Ultra-fast GCMS splitless headspace analysis of 56 EPA VOC using the Chromtech eTrapPlus Peltier-cold trap for cryofocussing

Aim:

The aim of the application is to significantly shorten the chromatographic runtime resulting in a higher sample throughput/day while maintaining the existing technical/analytical equipment.

Starting point:

The starting point for creating this application is an established VOC-GCMS method with a chromatographic runtime of approximately 20 minutes. The analysis is carried out with an Agilent 7890B/5977B GCMS system and a CTC PAL RTC autosampler. The capillary column used is a Agilent DB-624, 30 m x 0.25mm ID x 1.4 µm film. The oven temperature program ranges from 40 °C up to 260 °C. The Chromtech eTrap Plus Peltier cold trap device enables cryofocusing of the volatile analyses by performing lossless splitless injection of the headspace aliquot of 1 mL at -20 °C. Since the Chromtech eTrap Plus makes use of the thermo-electric cooling of Peltier devices, no cryogenic coolants like LN2 or LCO2 are required.

Optimization:

Since no additional analytical hardware was to be added according to the target, experiments were mainly carried out on the oven temperature program, injection and re-focusing of the sample using the Chromtech eTrap Plus cold trap device.

Results:

By increasing the oven start temperature from 40 °C to 100 °C, the retention time of the 1,2,3-trichlorobenzene (last eluting component in the chromatogram) can be reduced from 16.5 min to 5.5 min without affecting the signal quality of the early eluting components such as vinyl chloride or chloromethane. Even with these very volatile compounds, still narrow and easily evaluable signals are achieved. The reason for this is that after a splitless injection, the substances are refocused in the eTrap Plus at -25 °C and then by rapid heating transferred onto the analytical column (GC Oven Temp.@100°C) as narrow band.
The fact that the Chromtech eTrap PLus resides outside the hot GC oven is of crucial importance because thus it can be operated independently of the current GC oven temperature and therefore does not require any cryogenic media such as liquid nitrogen (LN2) or carbon dioxide (LCO2).
After carrying out these measures a tripling of the sample throughput can be achieved:
A new sample injection is possible after approx. every 6 minutes. Since the incubation time of the sample in this application lasts approx. 10 min, the 6-position agitator of the CTC-PAL is used in an „overlapping incubation“ mode, resulting in no waiting time for the next possible injection.

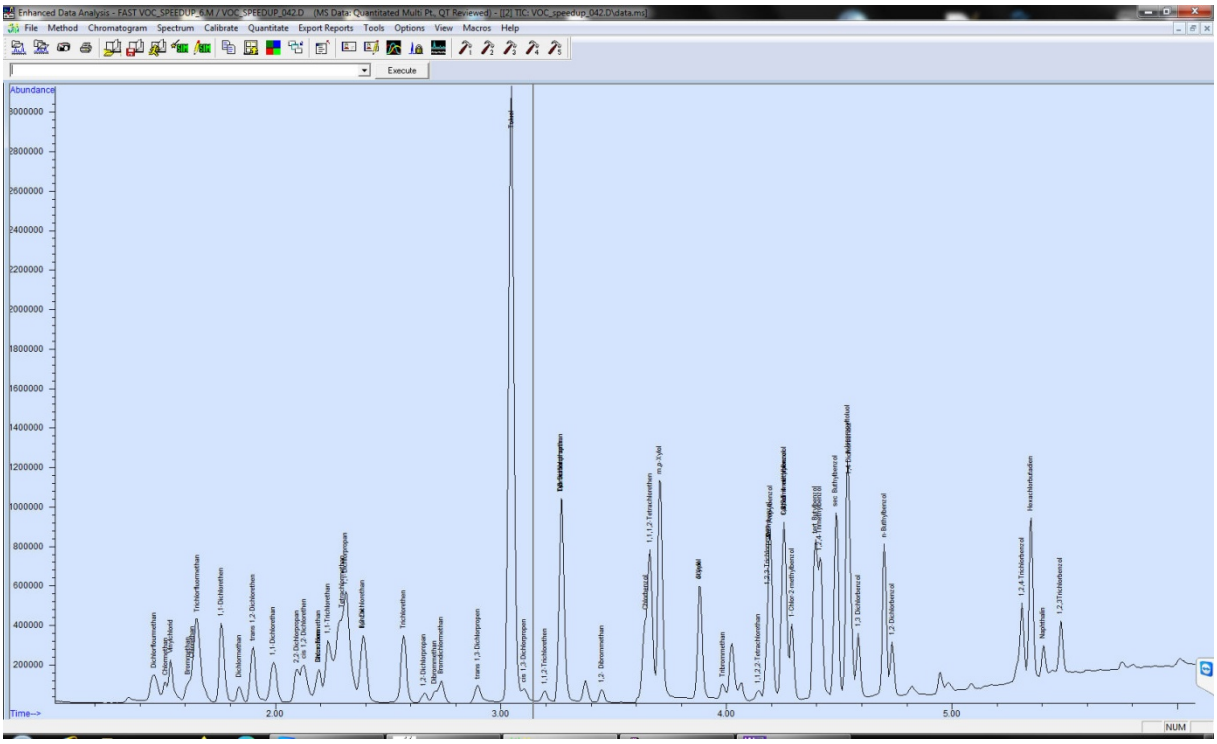

Abb.1: TIC chromatogram 56 EPA-VOCs

Based on a few elected analyses the following images illustrate the signal quality and chromatographic resolution when using the Chromtech eTrap Plus, despite the very fast retention times:

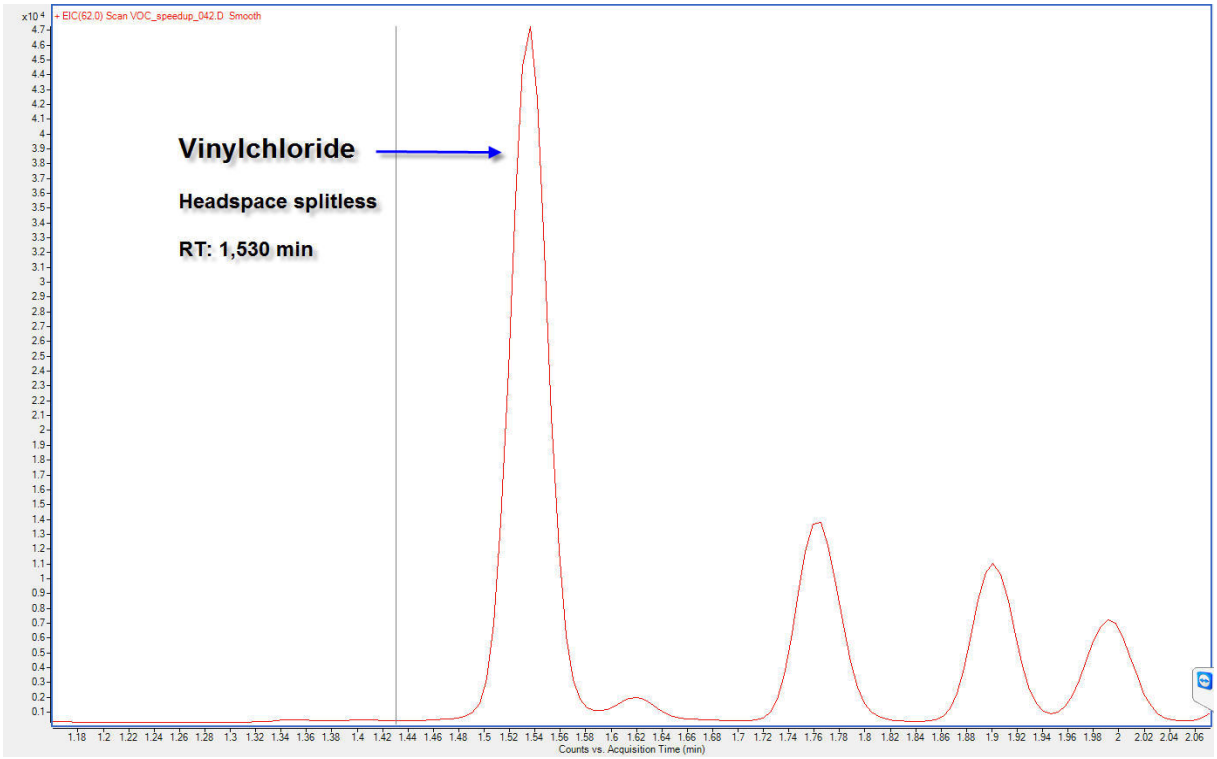

Abb.2: RT: 1,530 min Vinylchloride m/z= 62

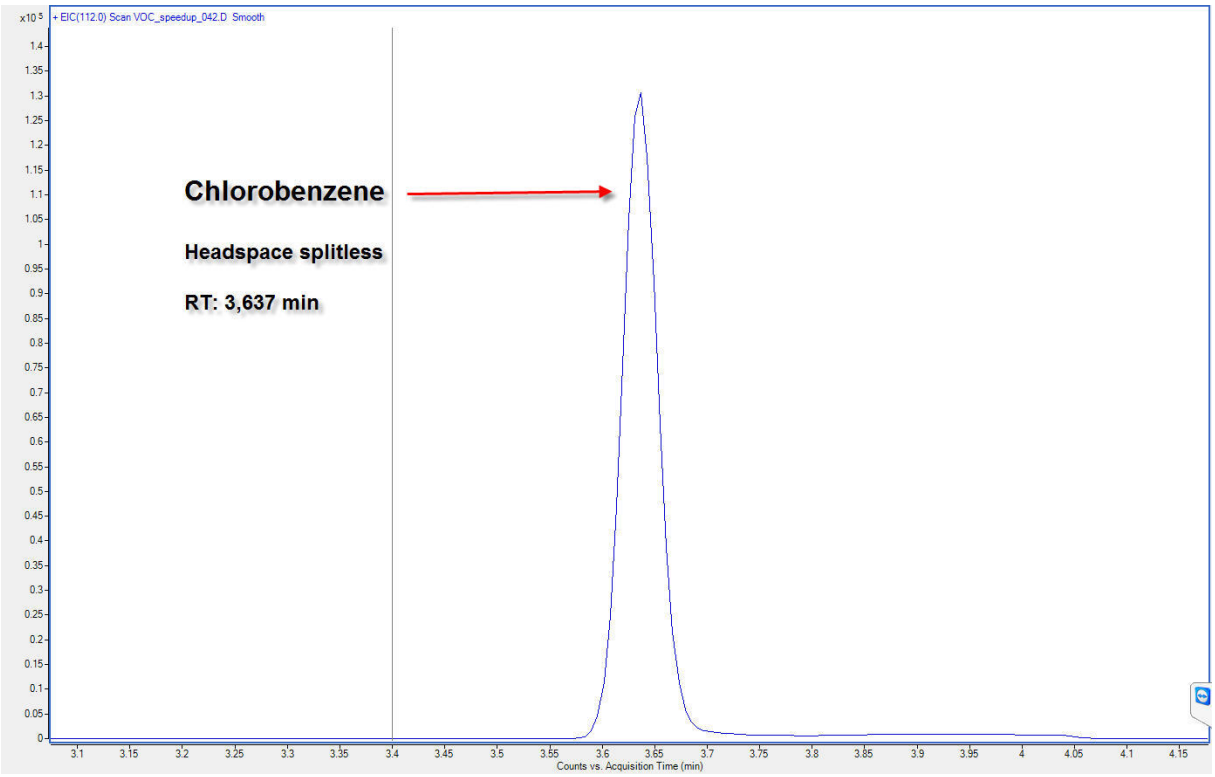

Abb.3: RT: 3,637 min Chlorobenzene m/z= 112

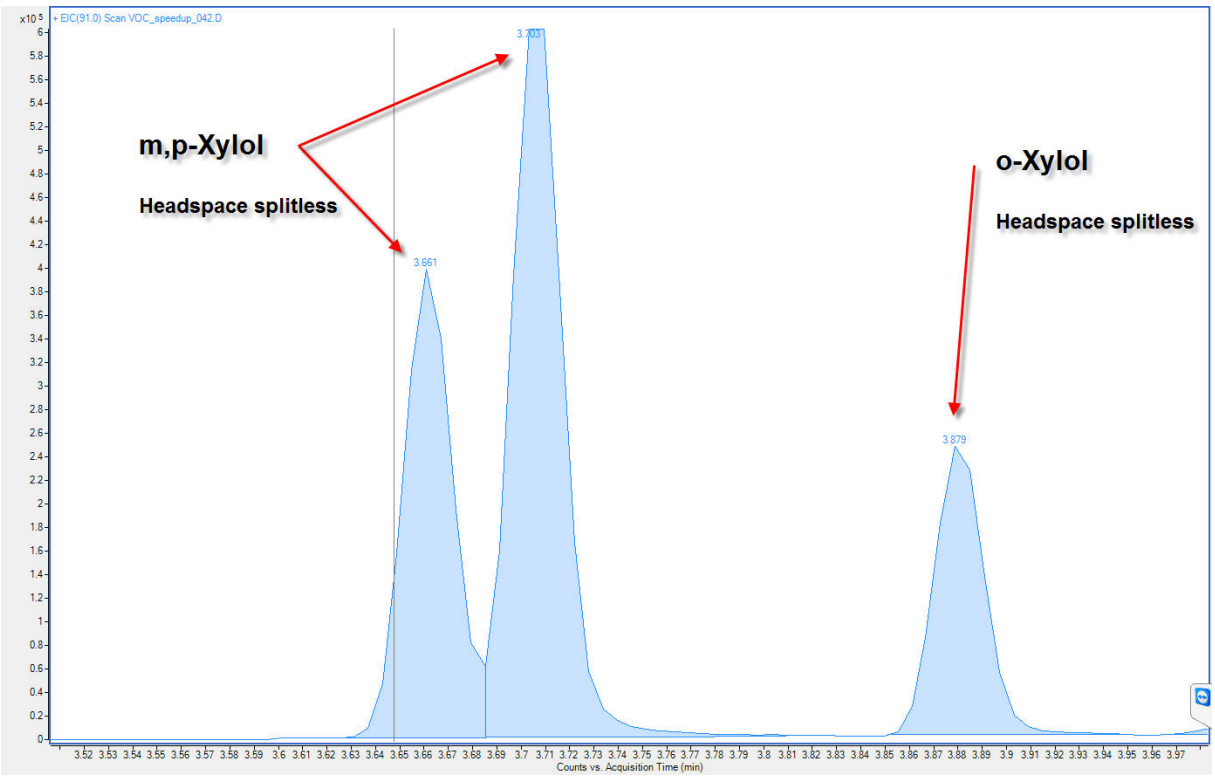

Abb.4: RT: 3,661 min m-Xylole m/z= 91

RT: 3,703 min p-Xylole m/z= 91

RT: 3,879 min o-Xylole m/z= 91

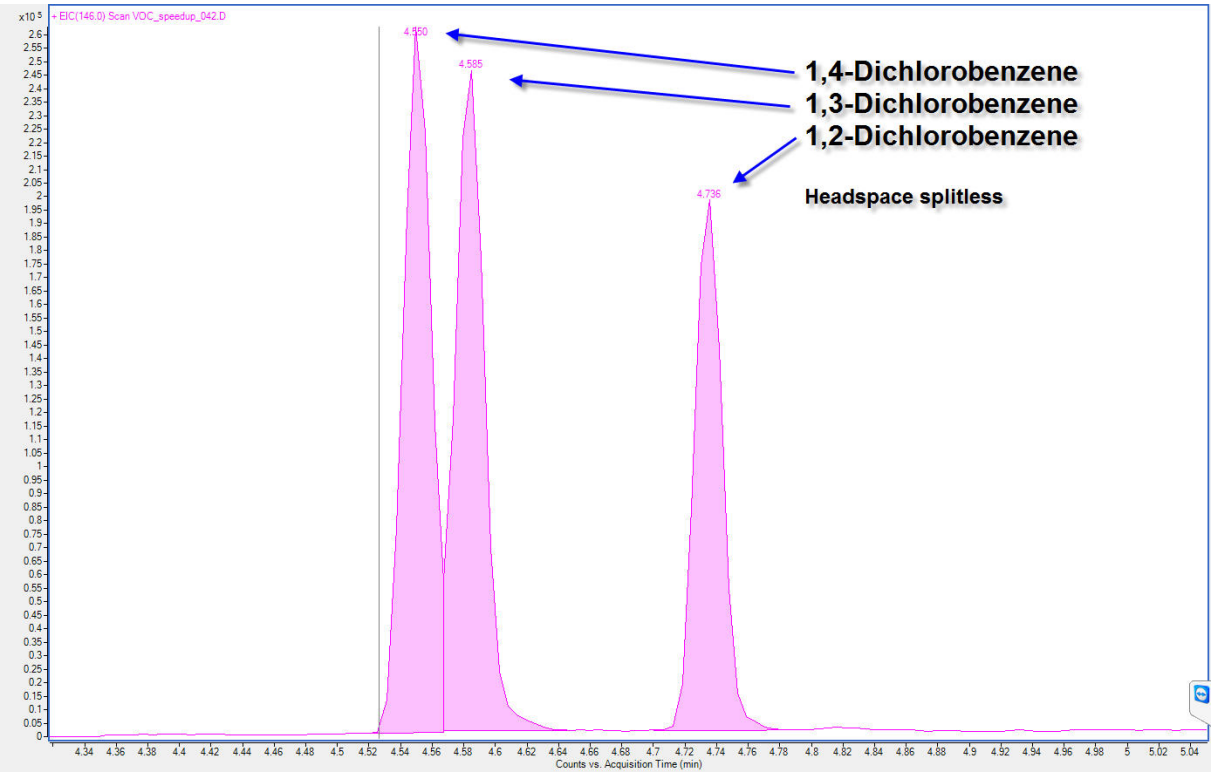

Abb.5: RT: 4,550 1,4-Dichlorobenzene m/z=146

RT: 4,585 1,3-Dichlorobenzene m/z=146

RT: 4,736 1,2-Dichlorobenzene m/z=146

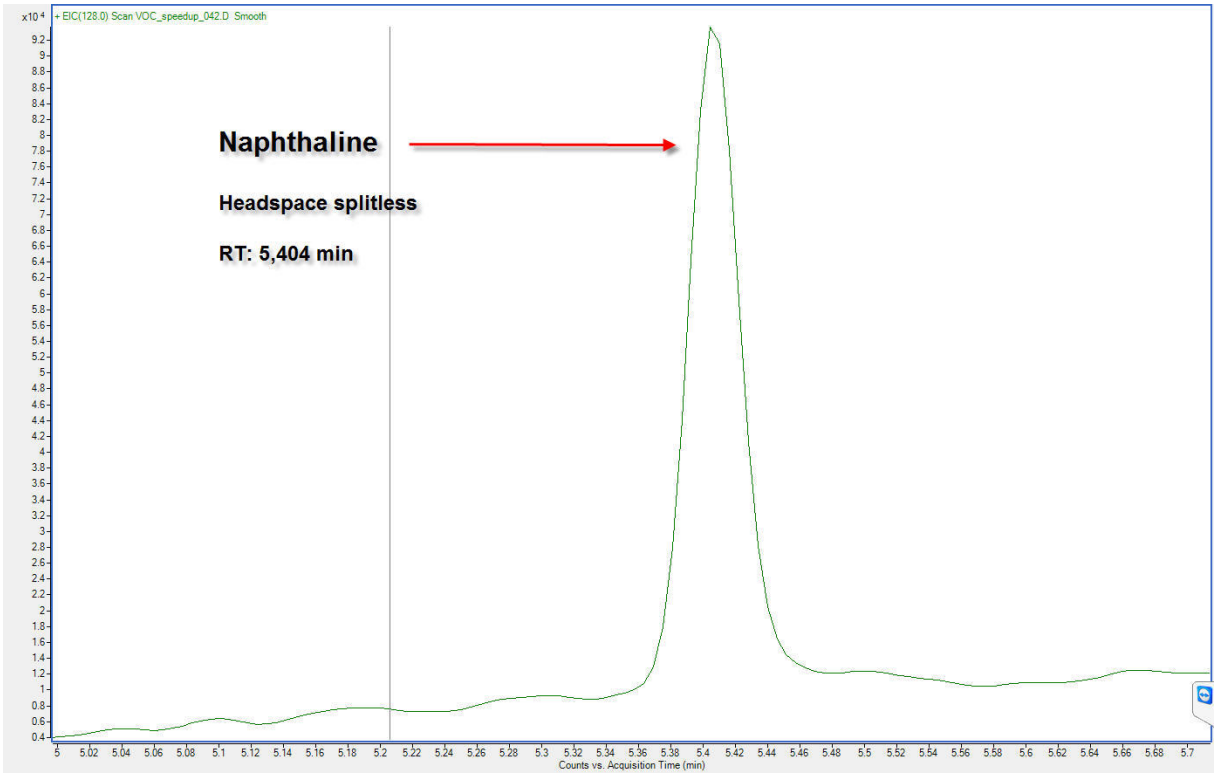

Abb.6: RT: 5,404 Naphthaline m/z= 128

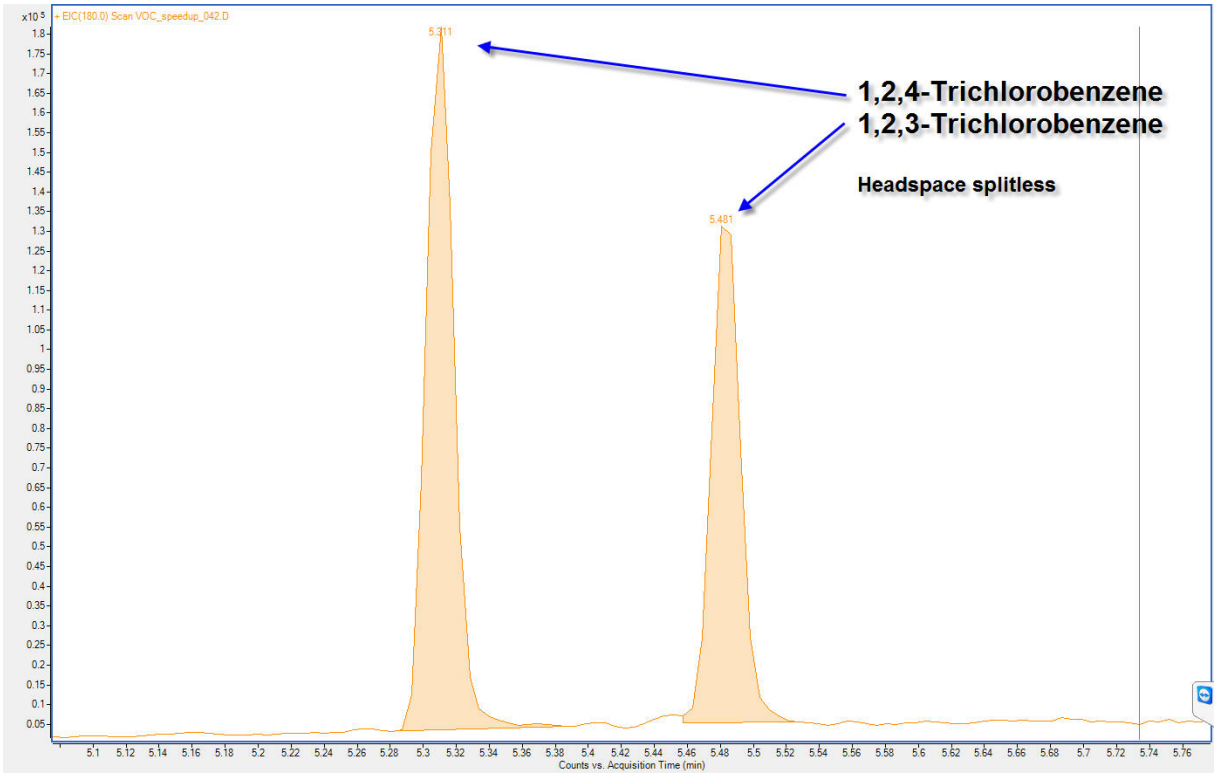

Abb.7: RT: 5,311 1,2,4-Trichlorobenzene m/z= 180

RT: 5,481 1,2,3-Trichlorobenzene m/z= 180

The following table shows all measured components with their respective retention time and target ions:

Compound	R.T.	m/z	Compound	R.T.	m/z
1) Chlormethan	1.513	50	30) Dibromchlormethan	3.272	129
2) Dichlorflourmethan	1.462	85	31) 1,2- Dibrommethan	3.449	107
3) Vinylchlorid	1.537	62	32) Chlorbenzol	3.637	112
4) Brommethan	1.607	96	33) 1,1,1,2-Tetrachlorethen	3.653	131
5) Chlorethan	1.622	64	34) m,p-Xylol	3.709	91
6) Trichlorfluormethan	1.654	101	35) o-Xylol	3.883	91
7) 1,1-Dichlorethen	1.764	61	36) Styrol	3.885	104
8) trans 1,2-Dichlorethen	1.903	61	37) Tribrommethan	3.985	173
9) Dichlormethan	1.841	84	38) 1,1,2,2-Tetrachlorethan	4.143	83
10) 1,1-Dichlorethan	1.994	65	39) Cumol	4.261	105
11) 2,2-Dichlorpropan	2.097	77	40) 1,2,3-Trichlorpropan	4.177	110
12) cis 1,2-Dichlorethen	2.128	96	41) Brombenzol	4.182	156
13) Chloroform	2.193	83	42) Propylbenzol	4.198	91
14) Bromchlormethan	2.196	130	43) 1-Chlor-4-methylbenzol	4.252	91
15) 1,1-Trichlorethan	2.237	97	44) 1,3,5-Trimethylbenzol	4.261	105
16) 1,1-Dichlorpropan	2.314	110	45) 1-Chlor-2-methylbenzol	4.291	126
17) Tetrachlormethan	2.289	117	46) tert Butylbenzol	4.396	119
18) 1,2-Dichlorethan	2.385	62	47) 1,2,4-Trimethylbenzol	4.421	105
19) Benzol	2.393	78	48) sec Buthylbenzol	4.489	105
20) Trichlorethen	2.571	130	49) p-Isopropyltoluol	4.540	119
21) 1,2-Dichlorpropan	2.664	63	50) 1,4-Dichlorbenzol	4.550	146
22) Bromdichlormethan	2.738	83	51) 1,3 Dichlorbenzol	4.586	146
23) Dibrommethan	2.708	174	52) 1,2-Dichlorbenzol	4.737	146
24) cis 1,3-Dichlorpropen	3.107	75	53) n-Buthylbenzol	4.703	91
25) Toluol	3.048	91	54) 1,2,4-Trichlorbenzol	5.313	180
26) trans 1,3-Dichlorpropen	2.898	75	55) Hexachlorbutadien	5.352	225
27) 1,1,2-Trichlorethen	3.196	97	56) Naphthalin	5.404	128
28) 1,3-Dichlorpropan	3.272	78	57) 1,2,3Trichlorbenzol	5.486	180
29) Tetrachlorethen	3.270	166			