

5 TD-GCMS 检测 VOCs 技术资料

5.1 仪器部件

热解吸仪	:	TD-20
气相色谱-质谱分析装置	:	GCMS-QP2010 Ultra

5.2 分析条件

5.2.1. TD 部

热解吸流量	:	60mL/min
热解吸时间	:	10min
阀温度	:	280°C
Trap 管冷却温度	:	-10°C
Trap 管加热温度	:	280°C
接口温度	:	250°C
样品吸附管温度	:	280°C
传输线温度	:	280°C

5.2.2. GC 部

色谱柱	:	Rtx-5 (Restek) 0.25mm×30m,df.0.25μm
程序升温条件	:	40°C(2min)→10°C/min→320°C(9min)
接口温度	:	280°C
柱前压	:	80kPa
分流比	:	100:1
载气	:	He (≧99.999%)
载气流量	:	1.4mL/min

5.2.3. MS 部

电离方式	:	EI
电子能量	:	70eV
离子源温度	:	260°C
分析模式	:	SCAN
质量范围	:	33~450 amu
扫描间隔	:	0.5sec
检测器电压	:	0.9kV

5.3 VOCs 样品在 TD 中热解吸流程图

VOCs 样品在 TD 中热解吸流程图见图 5 所示。下图左为第一次解吸，在通入氦气的条件下，将捕集好 VOCs 样品的 Tenax 采样管在 280°C 下热解吸，通过六通阀，然后在冷却至 -20°C 的 TD Trap 捕集管中富集。下图右为第二次解吸，在氦气氛围中，使富集了 VOCs 样品的 TD Trap 捕集管在 280°C 下热解吸，将解吸下来的气体导入 GC 中进行下一步检测。（在第二次解吸过程中继续往 Tenax 采样管中通入氦气，对 Tenax 采样管进行清洗老化。）

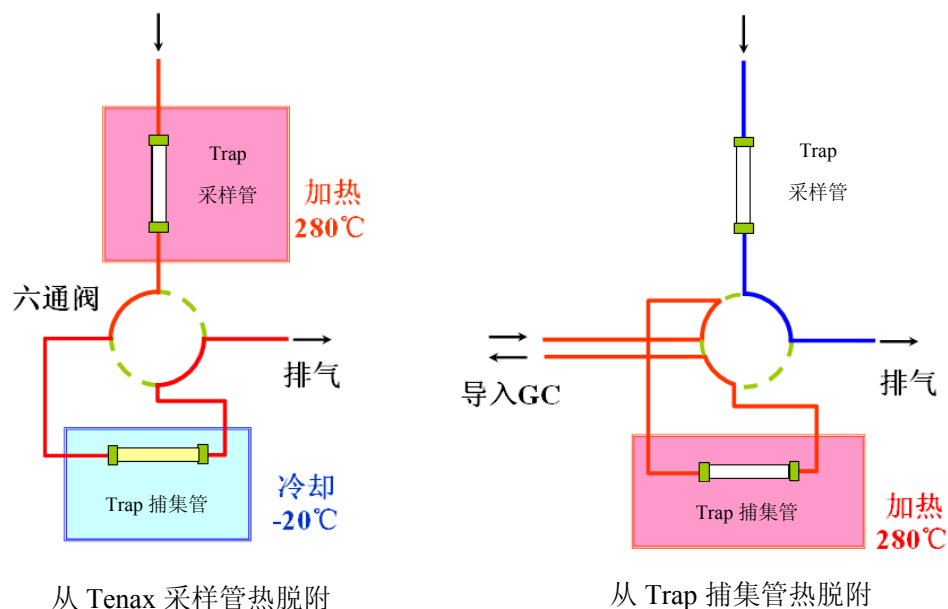


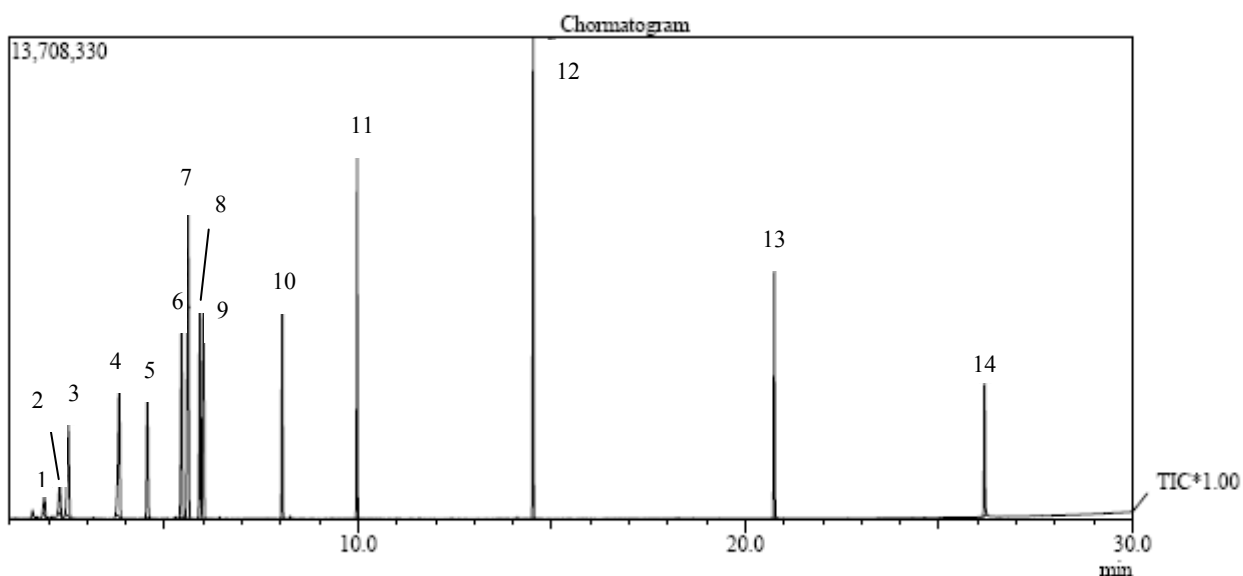
图 5. VOCs 样品在 TD 中热解吸流程图

检测方法

考虑到不同样品中 VOCs 组成成分的复杂性以及不同组分浓度差异很大，所以需要配置两条不同浓度梯度的混合标准曲线。混标中 VOCs 组成成分为 1,1-二氯乙烷, 1,2-二氯乙烷, 苯, 甲苯, 乙酸丁酯, 乙苯, *m,p*-二甲苯, *o*-二甲苯, 苯乙烯, *p*-二氯苯, 正十一烷, 正十四烷, DBP, DEHP, 仲丁威, 二嗪农, 毒死蜱；低浓度混标溶液的浓度梯度为 10、20、50、100、200 ng/采样管, 高浓度混标溶液的浓度梯度为 100、200、500、1000、2500 ng/采样管。配制后的混标溶液使用 TD-GCMS 进行分析检测。

5.4 检测结果

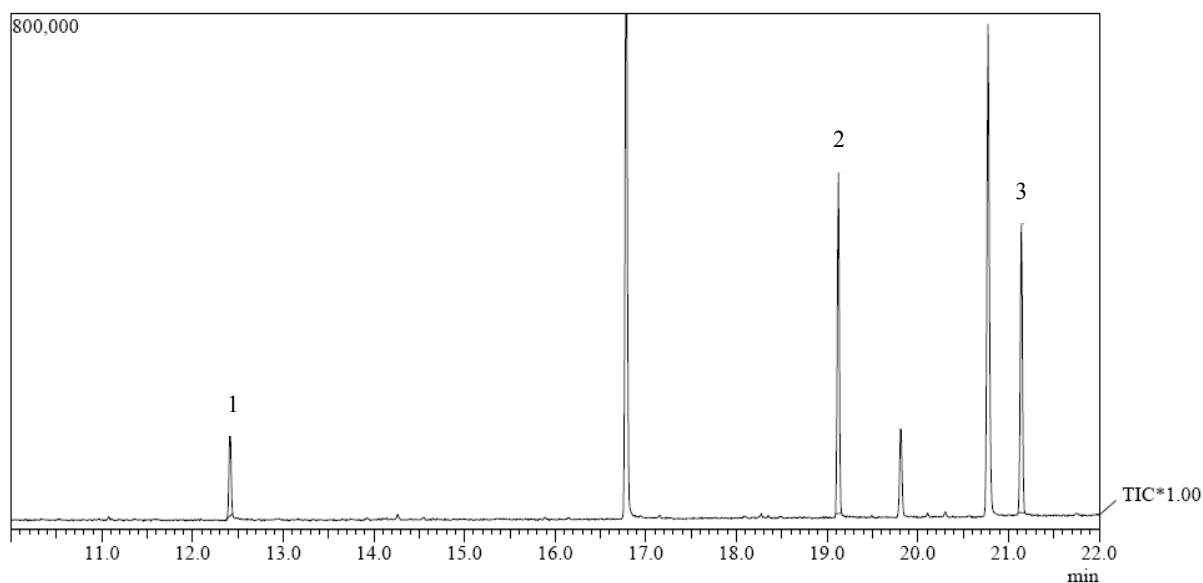
5.4.1 色谱图



14 种 VOCs 标准物质 TIC 图

No.	名称	保留时间	No.	名称	保留时间
1	1,1-二氯乙烷	1.884	8	苯乙烯 *	5.996
2	1,2-二氯乙烷	2.281	9	<i>o</i> -二甲苯 *	6.040
3	苯 *	2.436	10	<i>p</i> -二氯苯	8.081
4	甲苯 *	3.768	11	正十一烷	9.734
5	乙酸丁酯	4.573	12	正十四烷	14.340
6	乙苯 *	5.440	13	DBP	20.831
7	<i>m,p</i> -二甲苯 *	5.589	14	DEHP	26.143

注：带*为《乘用车内空气质量评价指南》中组分



3 种农残标准物质色谱图

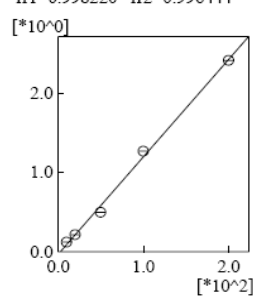
No.	名称	保留时间
1	仲丁威	12.413
2	二嗪农	19.124
3	毒死蜱	21.145

5.4.2 标准曲线

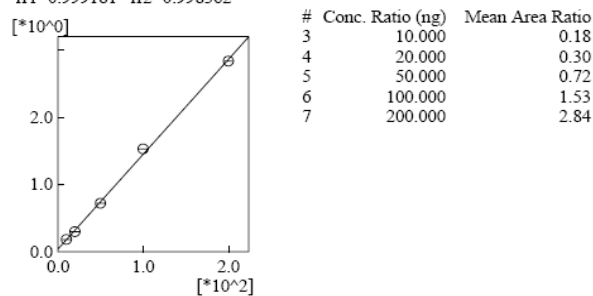
5.4.2.1 低浓度梯度标准曲线

Calibration

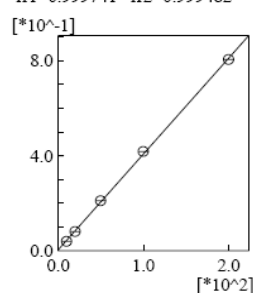
ID#:1 Mass:78.00 Name:Benzene (苯)
 $f(x)=0.012296*x-0.031770$
 $r1=0.998220$ $r2=0.996444$



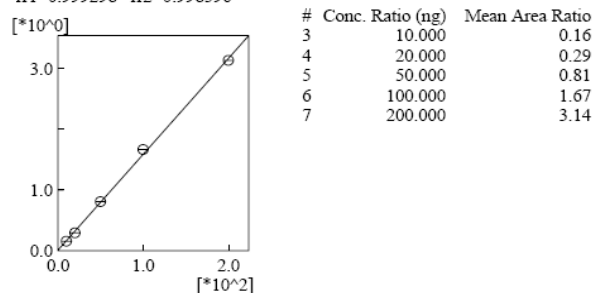
ID#:2 Mass:91.00 Name:Toluene (甲苯)
 $f(x)=0.014127*x+0.040255$
 $r1=0.999181$ $r2=0.998362$



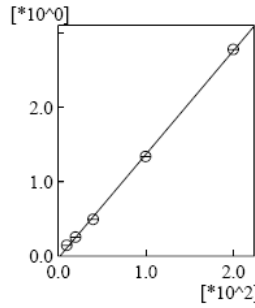
ID#:3 Mass:56.00 Name:n-Butyl acetate (乙酸丁酯)
 $f(x)=0.004037*x+0.004075$
 $r1=0.999741$ $r2=0.999482$



ID#:4 Mass:91.00 Name:Ethylbenzene (乙苯)
 $f(x)=0.015816*x+0.010749$
 $r1=0.999298$ $r2=0.998596$

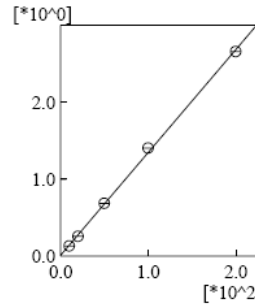


ID#5 Mass:91.00 Name:m,p-Xylene (m,p-二甲苯)
 $f(x)=0.013981*x-0.030421$
 $r1=0.999631$ $r2=0.999262$



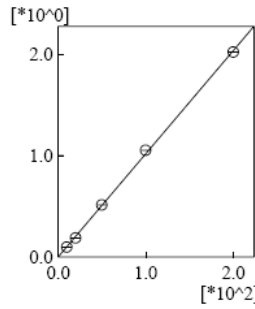
#	Conc. Ratio (ng)	Mean Area Ratio
2	10.000	0.15
3	20.000	0.26
4	40.000	0.49
5	100.000	1.34
6	200.000	2.78

ID#6 Mass:91.00 Name:o-Xylene (o-二甲苯)
 $f(x)=0.013383*x+0.011415$
 $r1=0.999487$ $r2=0.998974$



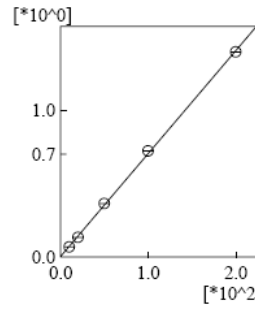
#	Conc. Ratio (ng)	Mean Area Ratio
3	10.000	0.13
4	20.000	0.26
5	50.000	0.69
6	100.000	1.41
7	200.000	2.66

ID#7 Mass:104.00 Name:Styrene (苯乙烯)
 $f(x)=0.010169*x+0.001722$
 $r1=0.999661$ $r2=0.999322$



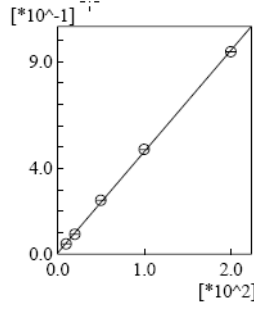
#	Conc. Ratio (ng)	Mean Area Ratio
3	10.000	0.10
4	20.000	0.19
5	50.000	0.51
6	100.000	1.05
7	200.000	2.02

ID#8 Mass:146.00 Name:p-Dichlorobenzene (p-二氯苯)
 $f(x)=0.006999*x+0.005256$
 $r1=0.999749$ $r2=0.999498$



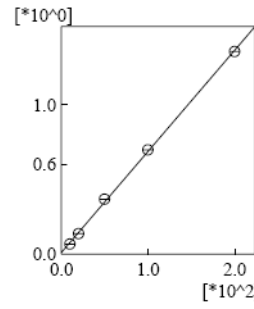
#	Conc. Ratio (ng)	Mean Area Ratio
3	10.000	0.07
4	20.000	0.13
5	50.000	0.36
6	100.000	0.72
7	200.000	1.40

ID#9 Mass:71.00 Name:Undecane (正十一烷)
 $f(x)=0.004734*x+0.005658$
 $r1=0.999687$ $r2=0.999374$



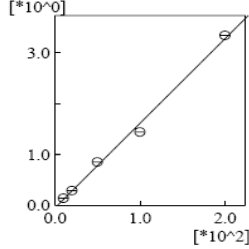
#	Conc. Ratio (ng)	Mean Area Ratio
3	10.000	0.05
4	20.000	0.09
5	50.000	0.25
6	100.000	0.49
7	200.000	0.95

ID#10 Mass:71.00 Name:Tetradecane (正十四烷)
 $f(x)=0.006769*x+0.010631$
 $r1=0.999682$ $r2=0.999363$



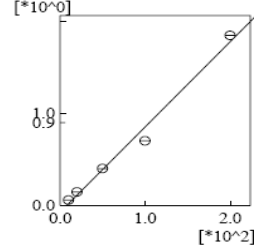
#	Conc. Ratio (ng)	Mean Area Ratio
3	10.000	0.07
4	20.000	0.14
5	50.000	0.37
6	100.000	0.70
7	200.000	1.36

ID#11 Mass:149.00 Name:Dibutyl phthalate (DBP)
 $f(x)=0.016614*x-0.046840$
 $r1=0.997097$ $r2=0.994203$



#	Conc. Ratio (ng)	Mean Area Ratio
3	10.000	0.14
4	20.000	0.29
5	50.000	0.86
6	100.000	1.44
7	200.000	3.34

ID#12 Mass:149.00 Name:Bis(2-ethylhexyl) phthalate (DEHP)
 $f(x)=0.009255*x-0.071422$
 $r1=0.992757$ $r2=0.985567$

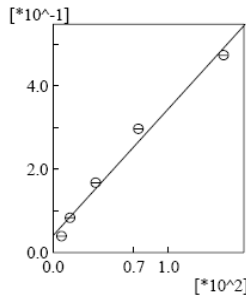


#	Conc. Ratio (ng)	Mean Area Ratio
3	10.000	0.06
4	20.000	0.15
5	50.000	0.40
6	100.000	0.70
7	200.000	1.85

ID#13 Mass:98.00 Name:Toluene-d8 (甲苯-d8)
 $f(x)=?$
 $r1=0.000000$ $r2=0.000000$

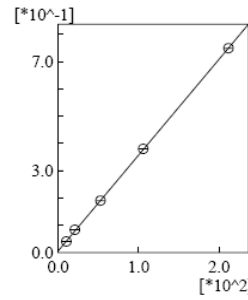
ISTD

Calibration
 ID#1 Mass:63.00 Name:1,1-Dichloroethane (1,1-二氯乙烷)
 $f(x)=0.003037*x+0.041163$
 $r1=0.991704$ $r2=0.983477$



#	Conc (ng)	Area
3	7.400	11912.00
4	14.800	25547.00
5	37.000	54121.00
6	74.000	95542.00
7	148.000	146055.00

ID#2 Mass:62.00 Name:1,2-Dichloroethane (1,2-二氯乙烷)
 $f(x)=0.003511*x+0.005805$
 $r1=0.999964$ $r2=0.999928$



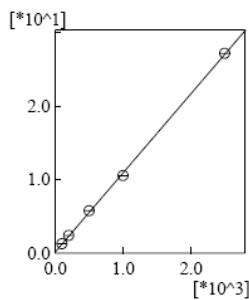
#	Conc (ng)	Area
3	10.600	12276.00
4	21.200	25546.00
5	53.000	61497.00
6	106.000	122412.00
7	212.000	231259.00

ID#3 Mass:98.00 Name:Toluene-d8 (甲苯-d8)
 $f(x)=?$
 $r1=0.000000$ $r2=0.000000$

ISTD

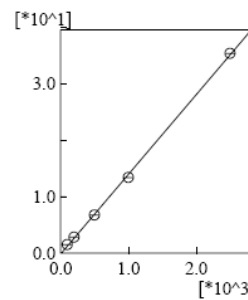
5.4.2.2 高浓度梯度标准曲线

Calibration
 ID#1 Mass:78.00 Name:Benzene (苯)
 $f(x)=0.010753*x+0.185914$
 $r1=0.999765$ $r2=0.999530$



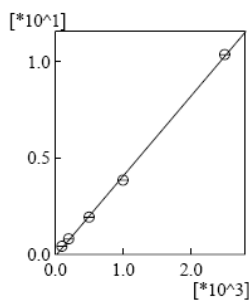
#	Conc. Ratio (ng)	Mean Area Ratio
6	100.000	1.27
7	200.000	2.41
8	500.000	5.76
9	1000.000	10.55
10	2500.000	27.18

ID#2 Mass:91.00 Name:Toluene (甲苯)
 $f(x)=0.014116*x-0.166894$
 $r1=0.999672$ $r2=0.999344$



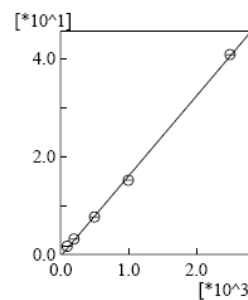
#	Conc. Ratio (ng)	Mean Area Ratio
6	100.000	1.53
7	200.000	2.84
8	500.000	6.77
9	1000.000	13.38
10	2500.000	35.35

ID#3 Mass:56.00 Name:n-Butyl acetate (乙酸丁酯)
 $f(x)=0.004153*x-0.094686$
 $r1=0.999511$ $r2=0.999023$



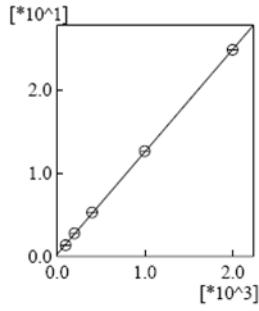
#	Conc. Ratio (ng)	Mean Area Ratio
6	100.000	0.42
7	200.000	0.81
8	500.000	1.94
9	1000.000	3.85
10	2500.000	10.37

ID#4 Mass:91.00 Name:Ethylbenzene (乙苯)
 $f(x)=0.016328*x-0.372852$
 $r1=0.999495$ $r2=0.998990$



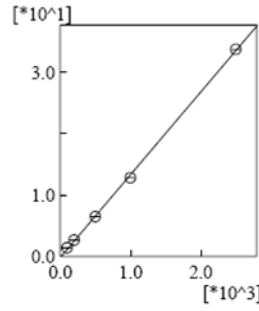
#	Conc. Ratio (ng)	Mean Area Ratio
6	100.000	1.67
7	200.000	3.14
8	500.000	7.64
9	1000.000	15.13
10	2500.000	40.77

ID#5 Mass:91.00 Name:m,p-Xylene (m,p-二甲苯)
 $f(x)=0.012334*x+0.267394$
 $r1=0.999942$ $r2=0.999884$



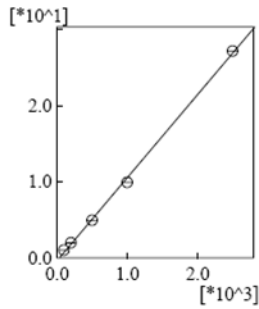
#	Conc. Ratio (ng)	Mean Area Ratio
5	100.000	1.34
6	200.000	2.78
7	400.000	5.29
8	1000.000	12.67
9	2000.000	24.89

ID#6 Mass:91.00 Name:o-Xylene (o-二甲苯)
 $f(x)=0.013509*x-0.185146$
 $r1=0.999739$ $r2=0.999479$



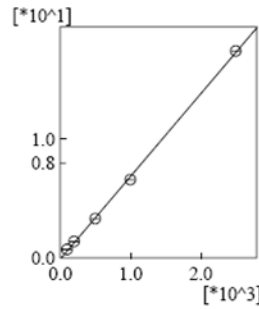
#	Conc. Ratio (ng)	Mean Area Ratio
6	100.000	1.41
7	200.000	2.66
8	500.000	6.49
9	1000.000	12.83
10	2500.000	33.78

ID#7 Mass:104.00 Name:Styrene (苯乙烯)
 $f(x)=0.010914*x-0.357865$
 $r1=0.999332$ $r2=0.998664$



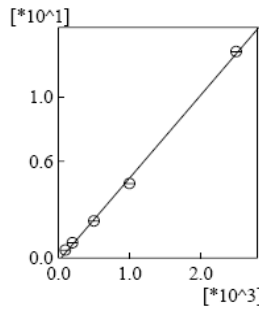
#	Conc. Ratio (ng)	Mean Area Ratio
6	100.000	1.05
7	200.000	2.02
8	500.000	4.96
9	1000.000	9.93
10	2500.000	27.18

ID#8 Mass:146.00 Name:p-Dichlorobenzene (p-二氯苯)
 $f(x)=0.006959*x-0.098983$
 $r1=0.999702$ $r2=0.999403$



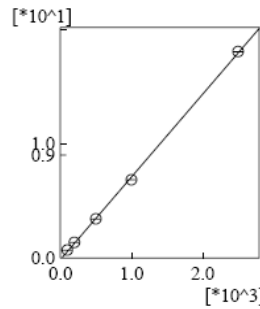
#	Conc. Ratio (ng)	Mean Area Ratio
6	100.000	0.72
7	200.000	1.40
8	500.000	3.31
9	1000.000	6.60
10	2500.000	17.41

ID#9 Mass:71.00 Name:Undecane (正十一烷)
 $f(x)=0.005148*x-0.193186$
 $r1=0.999151$ $r2=0.998303$



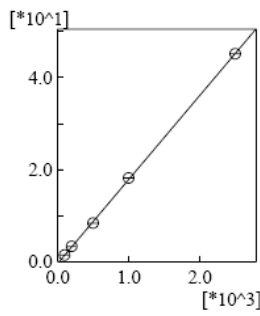
#	Conc. Ratio (ng)	Mean Area Ratio
6	100.000	0.49
7	200.000	0.95
8	500.000	2.30
9	1000.000	4.62
10	2500.000	12.81

ID#10 Mass:71.00 Name:Tetradecane (正十四烷)
 $f(x)=0.007232*x-0.155590$
 $r1=0.999766$ $r2=0.999532$



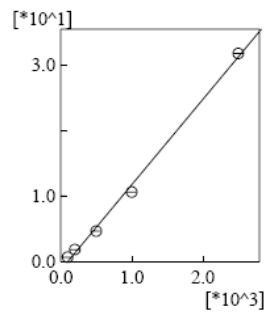
#	Conc. Ratio (ng)	Mean Area Ratio
6	100.000	0.70
7	200.000	1.36
8	500.000	3.42
9	1000.000	6.83
10	2500.000	18.02

ID#:11 Mass:149.00 Name:Dibutyl phthalate (DBP)
 $f(x)=0.018235*x-0.379408$
 $r1=0.999914$ $r2=0.999828$



#	Conc. Ratio (ng)	Mean Area Ratio
6	100.000	1.44
7	200.000	3.34
8	500.000	8.41
9	1000.000	18.18
10	2500.000	45.14

ID#:12 Mass:149.00 Name:Bis(2-ethylhexyl) phthalate (DEHP)
 $f(x)=0.013005*x-1.268196$
 $r1=0.998084$ $r2=0.996172$



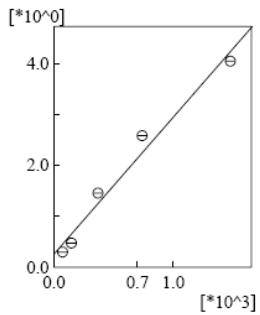
#	Conc. Ratio (ng)	Mean Area Ratio
6	100.000	0.70
7	200.000	1.85
8	500.000	4.67
9	1000.000	10.63
10	2500.000	31.73

ID#:13 Mass:98.00 Name:Toluene-d8 (甲苯-d8)
 $f(x)=?$
 $r1=0.000000$ $r2=0.000000$

ISTD

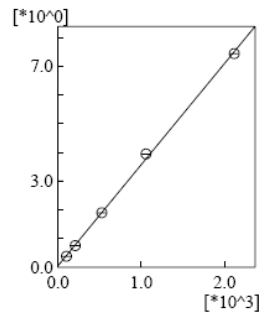
Calibration

ID#:1 Mass:63.00 Name:1,1-Dichloroethane (1,1-二氯乙烷)
 $f(x)=0.002684*x+0.259271$
 $r1=0.987225$ $r2=0.974613$



#	Conc (ng)	Area
6	74.000	95542.00
7	148.000	146055.00
8	370.000	457625.00
9	740.000	751443.00
10	1480.000	1252001.00

ID#:2 Mass:62.00 Name:1,2-Dichloroethane (1,2-二氯乙烷)
 $f(x)=0.003524*x+0.042592$
 $r1=0.999475$ $r2=0.998951$



#	Conc (ng)	Area
6	106.000	122412.00
7	212.000	231259.00
8	530.000	596597.00
9	1060.000	1148936.00
10	2120.000	2306181.00

ID#:3 Mass:98.00 Name:Toluene-d8 (甲苯-d8)
 $f(x)=?$
 $r1=0.000000$ $r2=0.000000$

ISTD

5.5. 精度管理

5.5.1. 定量下限

VOCs 类检测项共 17 种，定量下限均为 10 ng/采样管。

5.5.2. 线性评价 ($r>0.99$)

5.5.2.1. 低浓度范围工作曲线

检测项	苯	甲苯	乙酸丁酯	乙苯	<i>m,p</i> -二甲苯	<i>o</i> -二甲苯
R	0.99822	0.999181	0.999741	0.999298	0.999631	0.999487
检测项	苯乙烯	<i>p</i> -二氯苯	正十一烷	正十四烷	DBP	DEHP
R	0.999661	0.999749	0.999687	0.999682	0.997097	0.992757
检测项	1,1-二氯乙烷	1,2-二氯乙烷	仲丁威	二嗪农	毒死蜱	
R	0.991704	0.999964	0.996741	0.993783	0.991814	

5.5.2.2. 高浓度范围工作曲线

检测项	苯	甲苯	乙酸丁酯	乙苯	<i>m,p</i> -二甲苯	<i>o</i> -二甲苯
R	0.999765	0.999672	0.999511	0.999495	0.999942	0.999739
检测项	苯乙烯	<i>p</i> -二氯苯	正十一烷	正十四烷	DBP	DEHP
R	0.999332	0.999702	0.999151	0.999766	0.999914	0.998084
检测项	1,1-二氯乙烷	1,2-二氯乙烷	仲丁威	二嗪农	毒死蜱	
R	0.987225	0.999475	---	---	---	---

5.5.3. 相对误差评价 (|RE 值| <15%)

5.5.3.1. 低浓度范围工作曲线

配制浓度	RE 值					
	苯	甲苯	乙酸丁酯	乙苯	<i>m,p</i> -二甲苯	<i>o</i> -二甲苯
10ng	19.62	0.9230	-12.56	-8.602	19.89	-10.37
20ng	0.2155	-8.082	-5.038	-10.75	2.608	-7.819
50ng	-13.72	-3.575	2.126	0.9180	-6.159 (40ng)	0.8522
100ng	5.630	5.416	2.606	4.816	-1.906	4.146
200ng	-0.6123	-1.052	-0.7027	-1.132	0.6322	-0.9856

配制浓度	RE 值					
	苯乙烯	<i>p</i> -二氯苯	正十一烷	正十四烷	DBP	DEHP
10ng	-5.279	-9.012	-11.82	-16.28	14.99	42.18
20ng	-7.998	-7.322	-8.280	-6.752	2.415	13.98
50ng	0.7682	2.616	3.960	5.394	8.655	2.158
100ng	3.306	2.386	2.257	1.479	-10.21	-14.65
200ng	-0.7814	-0.6643	-0.6994	-0.5986	1.950	3.658

配制浓度	RE 值				
	1,1-二氯乙烷	1,2-二氯乙烷	仲丁威	二嗪农	毒死蜱
10ng	-38.38(7.4ng)	-6.075(10.6ng)	-7.910	37.97	47.67
20ng	-6.487(14.6ng)	3.958(21.2ng)	-2.575	1.310	-8.940
50ng	22.71(37ng)	-1.089(53ng)	14.44	-8.328	-12.80
100ng	18.56(74ng)	0.564(106ng)	7.528	-12.94	-15.61
200ng	-8.743(148ng)	-0.535(212ng)	-2.542	4.017	4.525

5.5.3.2. 高浓度范围工作曲线

配制浓度	RE 值					
	苯	甲苯	乙酸丁酯	乙苯	<i>m,p</i> -二甲苯	<i>o</i> -二甲苯
200ng	3.523	6.360	8.432	7.517	1.998	5.368
500ng	3.693	-1.708	-2.130	-1.878	1.839 (400 ng)	-1.240
1000ng	-3.629	-4.039	-4.933	-5.058	0.5646	-3.656
2500ng	0.4095	0.6416	0.7828	0.7962	-0.2023 (2000 ng)	0.5718

配制浓度	RE 值					
	苯乙烯	<i>p</i> -二氯苯	正十一烷	正十四烷	DBP	DEHP
200ng	8.920	7.393	10.64	4.531	2.004	13.40
500ng	-2.491	-2.054	-3.108	-1.254	-3.585	-8.672
1000ng	-5.747	-3.770	-6.420	-3.428	1.768	-8.535
2500ng	0.9154	0.6093	1.031	0.5410	-0.1524	1.503

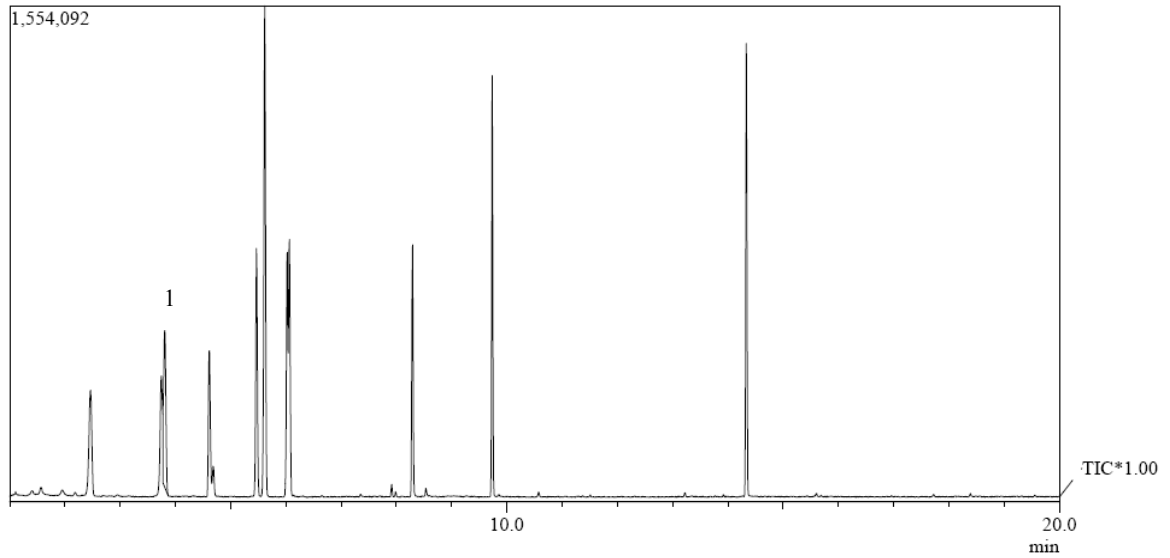
配制浓度	RE 值				
	1,1-二氯乙烷	1,2-二氯乙烷	仲丁威	二嗪农	毒死蜱
200ng	-8.743(148ng)	-0.535(212ng)	---	---	---
500ng	19.97(370ng)	-1.051(530ng)	---	---	---
1000ng	16.51(740ng)	4.160(1060ng)	---	---	---
2000ng	-6.114(1480ng)	-1.389(2120ng)	---	---	---

*RE 值=(实测值-配制浓度)/ 配制浓度×100

5.6. TVOC 值的计算

TVOC 值由样品中 C₆~C₁₆ 的色谱峰积分总面积与 100ng 甲苯色谱峰积分面积的比较计算得出 (JASO M 902: 2007)。

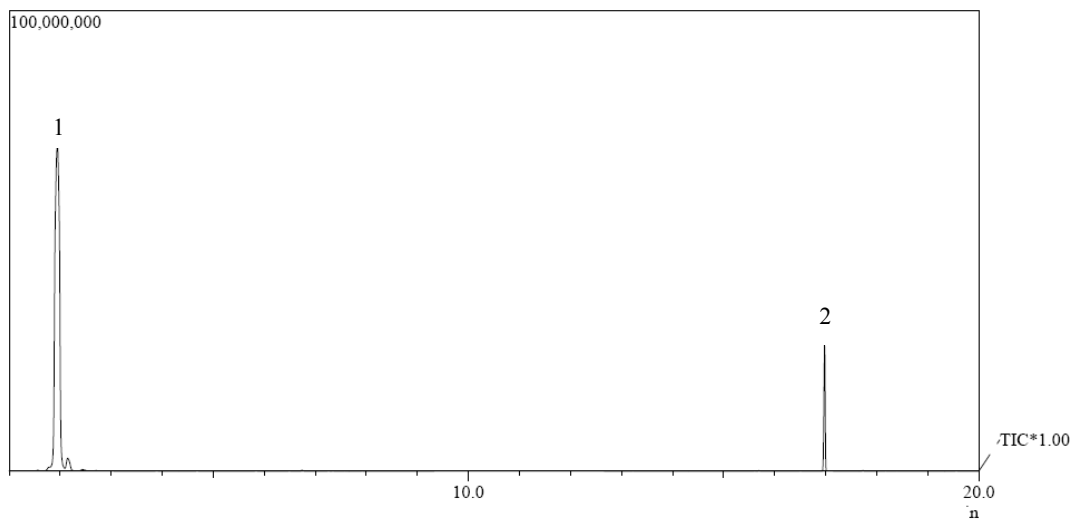
5.6.1. 100ng 甲苯的色谱图



TIC 图

峰号	保留时间	面积	名称
1	3.807	1359085	甲苯

5.6.2. C₆~C₁₆ 保留时间确定



TIC 图

峰号	保留时间	面积	名称
1	1.946	457717721	正己烷
2	16.977	45432646	正十六烷

5.6.3. TVOC 计算表格

样品 C ₆ ~C ₁₆ 的色谱 峰积分总面积	甲苯 100ng 色谱峰 积分面积	采样管中 TVOC 量	样品中 TVOC 浓度
A	A _T	m(μg/采样管)	C _m (μg/L)
$m(\mu\text{g}/\text{采样管})=A/A_T \times 100/1000; C_m(\mu\text{g}/\text{L})=m \times L_o/L_T$			
TVOC 计算公式:	注: L _o 为充入采样袋中氮气的体积		
	L _T 为采样管采样体积		