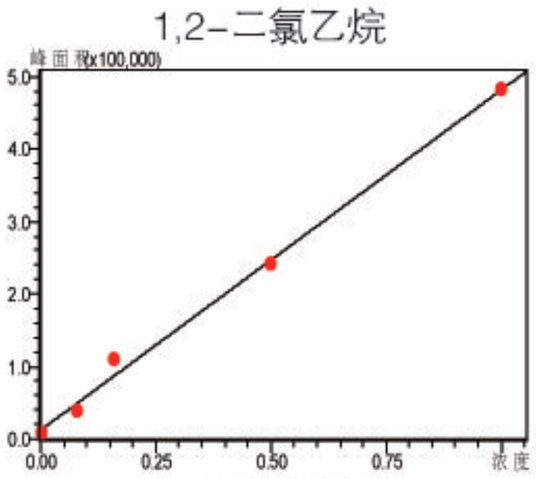

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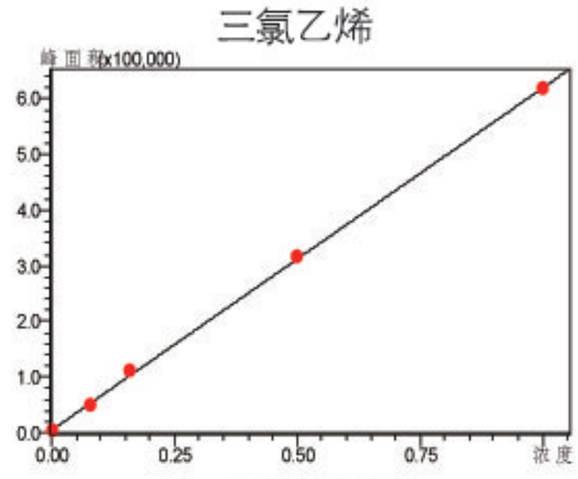
三氯乙烯



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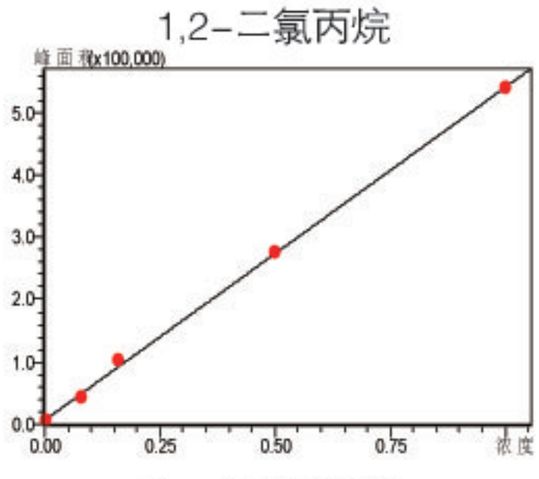

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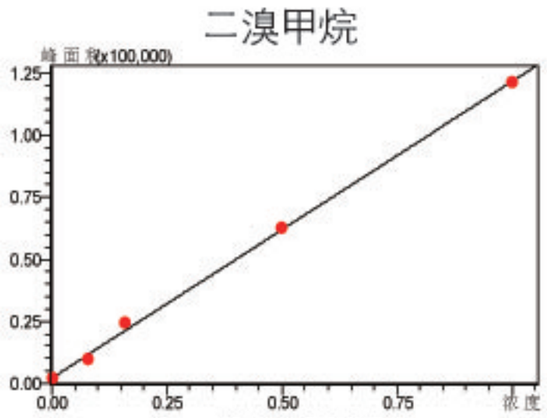
二溴甲烷



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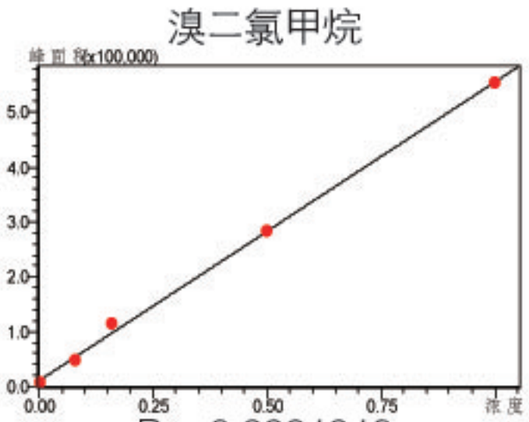
溴二氯甲烷



R = 0.9991918

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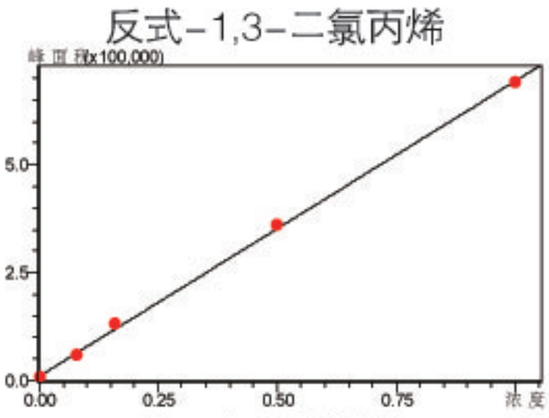

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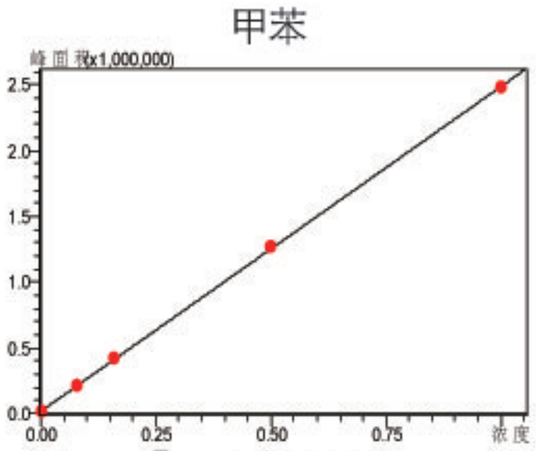
甲苯



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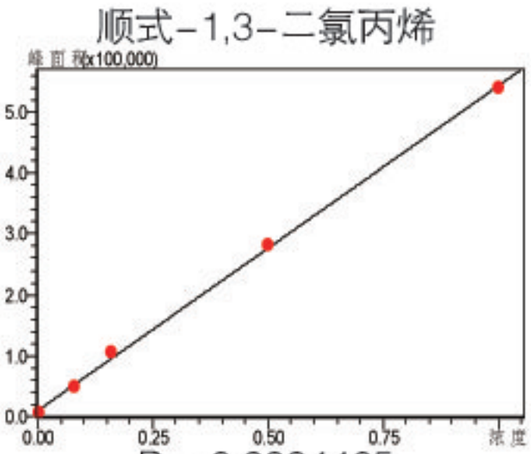
顺式-1,3-二氯丙烯



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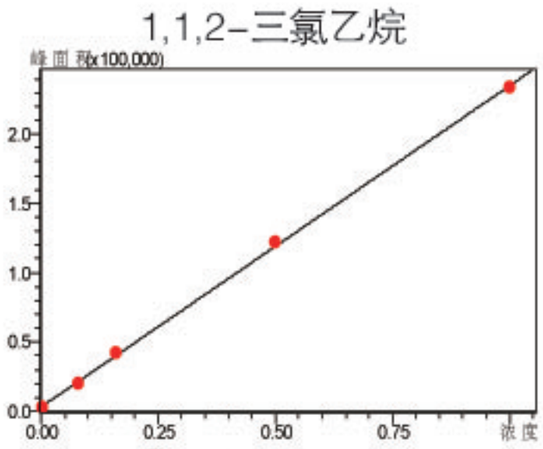
1,1,2-三氯乙烷



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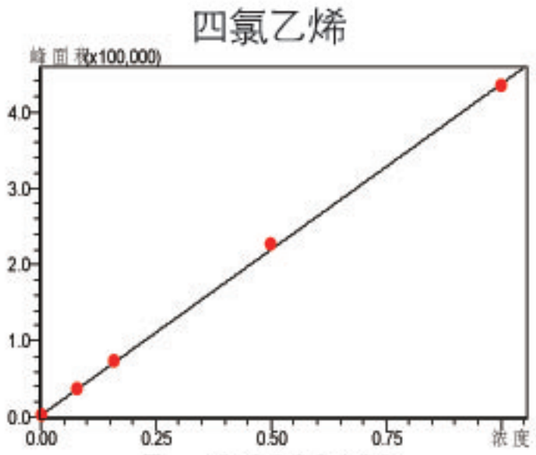
四氯乙烯



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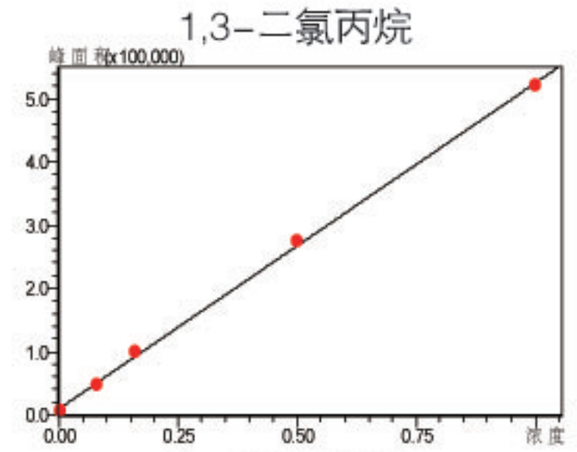

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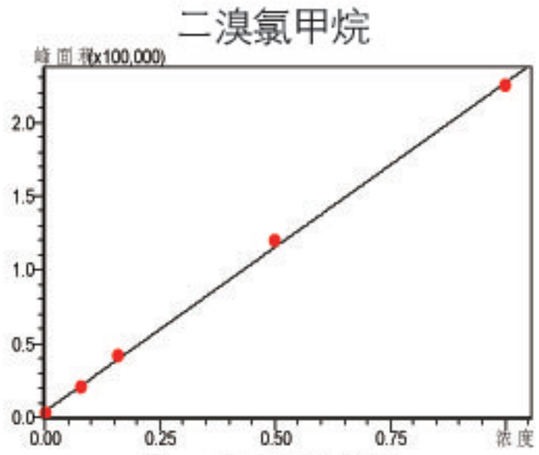
二溴氯甲烷



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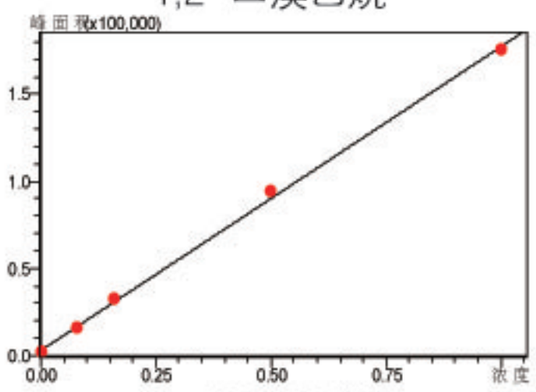

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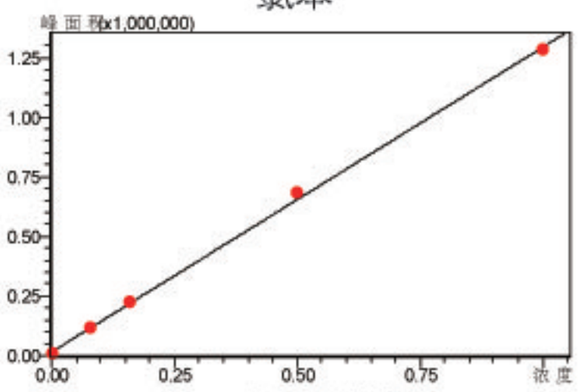
氯苯



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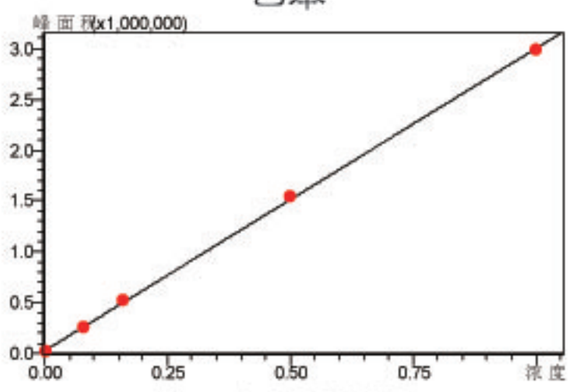

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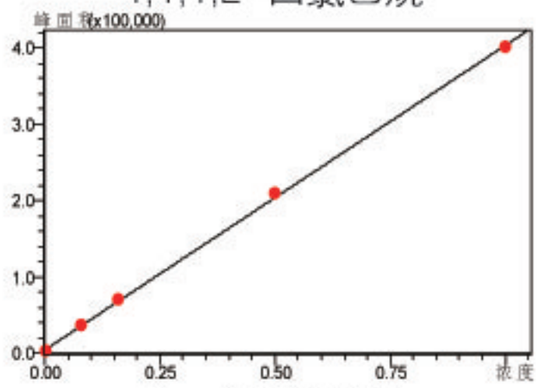
1,1,1,2-四氯乙烷



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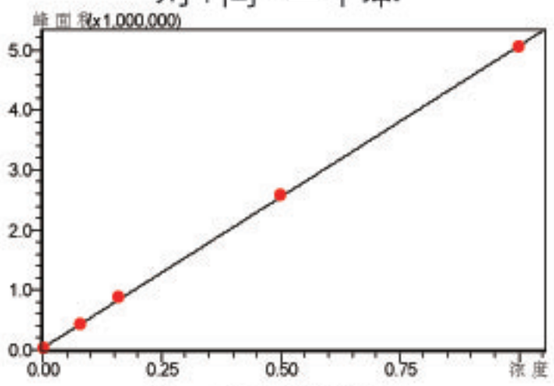
对+间-二甲苯



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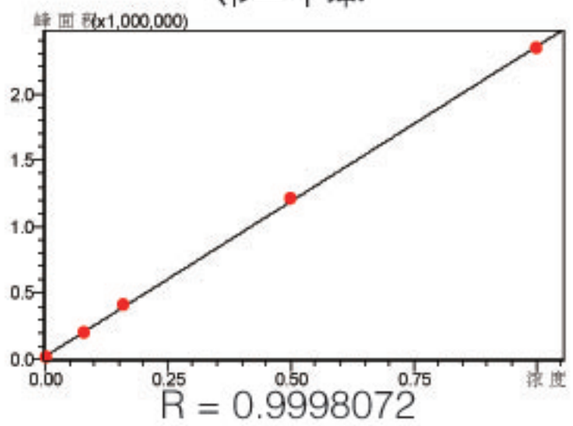
邻二甲苯



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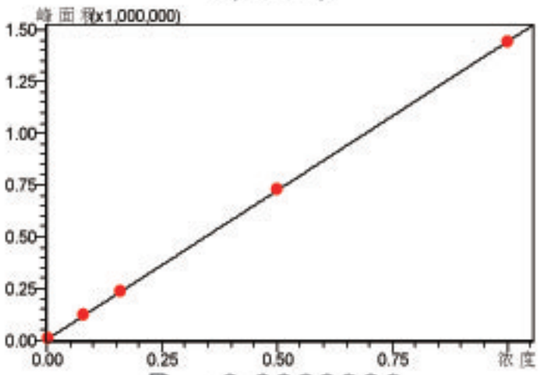
苯乙烯



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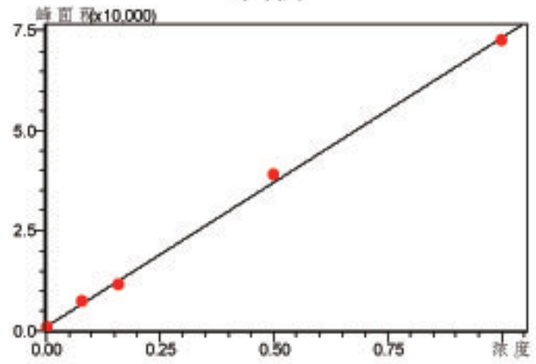

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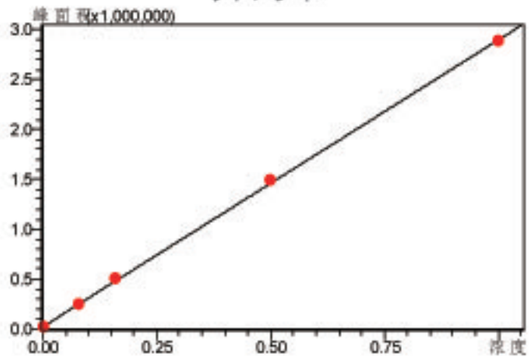
异丙苯



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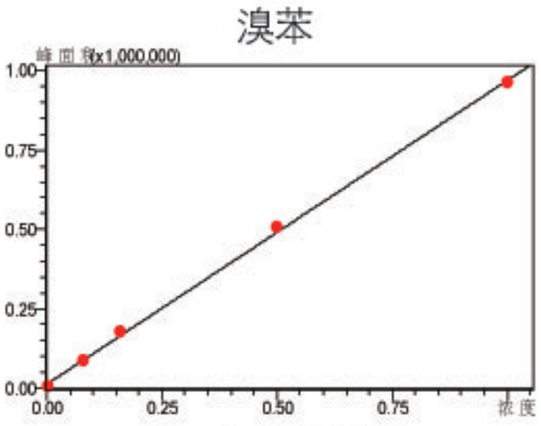
溴苯



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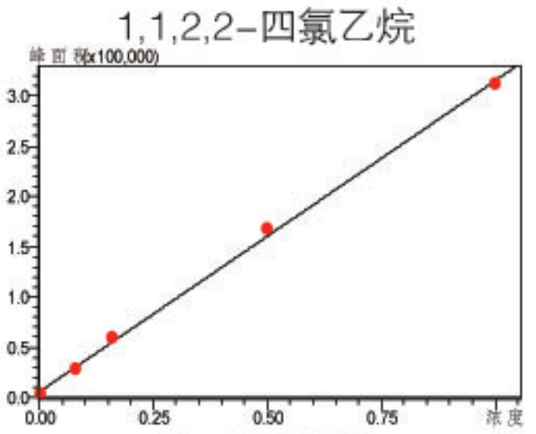

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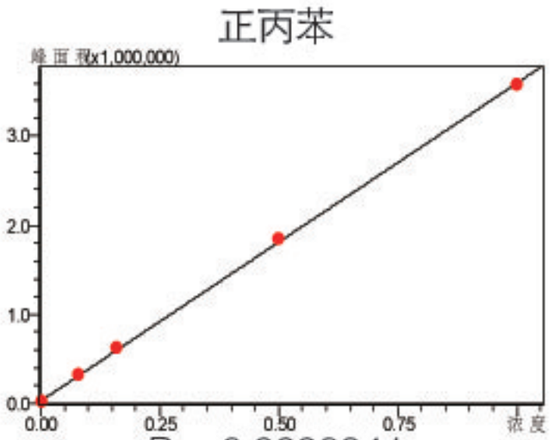
正丙苯



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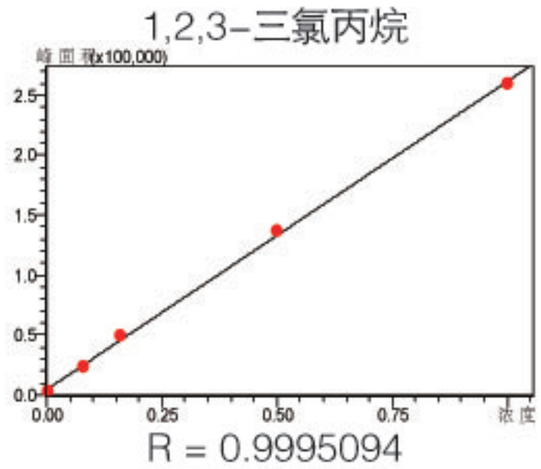

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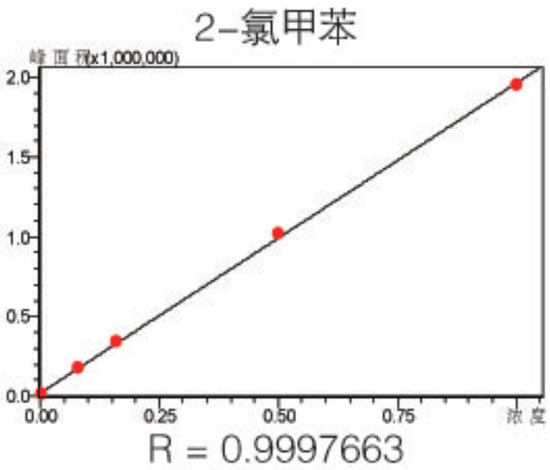
2-氯甲苯



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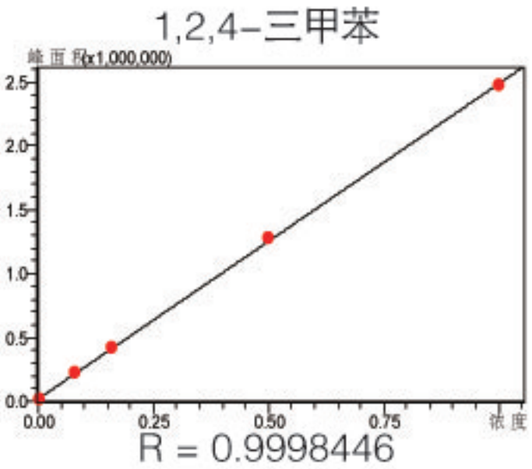

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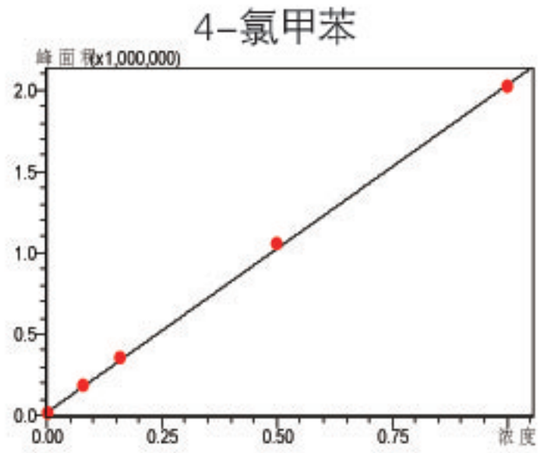
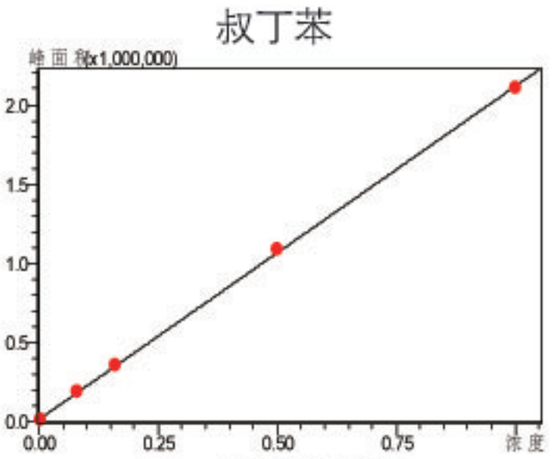


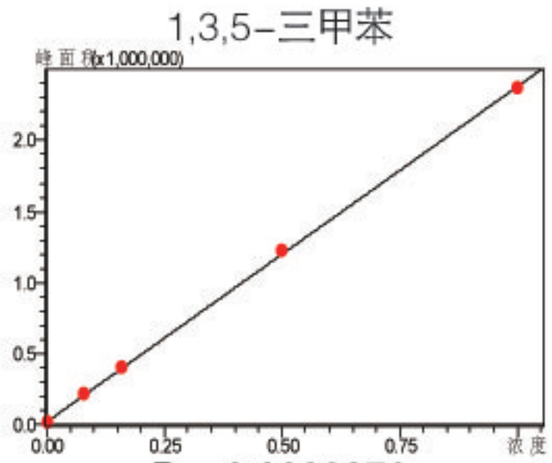
R = 0.9997627

叔丁苯



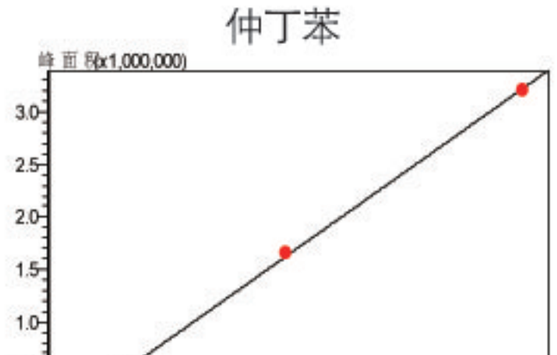
R = 0.9998765

1,3,5-三甲苯



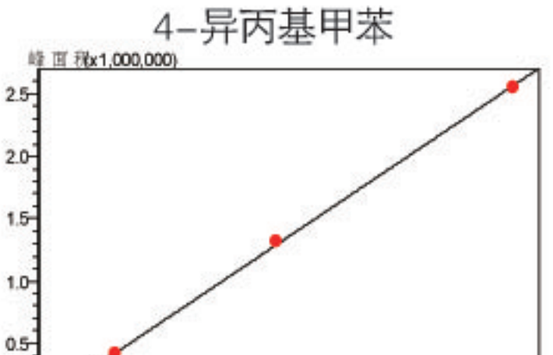
R = 0.9998372

仲丁苯



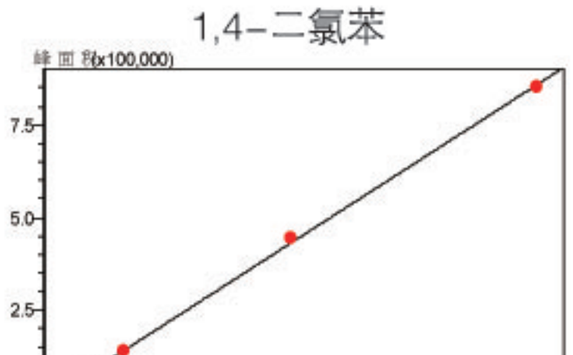
R = 0.9998668

4-异丙基甲苯



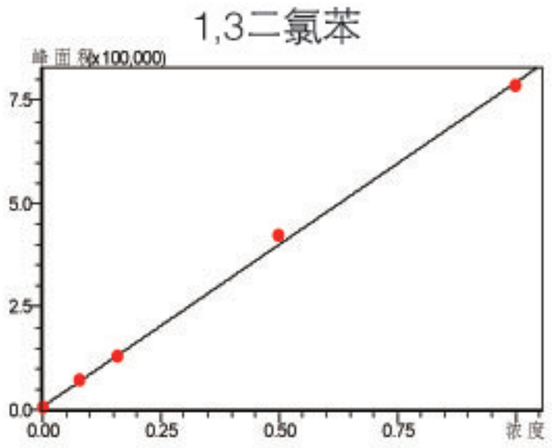
R = 0.9998835

1,4-二氯苯



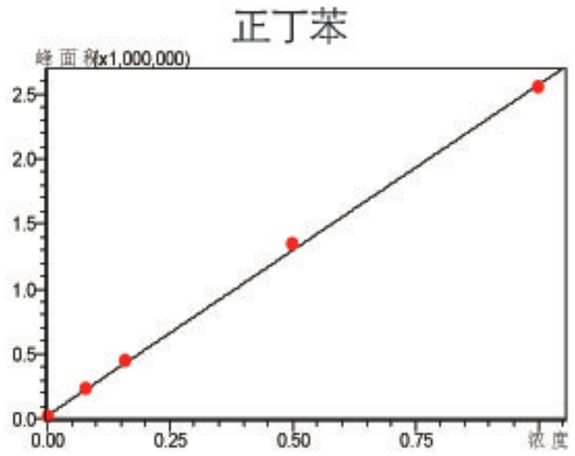
R = 0.9997799

1,3二氯苯



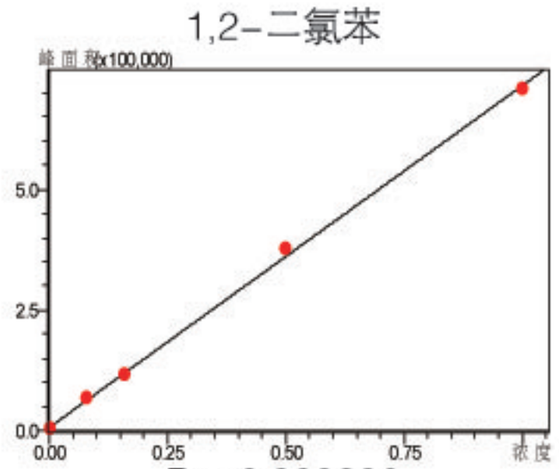
R = 0.9993706

正丁苯



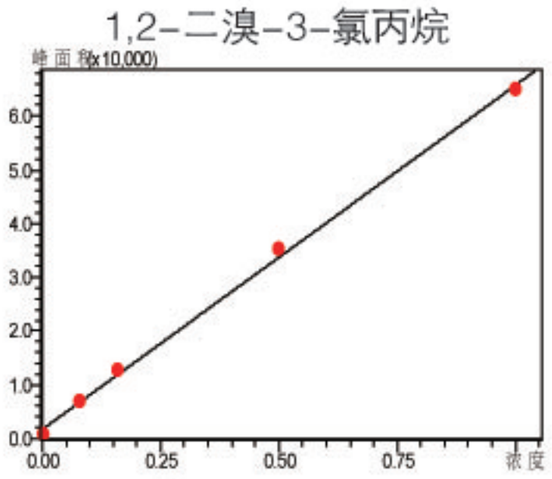
R = 0.9996953

1,2-二氯苯



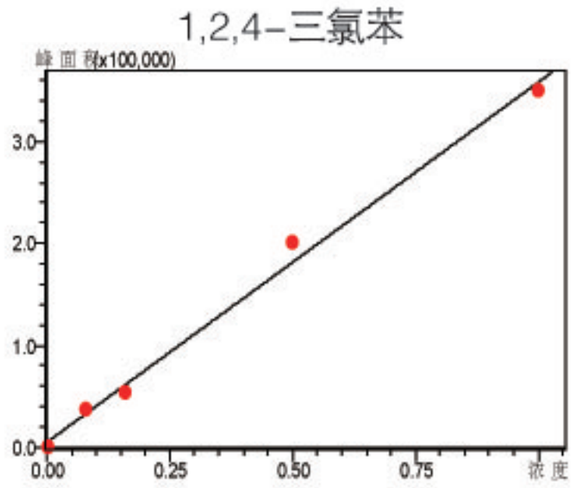
R = 0.999396

1,2-二溴-3-氯丙烷



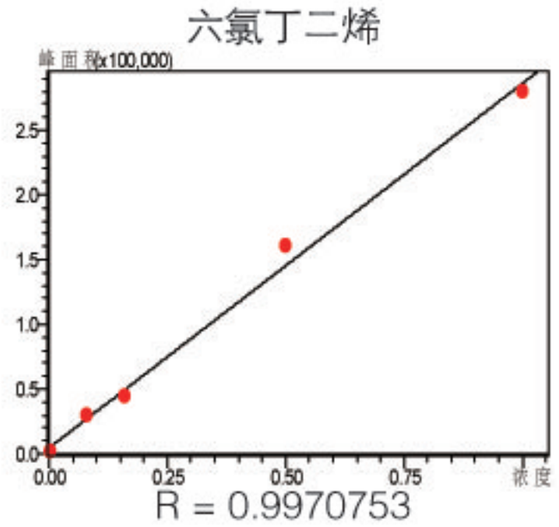
R = 0.999092

1,2,4-三氯苯



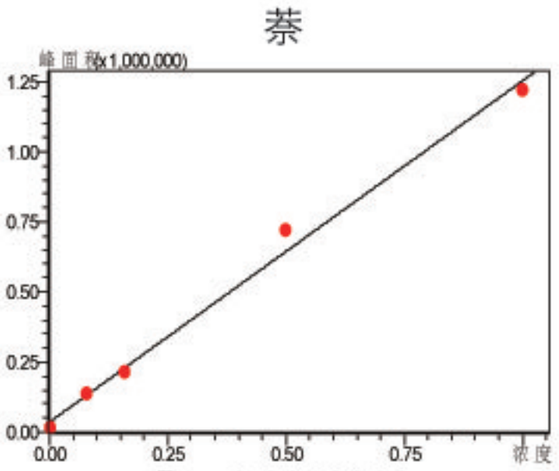
R = 0.9966133

六氯丁二烯



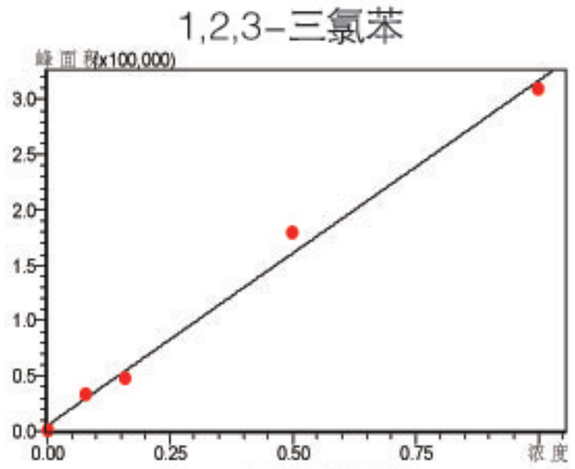
R = 0.9970753

萘



R = 0.9959826

1,2,3-三氯苯



R = 0.9963477

表2 54种挥发性有机物定量离子

化合物名称	定量离子	化合物名称	定量离子	化合物名称	定量离子
1,1-二氯乙烯	61	甲苯	91	1,2,3-三氯丙烷	75
二氯甲烷	49	顺式-1,3-二氯丙烯	75	2-氯甲苯	91
反式-1,2-二氯乙烯	61	1,1,2-三氯乙烷	97	1,2,4-三甲苯	105
1,1-二氯乙烷	63	四氯乙烯	129	4-氯甲苯	91
2,2-二氯丙烷	77	1,3-二氯丙烷	76	叔丁苯	119
顺式-1,2-二氯乙烯	96	二溴氯甲烷	129	1,3,5-三甲苯	105
溴氯甲烷	130	1,2-二溴乙烷	107	仲丁苯	105
氯仿	83	氯苯	112	4-异丙基甲苯	119
1,1,1-三氯乙烷	97	乙苯	91	1,4-二氯苯	146
四氯化碳	117	1,1,1,2-四氯乙烷	131	1,3 二氯苯	146
1,1-二氯丙烯	75	对+间-二甲苯	91	正丁苯	91
苯	78	邻二甲苯	91	1,2-二氯苯	146
1,2-二氯乙烷	62	苯乙烯	104	1,2-二溴-3-氯丙烷	75
三氯乙烯	95	溴仿	173	1,2,4-三氯苯	180
1,2-二氯丙烷	63	异丙苯	105	六氯丁二烯	225
二溴甲烷	93	溴苯	77	萘	128
溴二氯甲烷	83	1,1,2,2-四氯乙烷	83	1,2,3-三氯苯	180
反式-1,3-二氯丙烯	75	正丙苯	91		

3、重现性测试

取0.05ppm标液进行重现性测试，结果见表3、表4。结果表明重现性良好。

表3 面积重现性测试（ n=5 ）

化合物名称	1	2	3	4	5	RSD（%）
1,1-二氯乙烯	850557	898534	925351	896586	923376	3.36%
二氯甲烷	476927	503512	521318	501087	518687	3.51%
反式-1,2-二氯乙烯	821335	868533	897067	866251	894826	3.51%
1,1-二氯乙烷	907632	964276	996910	961088	993709	3.72%
2,2-二氯丙烷	770602	802021	814365	794258	806714	2.10%
顺式-1,2-二氯乙烯	483504	515836	532820	497889	517577	3.75%
溴氯甲烷	147108	154962	159795	150039	154814	3.20%
氯仿	677872	717527	738597	712732	735470	3.39%
1,1,1-三氯乙烷	734380	776334	794159	769351	788339	3.03%
四氯化碳	612709	647822	662917	642097	655921	3.00%
1,1-二氯丙烯	870154	921631	945628	918305	942284	3.28%
苯	2192554	2326298	2403685	2322072	2397424	3.65%
1,2-二氯乙烷	288469	300875	309064	295165	302914	2.62%
三氯乙烯	554987	586702	602606	582626	598716	3.21%
1,2-二氯丙烷	458395	487299	503265	480313	496749	3.58%
二溴甲烷	103927	108657	111486	100164	103489	4.26%
溴二氯甲烷	407377	426110	437180	419836	431045	2.69%
反式-1,3-二氯丙烯	580525	605454	619655	600934	613441	2.48%
甲苯	2409847	2548202	2606178	2544219	2596915	3.09%
顺式-1,3-二氯丙烯	422226	436024	442841	430741	436580	1.78%
1,1,2-三氯乙烷	227333	238722	244194	224201	231355	3.52%
四氯乙烯	437167	460828	467307	454797	462267	2.56%
1,3-二氯丙烷	453739	475667	487944	469865	482301	2.78%
二溴氯甲烷	206090	213970	217609	204128	208858	2.66%
1,2-二溴乙烷	175512	183137	186410	173499	179456	2.96%
氯苯	1335550	1404085	1425908	1398567	1420769	2.59%
乙苯	2759168	2901460	2931374	2891382	2921111	2.42%
1,1,1,2-四氯乙烷	370072	387779	394578	380071	383827	2.38%
对+间-二甲苯	4432389	4651148	4699296	4643070	4684075	2.35%
邻二甲苯	2088892	2183337	2203559	2176948	2196540	2.14%
苯乙烯	1432012	1483962	1523457	1420740	1425914	3.08%
溴仿	81513	81263	80168	81203	77595	2.02%
异丙苯	2698473	2833472	2840493	2828784	2837084	2.18%
溴苯	824948	859630	868412	854158	863840	2.01%
1,1,2,2-四氯乙烷	297946	308707	314007	301844	306329	2.03%
正丙苯	3213863	3360234	3342760	3354361	3338201	1.84%
1,2,3-三氯丙烷	221901	231040	233610	221193	223347	2.52%
2-氯甲苯	1731301	1800336	1798652	1793159	1794367	1.65%
1,2,4-三甲苯	2201596	2294959	2276020	2290156	2272888	1.67%
4-氯甲苯	1748989	1818866	1808434	1813334	1803860	1.58%
叔丁苯	1899041	2014323	1996478	2009841	1991806	2.39%
1,3,5-三甲苯	2086591	2179026	2150983	2174210	2144862	1.72%

表4 保留时间重现性测试（ n=5 ）

化合物名称	1	2	3	4	5	RSD（%）
1,1-二氯乙烯	6.950min	6.958min	6.962min	6.962min	6.958min	0.070%
二氯甲烷	8.036min	8.046min	8.050min	8.050min	8.046min	0.071%
反式-1,2-二氯乙烯	8.481min	8.492min	8.496min	8.496min	8.492min	0.072%
1,1-二氯乙烷	9.466min	9.477min	9.482min	9.482min	9.477min	0.069%
2,2-二氯丙烷	10.668min	10.681min	10.687min	10.687min	10.681min	0.073%
顺式-1,2-二氯乙烯	10.735min	10.750min	10.754min	10.754min	10.750min	0.073%
溴氯甲烷	11.301min	11.316min	11.320min	11.320min	11.316min	0.069%
氯仿	11.403min	11.419min	11.424min	11.424min	11.419min	0.076%
1,1,1-三氯乙烷	11.765min	11.780min	11.785min	11.785min	11.780min	0.070%
四氯化碳	12.048min	12.066min	12.070min	12.070min	12.066min	0.076%
1,1-二氯丙烯	12.131min	12.146min	12.151min	12.151min	12.146min	0.068%
苯	12.633min	12.650min	12.656min	12.656min	12.650min	0.075%
1,2-二氯乙烷	12.870min	12.889min	12.892min	12.892min	12.889min	0.072%
三氯乙烯	14.196min	14.216min	14.222min	14.222min	14.216min	0.075%
1,2-二氯丙烷	14.946min	14.967min	14.973min	14.973min	14.967min	0.074%
二溴甲烷	15.279min	15.300min	15.307min	15.307min	15.300min	0.075%
溴二氯甲烷	15.624min	15.648min	15.653min	15.653min	15.648min	0.077%
反式-1,3-二氯丙烯	16.869min	16.892min	16.898min	16.898min	16.892min	0.071%
甲苯	17.670min	17.698min	17.703min	17.703min	17.698min	0.078%
顺式-1,3-二氯丙烯	18.547min	18.576min	18.581min	18.581min	18.576min	0.077%
1,1,2-三氯乙烷	19.100min	19.131min	19.137min	19.137min	19.131min	0.081%
四氯乙烯	19.184min	19.216min	19.221min	19.221min	19.216min	0.081%
1,3-二氯丙烷	19.644min	19.676min	19.679min	19.679min	19.676min	0.077%
二溴氯甲烷	20.226min	20.256min	20.266min	20.266min	20.261min	0.083%
1,2-二溴乙烷	20.646min	20.681min	20.684min	20.684min	20.681min	0.079%
氯苯	22.132min	22.173min	22.179min	22.179min	22.173min	0.090%
乙苯	22.371min	22.413min	22.419min	22.419min	22.413min	0.091%
1,1,1,2-四氯乙烷	22.437min	22.479min	22.484min	22.484min	22.479min	0.089%
对+间-二甲苯	22.791min	22.833min	22.837min	22.837min	22.833min	0.087%
邻二甲苯	24.191min	24.239min	24.245min	24.245min	24.239min	0.095%
苯乙烯	24.296min	24.342min	24.348min	24.348min	24.342min	0.091%
溴仿	25.049min	25.094min	25.098min	25.098min	25.094min	0.084%
异丙苯	25.410min	25.461min	25.466min	25.466min	25.461min	0.095%
溴苯	26.624min	26.677min	26.682min	26.682min	26.677min	0.094%
1,1,2,2-四氯乙烷	26.781min	26.837min	26.838min	26.838min	26.837min	0.094%
正丙苯	26.840min	26.894min	26.898min	26.898min	26.894min	0.093%
1,2,3-三氯丙烷	26.967min	27.014min	27.023min	27.023min	27.020min	0.089%
2-氯甲苯	27.242min	27.296min	27.300min	27.300min	27.296min	0.092%
1,2,4-三甲苯	27.480min	27.538min	27.543min	27.543min	27.538min	0.099%
4-氯甲苯	27.653min	27.708min	27.712min	27.712min	27.708min	0.092%
叔丁苯	28.544min	28.604min	28.606min	28.606min	28.604min	0.095%
1,3,5-三甲苯	28.774min	28.833min	28.838min	28.838min	28.833min	0.096%

4、回收率测试

分别取2g沙子和花园表层土于顶空瓶中，加入一定量的0.05ppm标液，再加入10mL基质修正液，顶空处理后，进行回收率测试，回收率在83%~105%之间。与EPA8260中选用沙子和花园表层土做回收率测试的表述是一致的。

结论

应用顶空技术对土壤中VOCs经前处理后，能最大限度的避免了VOCs的挥发损失。选择本方法测试完全能满足土壤中VOCs的分析灵敏度，方法操作简单，干扰少，重复性好。