Large Volume Injection for Capillary Gas Chromatography Using new PTV Injector with a Liner in the Shape of a Stomach

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[Introduction] We have developed new PTV injector for capillary gas chromatography with “stomach” shaped liner inserted in it. At beginning, injection temperature is kept just below the boiling point of the solvent, and injected sample can stay in the liner as liquid. This unique “stomach” shaped liner has brought many advantages for large volume injection.

[Large Volume Injection method]

1st stage; The injector is kept at a temperature lower than the boiling point of sample solvent. Sample is injected into the liner, and stays there as liquid state.

2nd stage; While the evaporated sample solvent is exhausted in the split purge mode, the target compounds are concentrated in the liner. 3rd stage; Target compounds are transferred to the capillary column at an elevated injector temperature in the splitless mode. 4th stage; Matrix compounds are eliminated from the liner in the split purge at further elevated injector temperature.

Fig. 1 “Stomach” shaped liner

[Results and Discussion]

We have studied the performance of large volume injection of this injector. We have used, as sample, n-hydrocarbons, PAHs, PCBs and pesticides. Good linearity has been obtained between each peak area of n-hydrocarbons (n-C12-C30) and its injection volume (i.e. 10, 20, 30, 40, 50 μL). Sample of 50 μL volume was injected and analyzed repeatedly (n=7). We have got good repeatability of 2% or less RSD (Relative Standard Deviation) on each n-hydrocarbon peak area.

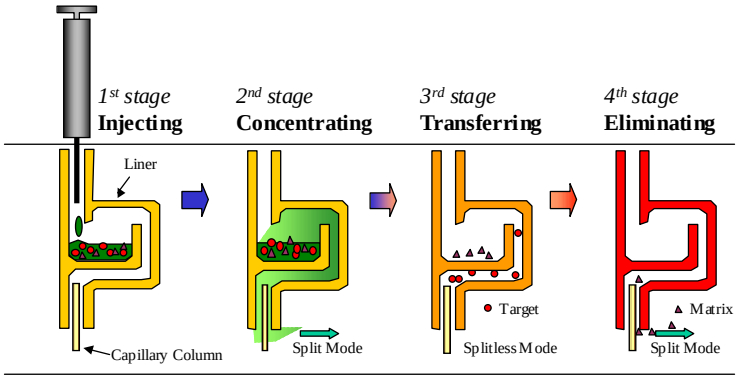

Fig. 2 Scheme of large volume injection method

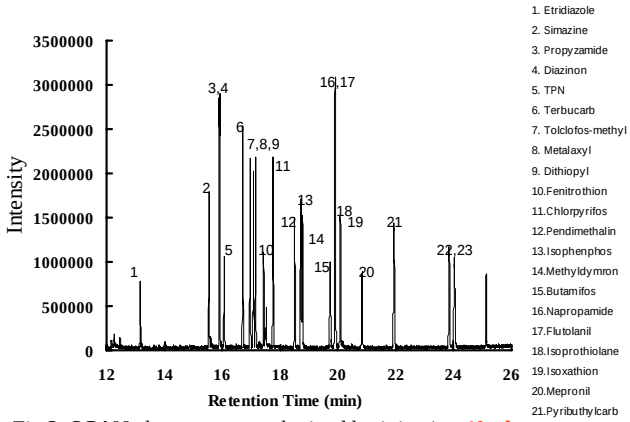

Fig.3 SCAN chromatogram obtained by injecting 40 μl (LVI) of pesticides in Acetone

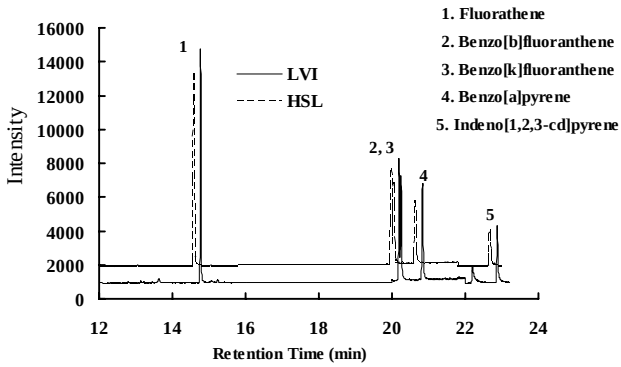

Fig. 4 Total ion chromatogram obtained by injecting 200 μl (LVI) of PAHs **in hexane** (**0.1pg/μl**) and 2 μl (HSL) of PAHs **in hexane** (**10pg/μl**)

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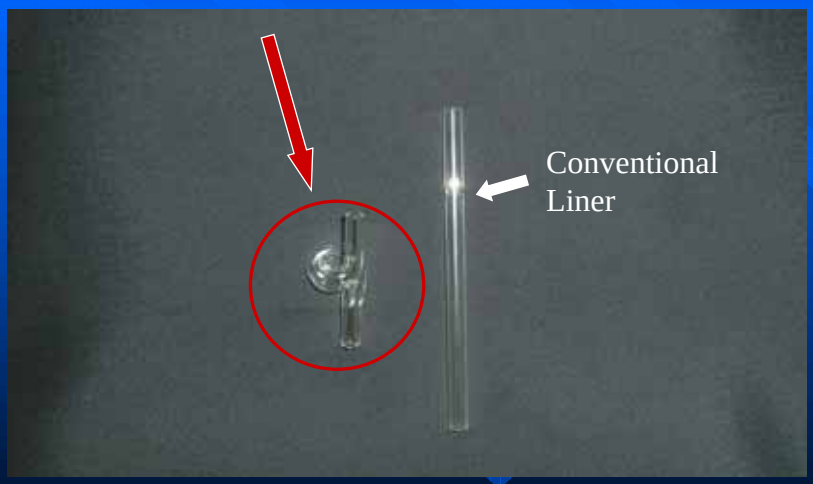
“Stomach” Shaped Liner



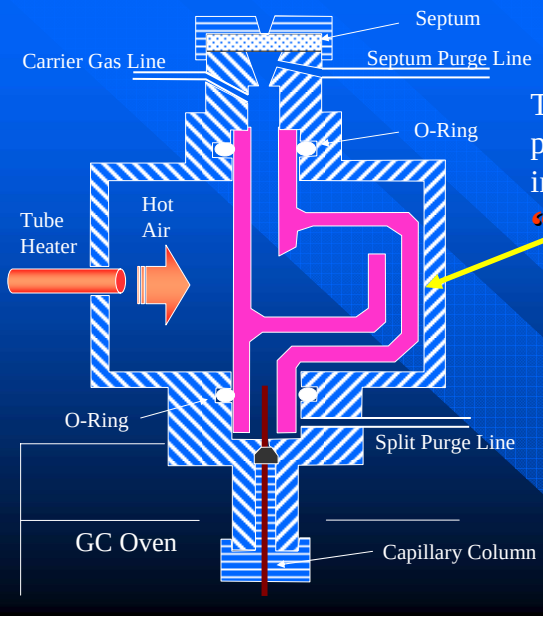
Abstract

We have developed new PTV injector for capillary gas chromatography with **“stomach” shaped liner** inserted in it. At beginning, injection temperature is kept just below the boiling point of the solvent, and injected sample can stay in the liner as liquid.

This unique “stomach” shaped liner has brought many advantages for **large volume injection**. Here, we have discussed on many parameters like a type of solvent, injection volume, split purge flow rate, and split/splitless time. Some of these parameters often give important effect on large volume injection technique obtaining good sensitivity, repeatability, or accuracy of data.

We have studied large volume injection technique using this injector by injecting n-hydrocarbons, PAHs, PCBs and pesticides. We have determined optimum conditions of the injector to get best results in various type of solvent.

New Injection System



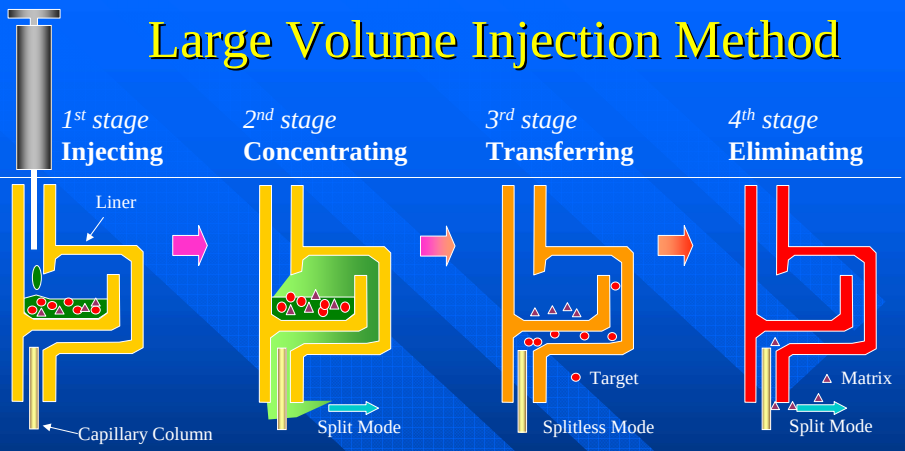
The injection system consisted of a programmed-temperature vaporizing injector with

"stomach" shaped liner.

Multi-Injector

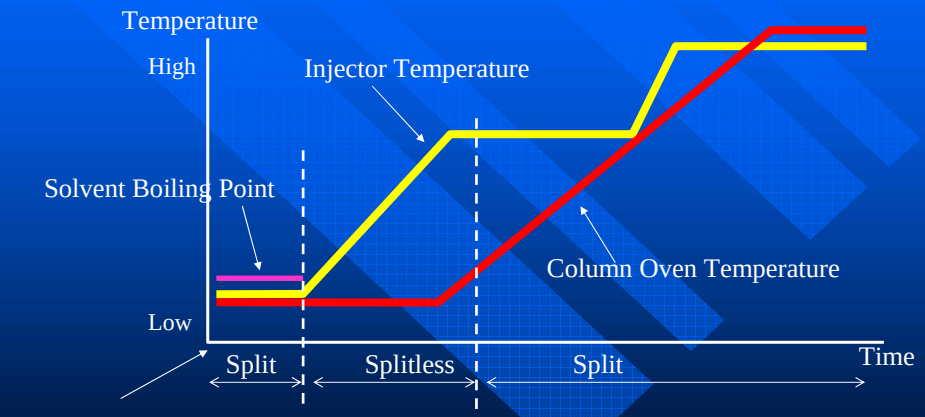
- Split, Splitless Injection
- Cold Split, Cold Splitless
- On-column Injection
- **Large Volume Injection**
- **Derivatizating Injection**
- **Interface of On-Line GC**

Large Volume Injection Method



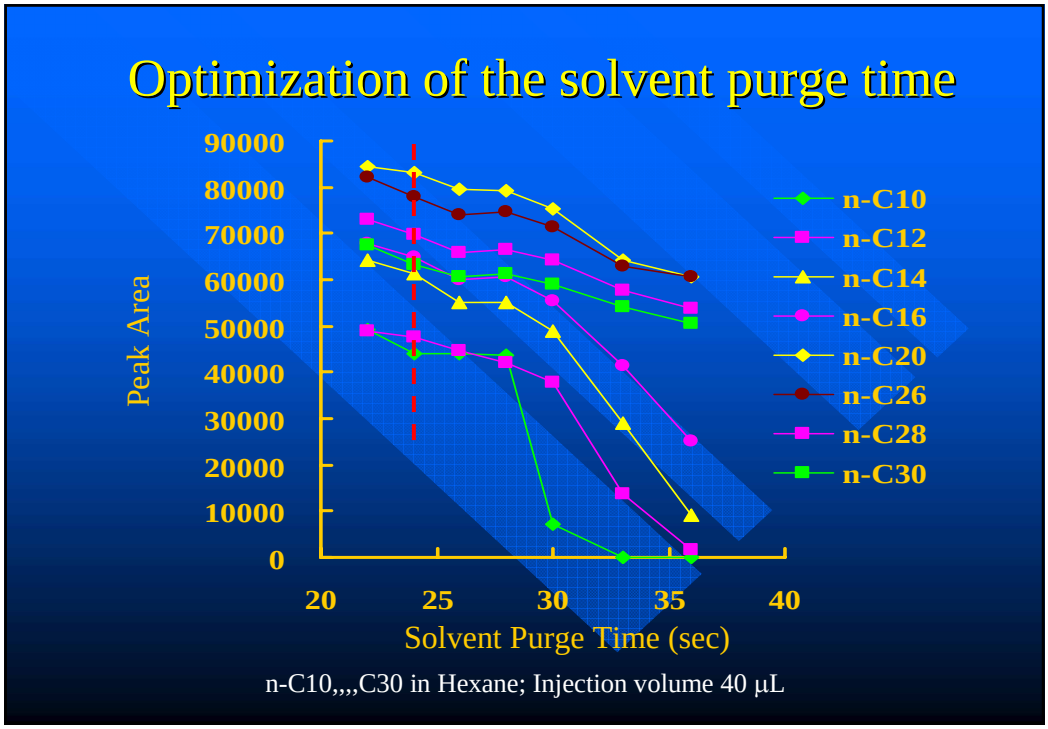
1st stage Injecting	2nd stage Concentrating	3rd stage Transferring	4th stage Eliminating
The injector is kept at a temperature lower than the boiling point of sample solvent. The sample is injected into the liner, and stays as liquid state.	While the evaporated sample solvent is exhausted in the split purge mode, target compounds are concentrated in the liner.	Target compounds are transferred to the capillary column at an elevated injector temperature in the splitless mode.	Matrix compounds are eliminated from the liner in the split purge mode at further elevated injector temperature.

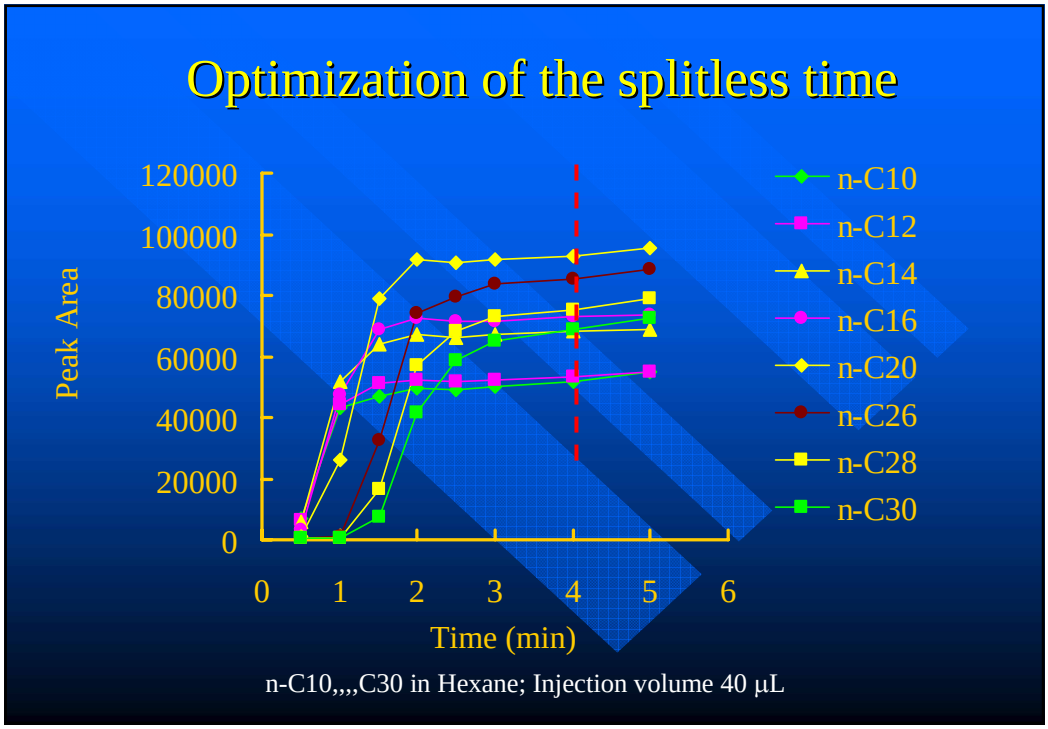
The Scheme of GC Conditions for Large Volume Injection



Operating Conditions of Injector and GC/MS

Injector	LaviStoma (EMINET)
Injector Oven Temp.	69℃-100℃/min-270℃(20min)
Solvent Purge Time	12 sec
Auto-Sampler	AOC-20i (Shimadzu)
GC/MS	QP5050A (Shimadzu)
Pre-column	Deactivated silica capillary tube 0.53mm×0.5m
Column	DB-5MS 0.25mm×30m, 0.25μm
Column Oven Temp.	50℃(4min)-15℃/min-315℃(3min)
Detector Temp	300℃
MS Method	SIM
Carrier Gas Press	20kPa-60kPa(4min)-6.3kPa/min-171kPa(3min)
Splitpurge Flow	150 ml/min
Splitless Time	4 min


Optimization of the solvent purge time
Peak Area
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
20
25
30
35
40
Solvent Purge Time (sec)
n-C10
n-C12
n-C14
n-C16
n-C20
n-C26
n-C28
n-C30
n-C10,,,,C30 in Hexane; Injection volume 40 µL


Optimization of the splitless time
Peak Area
120000
100000
80000
60000
40000
20000
0
0
1
2
3
4
5
6
Time (min)
n-C10
n-C12
n-C14
n-C16
n-C20
n-C26
n-C28
n-C30
n-C10,,,,C30 in Hexane; Injection volume 40 µL

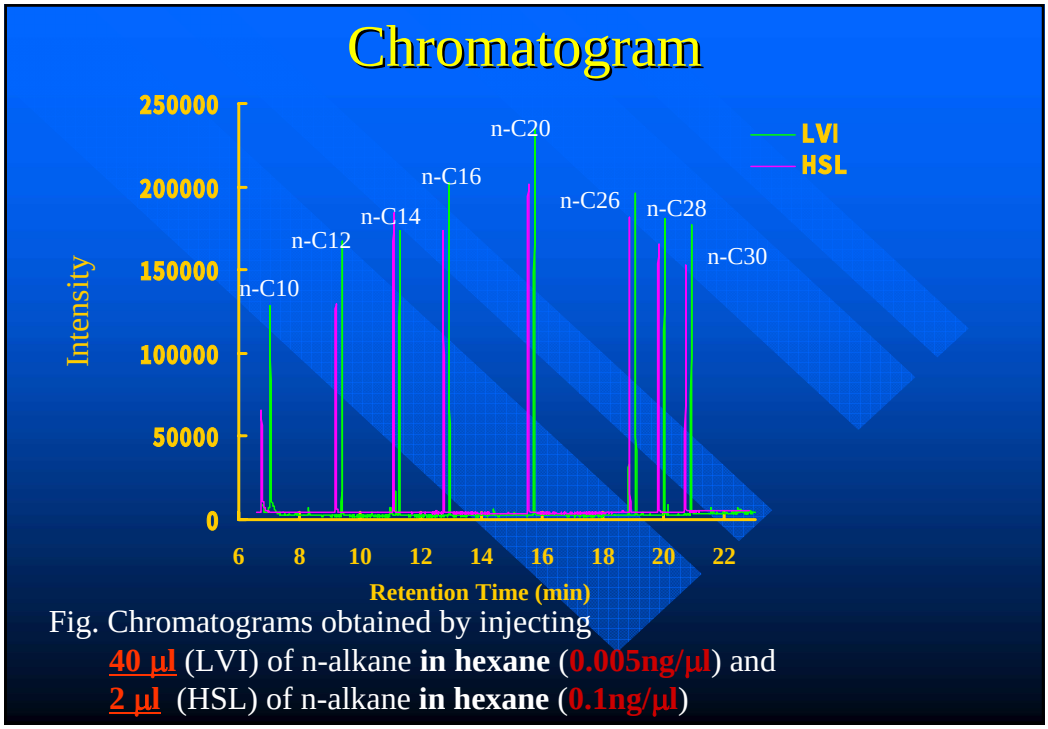


Fig. Chromatograms obtained by injecting
40 µl (LVI) of n-alkane **in hexane** (0.005ng/µl) and
2 µl (HSL) of n-alkane **in hexane** (0.1ng/µl)

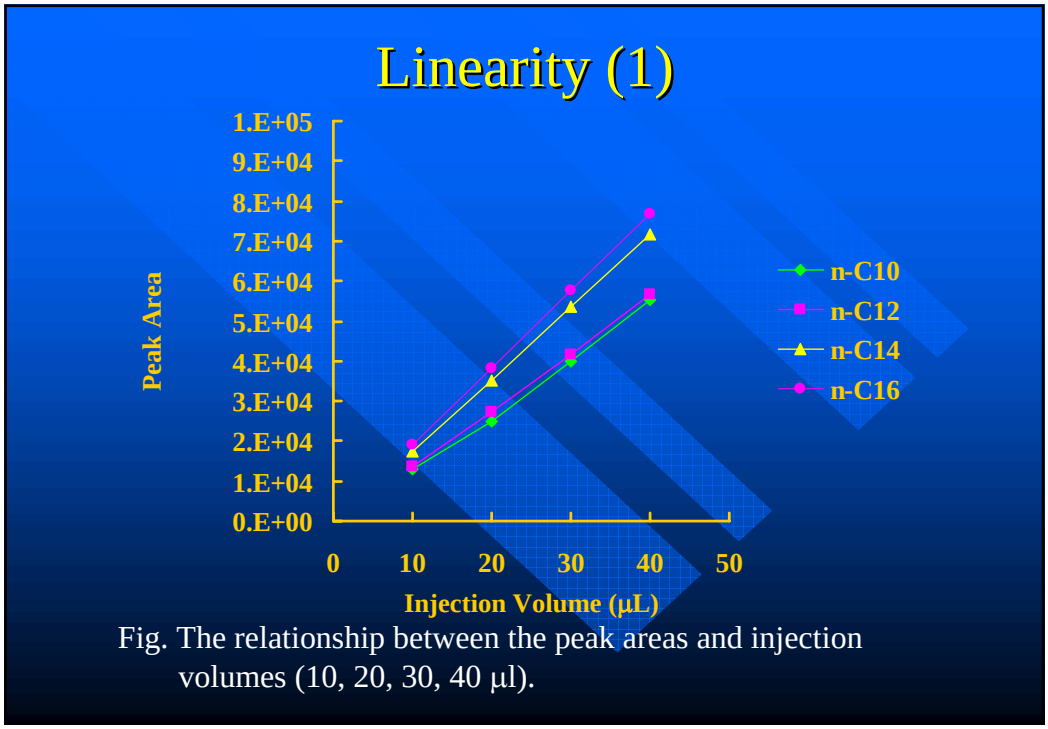


Fig. The relationship between the peak areas and injection volumes (10, 20, 30, 40 µl).

Linearity (2)

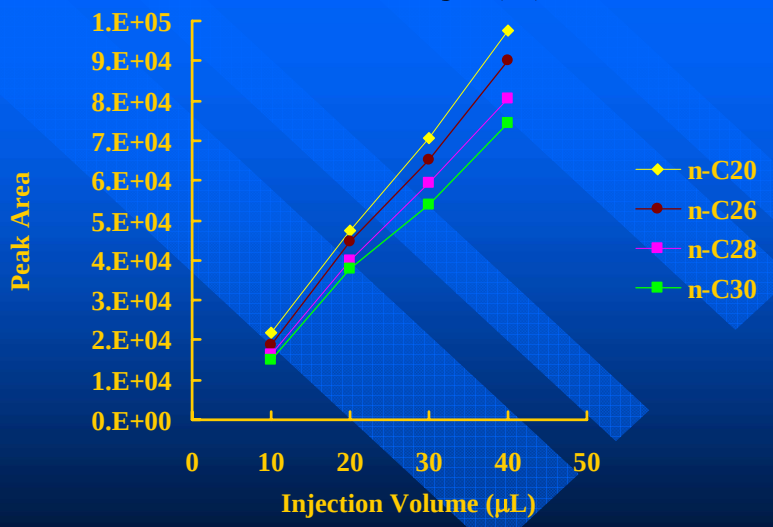


Fig. The relationship between the peak areas and injection volumes (10, 20, 30, 40 µl).

Reproducibility

Table Peak areas of the n-alkanes, average areas and relative standard deviations (R.S.D.).

Compound	#1	#2	#3	#4	#5	#6	#7	#8
n-C10	57465	51172	49832	52175	49285	48795	48666	52475
n-C12	57007	55262	54955	55701	54556	53511	54183	56555
n-C14	71474	69488	68903	69481	67529	66156	68386	70176
n-C16	76798	75169	74463	74394	73390	73021	75292	75571
n-C20	97979	95868	96234	95794	94827	94423	96356	96473
n-C26	90071	91688	89817	90662	87406	87001	89921	89811
n-C28	82609	81358	79343	80507	78297	78564	80017	80723
n-C30	75970	74822	73243	75688	74151	73492	74987	75817

Compound	#9	#10	#11	#12	#13	#14	#15	Ave.	RSD(%)
n-C10	57813	54758	63663	66097	51324	51415	52858	53853	9.81
n-C12	54558	53766	56513	56928	55022	55649	55608	55318	2.00
n-C14	68280	66573	70789	70938	68802	69554	69727	69084	2.21
n-C16	73940	71708	76300	76578	74089	76538	75586	74856	1.96
n-C20	95321	94970	98971	98405	96841	97975	97946	96559	1.47
n-C26	91589	92683	95061	95372	93360	94678	94747	91591	2.93
n-C28	80805	82380	85617	85720	82771	85824	85186	81981	3.18
n-C30	77339	78448	79743	79869	79956	80383	79710	76908	3.35

A 40 µl injection of a standard sample of 0.005 ng/µl concentration was repeated 15 times.

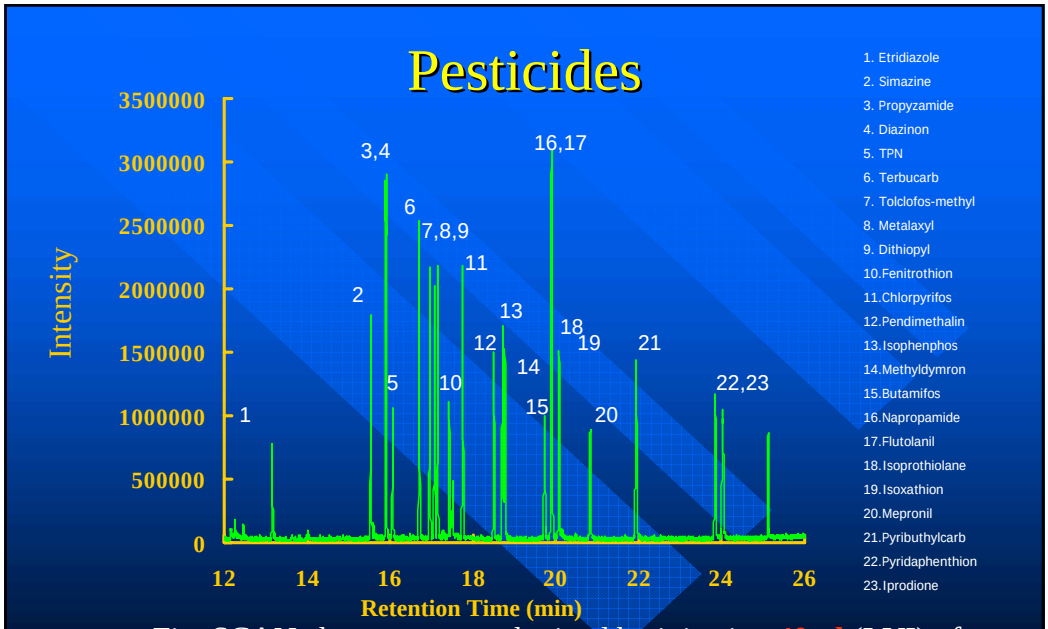


Fig. SCAN chromatogram obtained by injecting 40 µl (LVI) of pesticides in Acetone

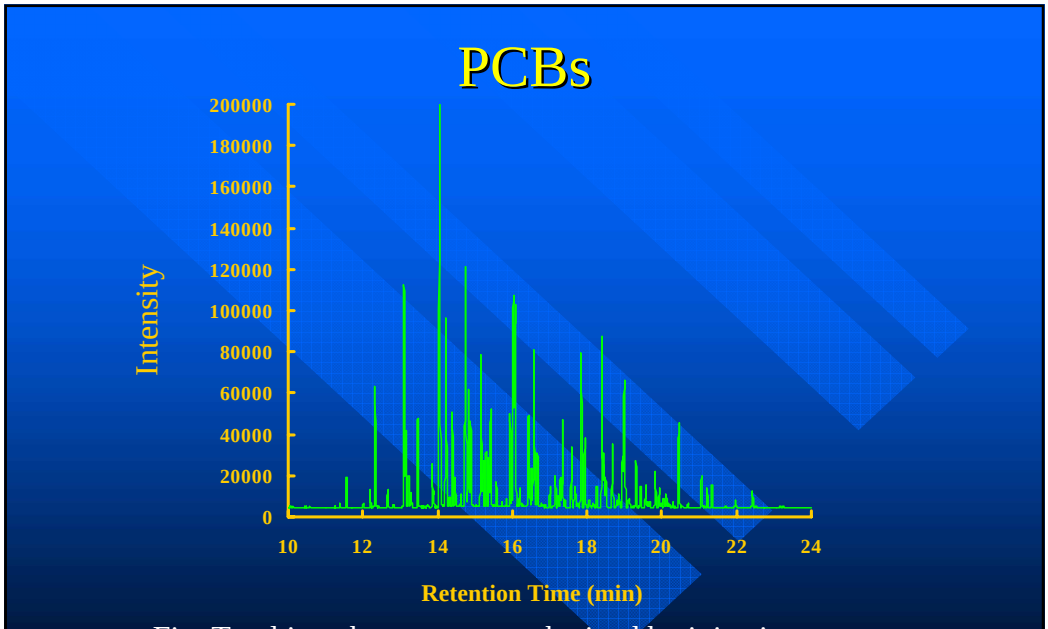


Fig. Total ion chromatogram obtained by injecting 20 µl (LVI) of PCBs in toluene

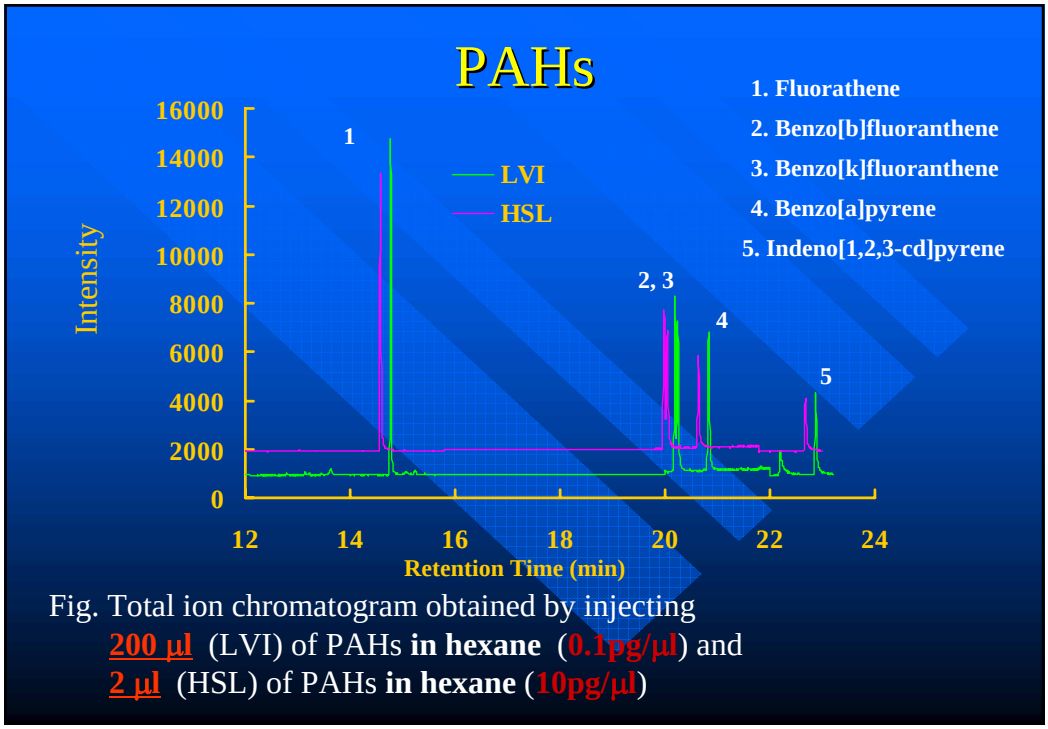


Fig. Total ion chromatogram obtained by injecting
200 μl (LVI) of PAHs **in hexane** (0.1pg/μl) and
2 μl (HSL) of PAHs **in hexane** (10pg/μl)