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

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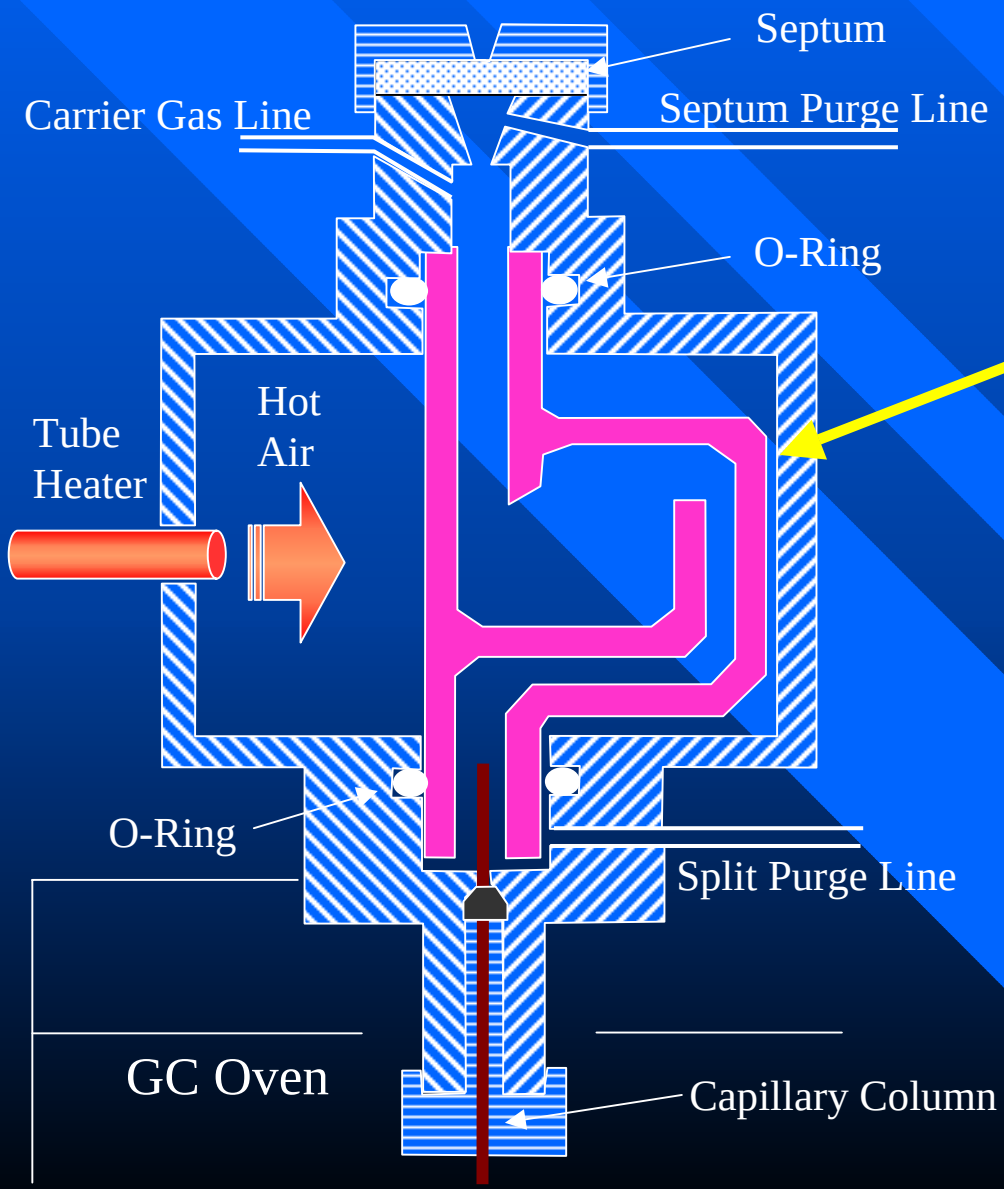
Abstract

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, injection temperature, initial gas pressure, 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



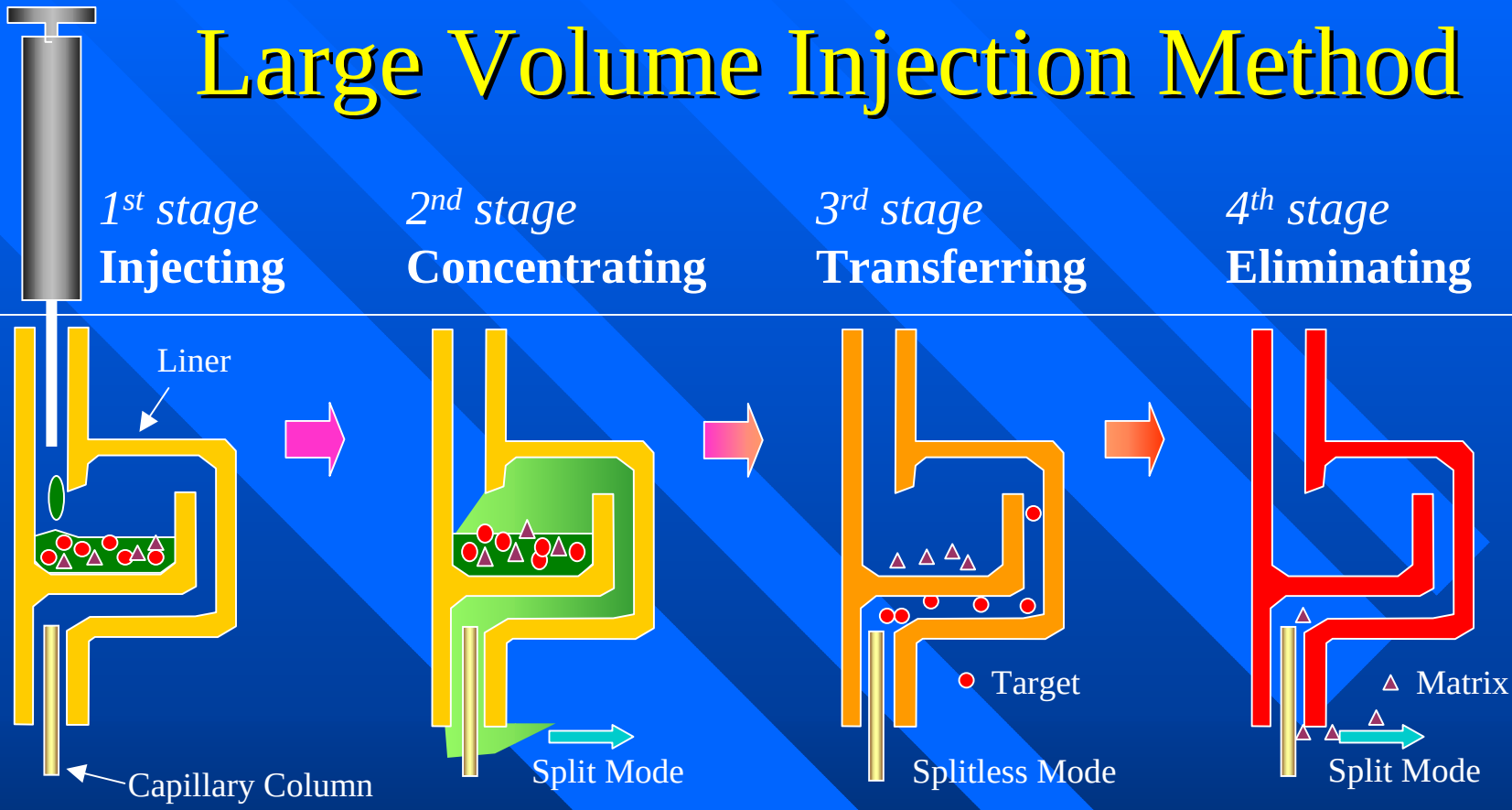
The injection system consisted of a programmed-temperature vaporizing injector with

"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



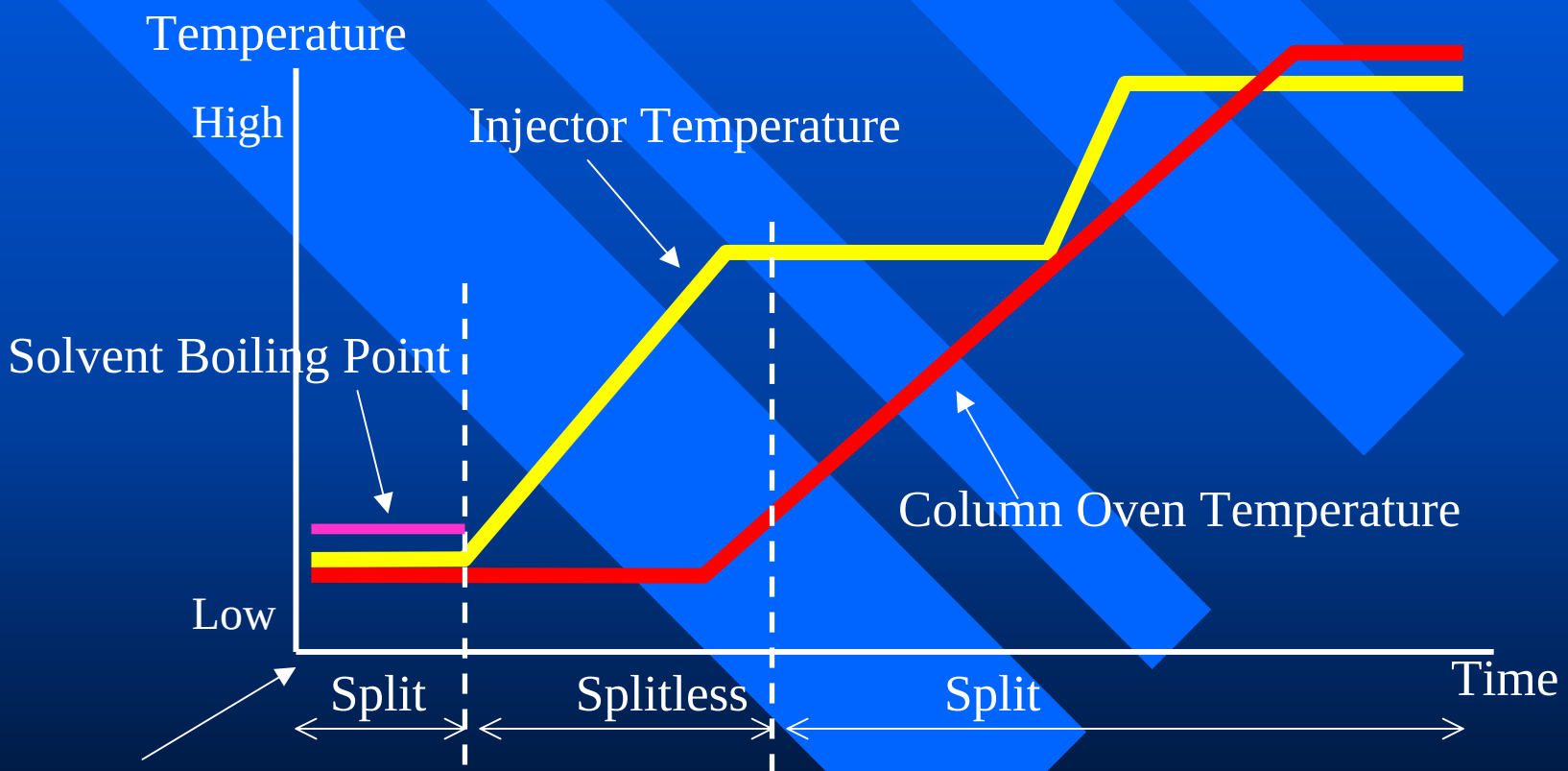
The injector was kept at a temperature lower than the boiling point of sample solvent.
The sample was injected into the liner, and was stayed with liquid state.

While the evaporated sample solvent was exhausted with the split purge, the target compounds were concentrated in the liner.

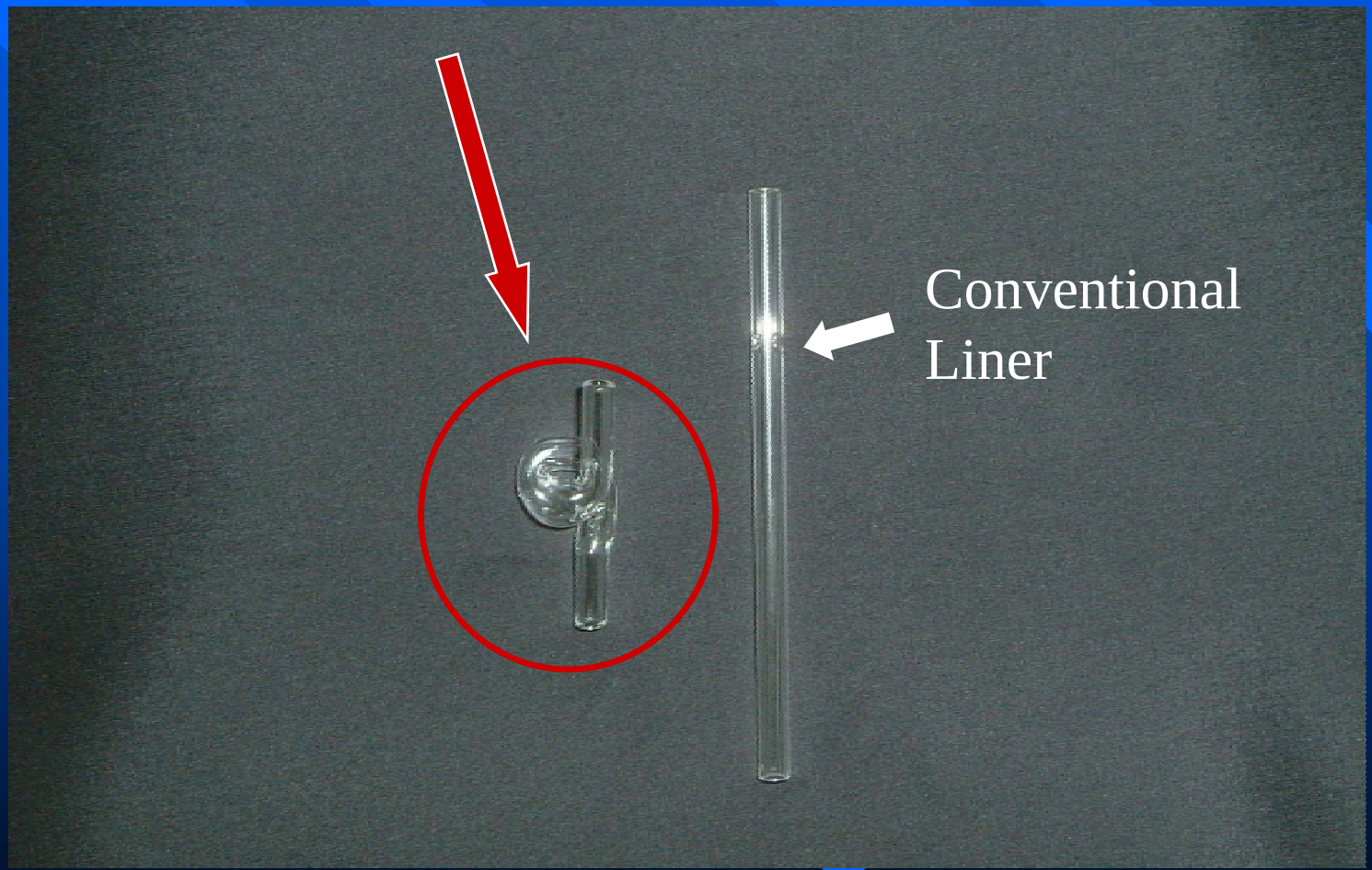
The target compounds were transferred to the capillary column at an elevated injector temperature with the splitless mode.

Matrix compounds were Eliminated from the liner with the split purge at further elevated injector temperature

The Scheme of GC Conditions for Large Volume Injection

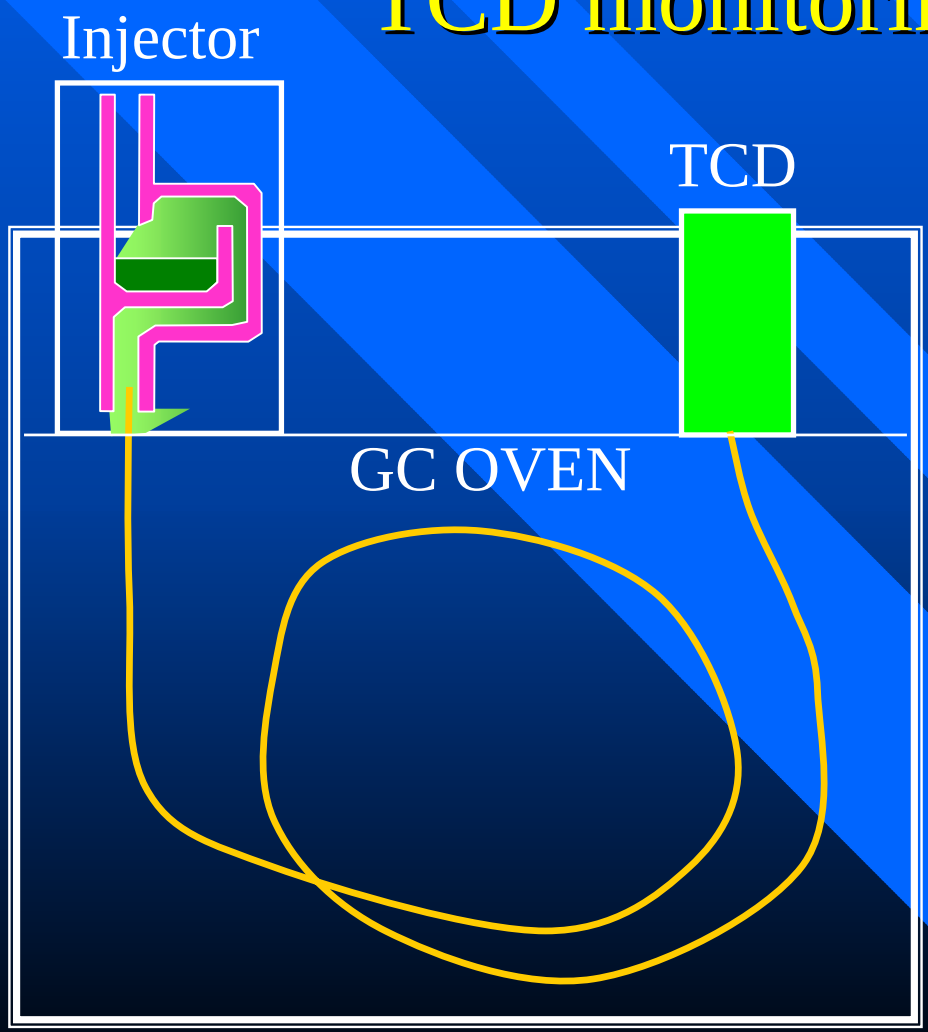


“Stomach” Shaped Liner



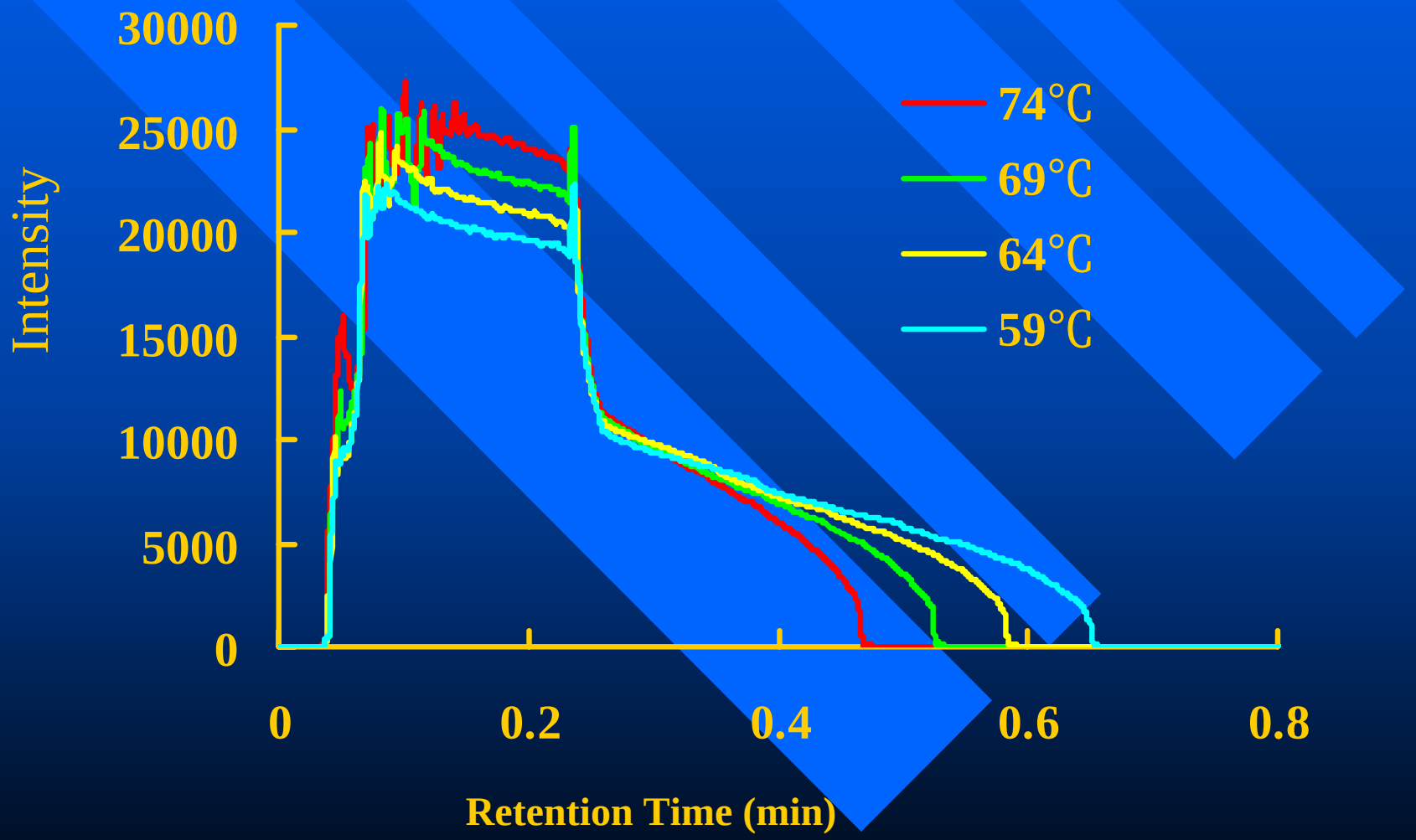
Experiment

TCD monitoring of solvent peak



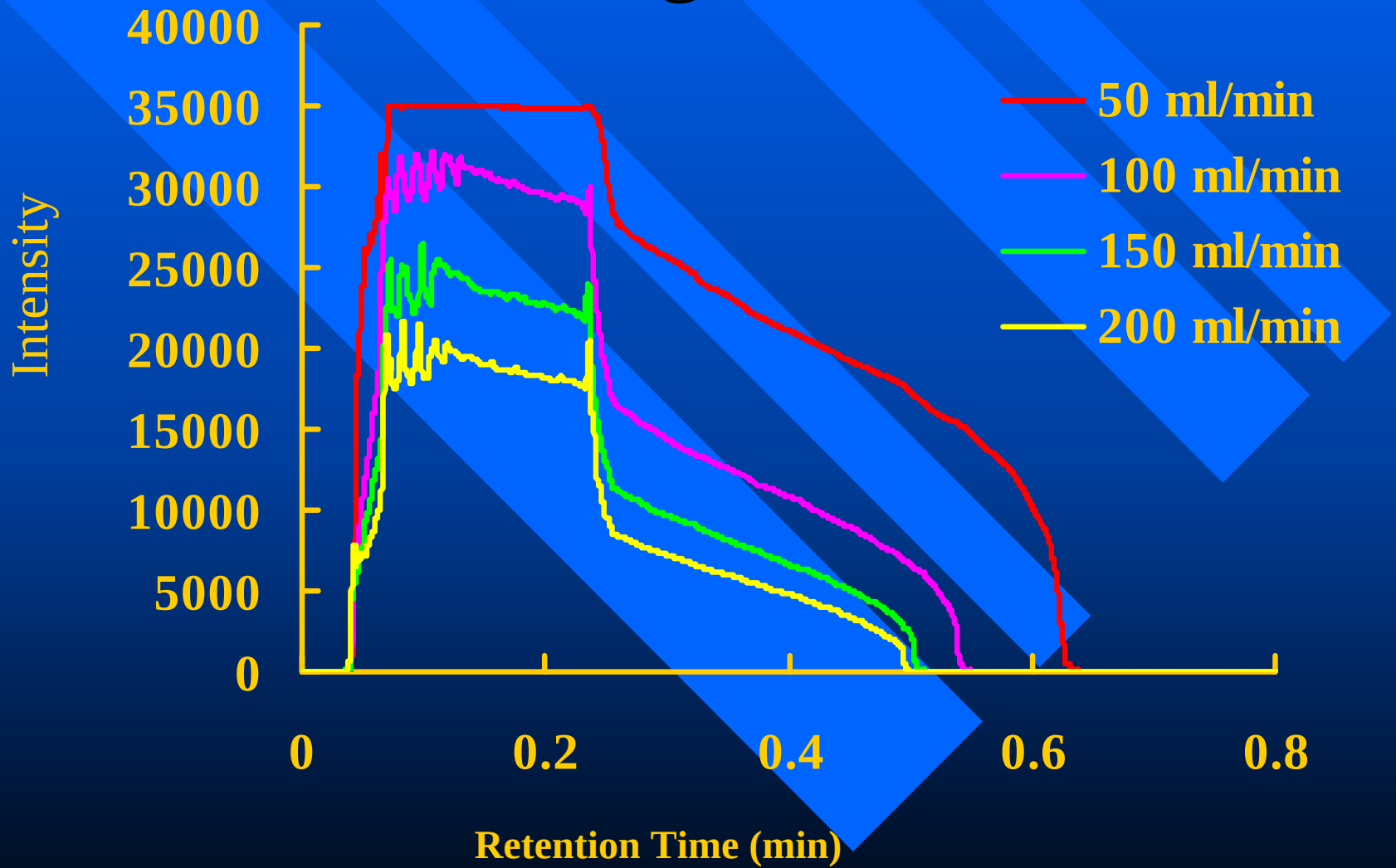
Column; 0.25mm I.d.✕1m

Optimization of the split purge time -Injection Temp-



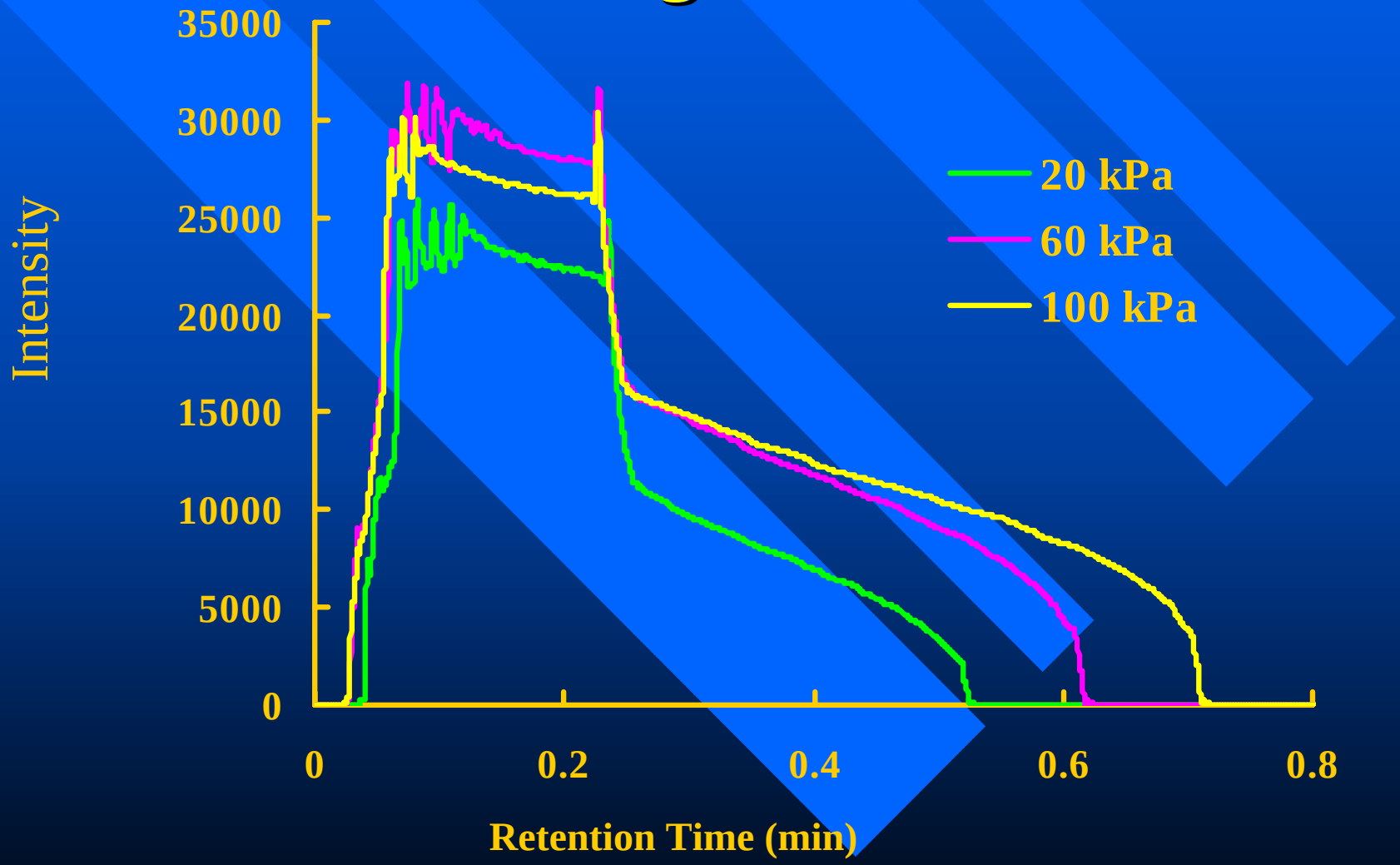
Injection volume 40 μL ; Hexane

Optimization of the split purge time -Purge Flow-



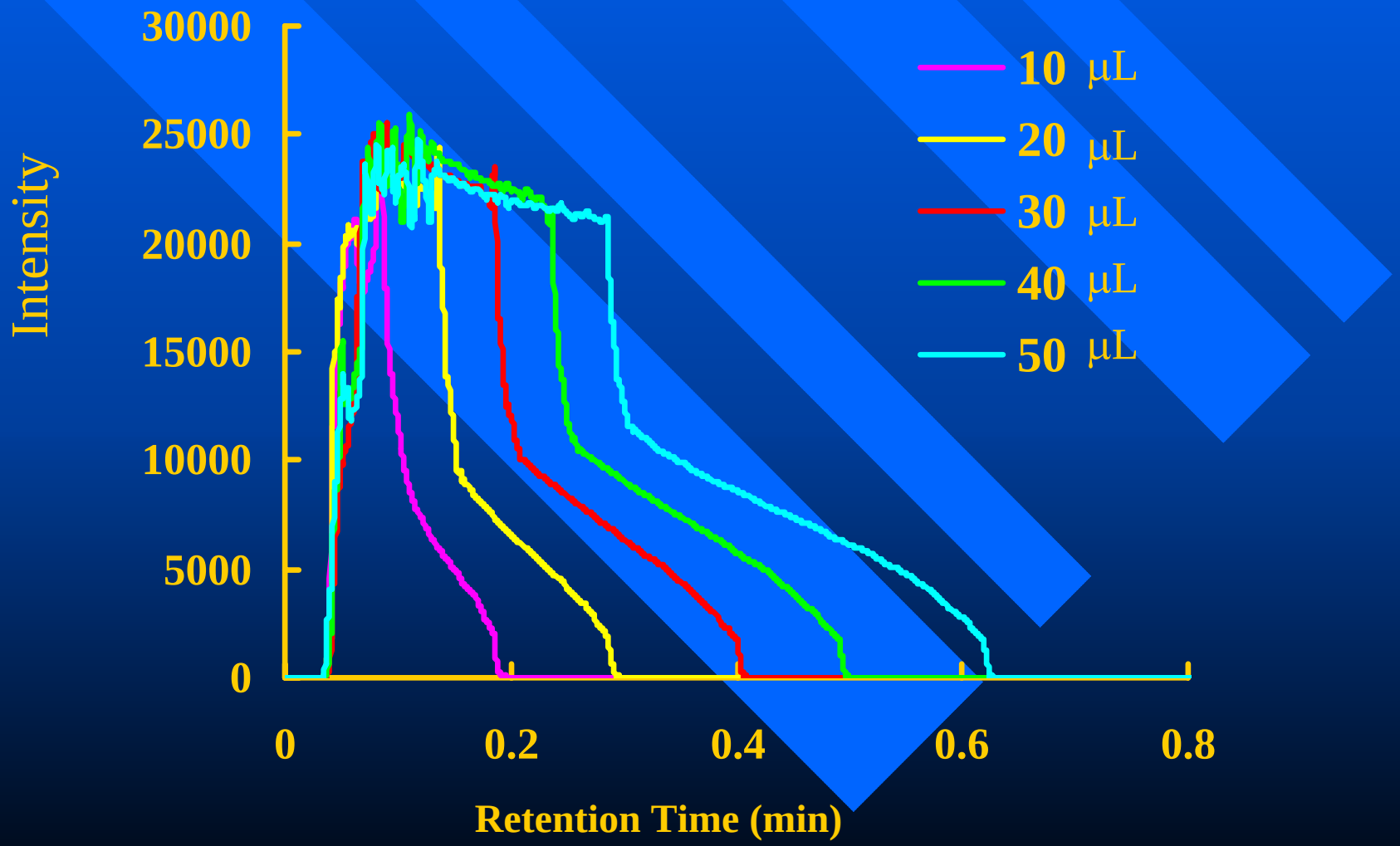
Injection volume 40 μL ; Hexane

Optimization of the split purge time -Purge Press-



Injection volume 40 μL ; Hexane

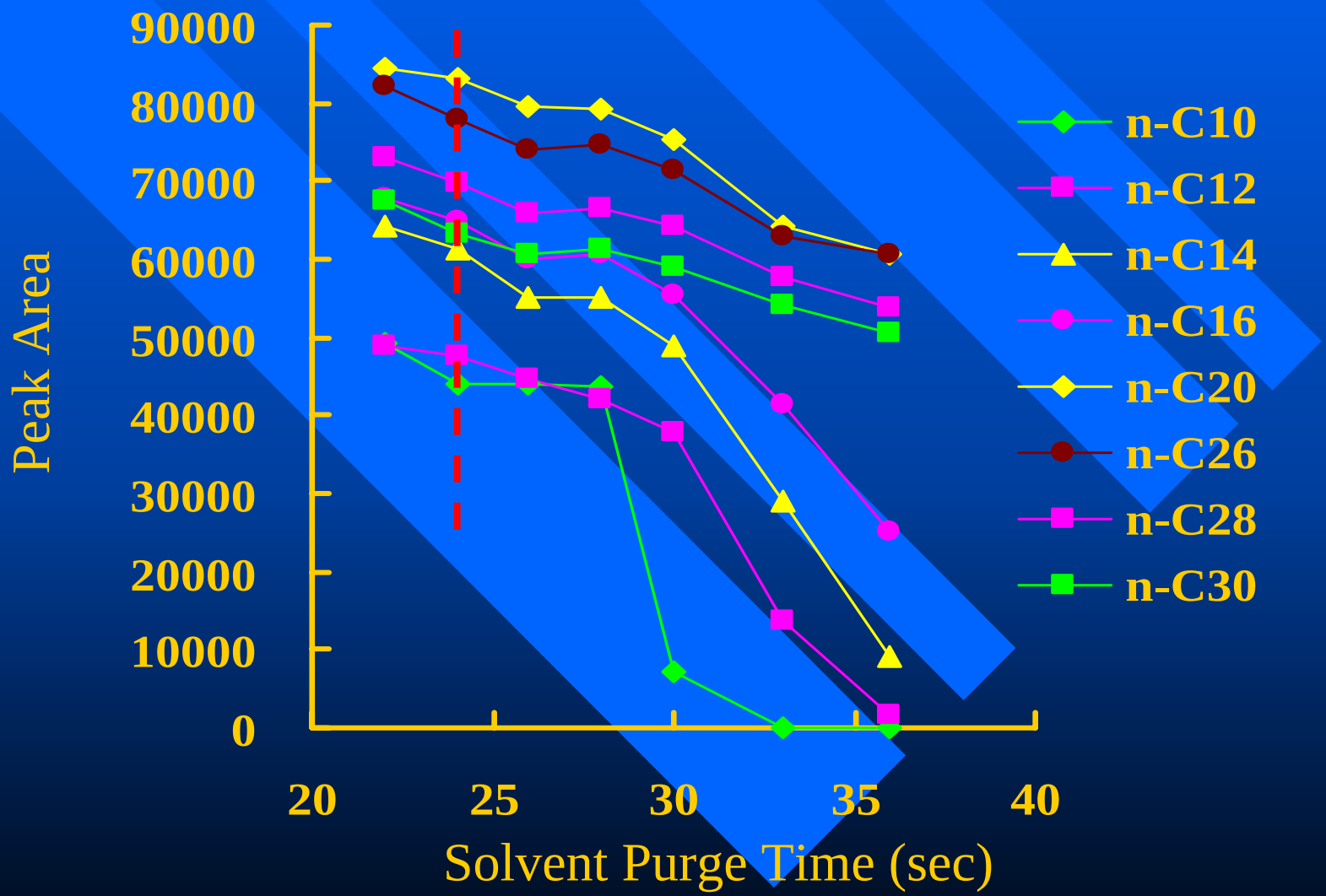
Optimization of the split purge time -Injection Volume Hexane-



Operating Conditions of GC/MS and Injector

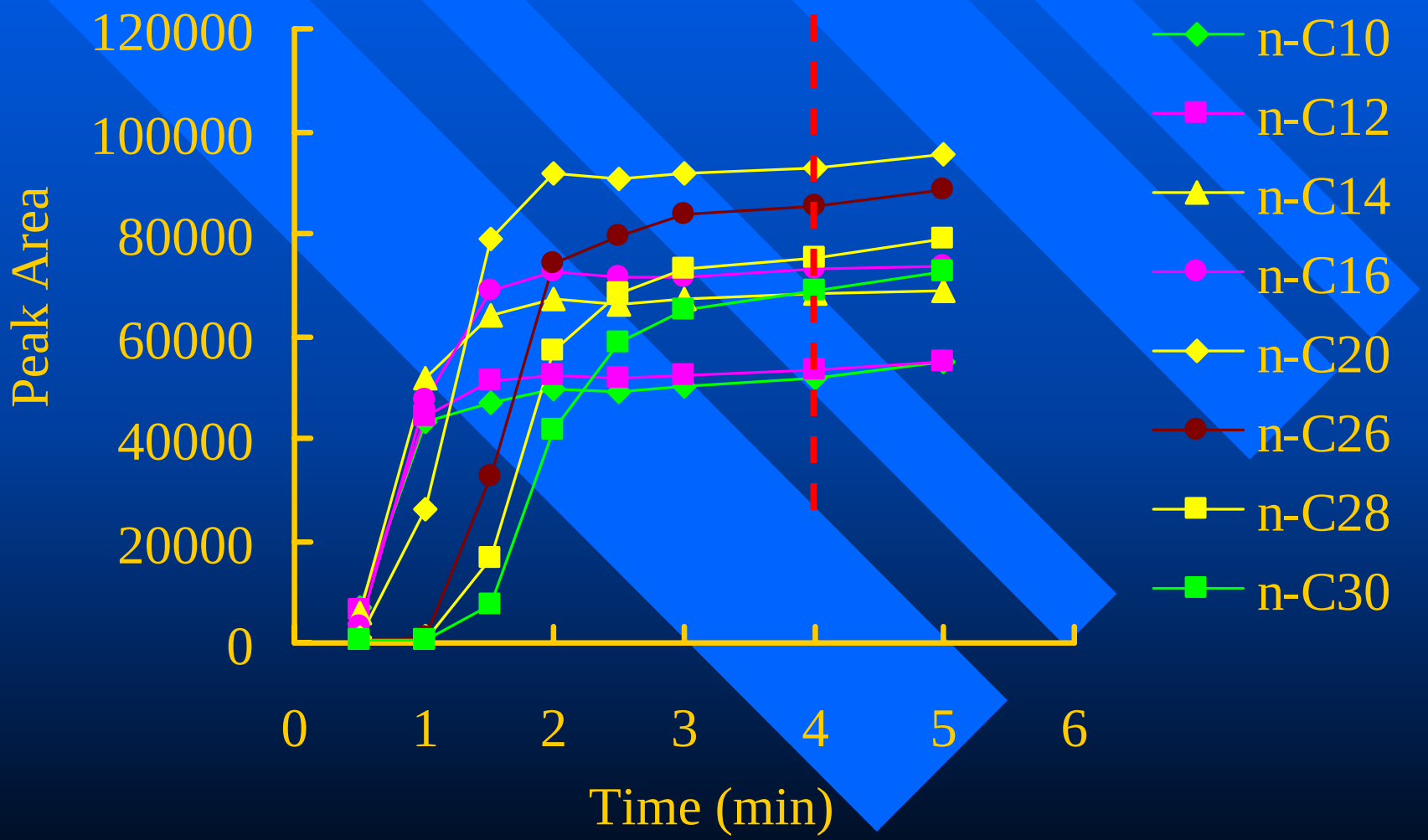
Injector	LaviStoma (EMINET)
Injector Oven Temp.	69℃-100℃/min-270℃(20min)
Solvent Purge Time	12 sec
GC/MS	QP5050A (Shimadzu)
Pre-column	Deactivated silica capillary tube 0.53mm×0.5m
Column	DB-5MS 0.25mm×30m, 0.25μm
Column Oven Temp.	50℃(4min)-15℃/min-315℃(3min)
Detector Temp	300℃
MS Method	SIM
Carrier 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



n-C10,,,,C30 in Hexane; Injection volume 40 µL

Optimization of the splitless time



n-C10,,,,C30 in Hexane; Injection volume 40 µL

Chromatogram

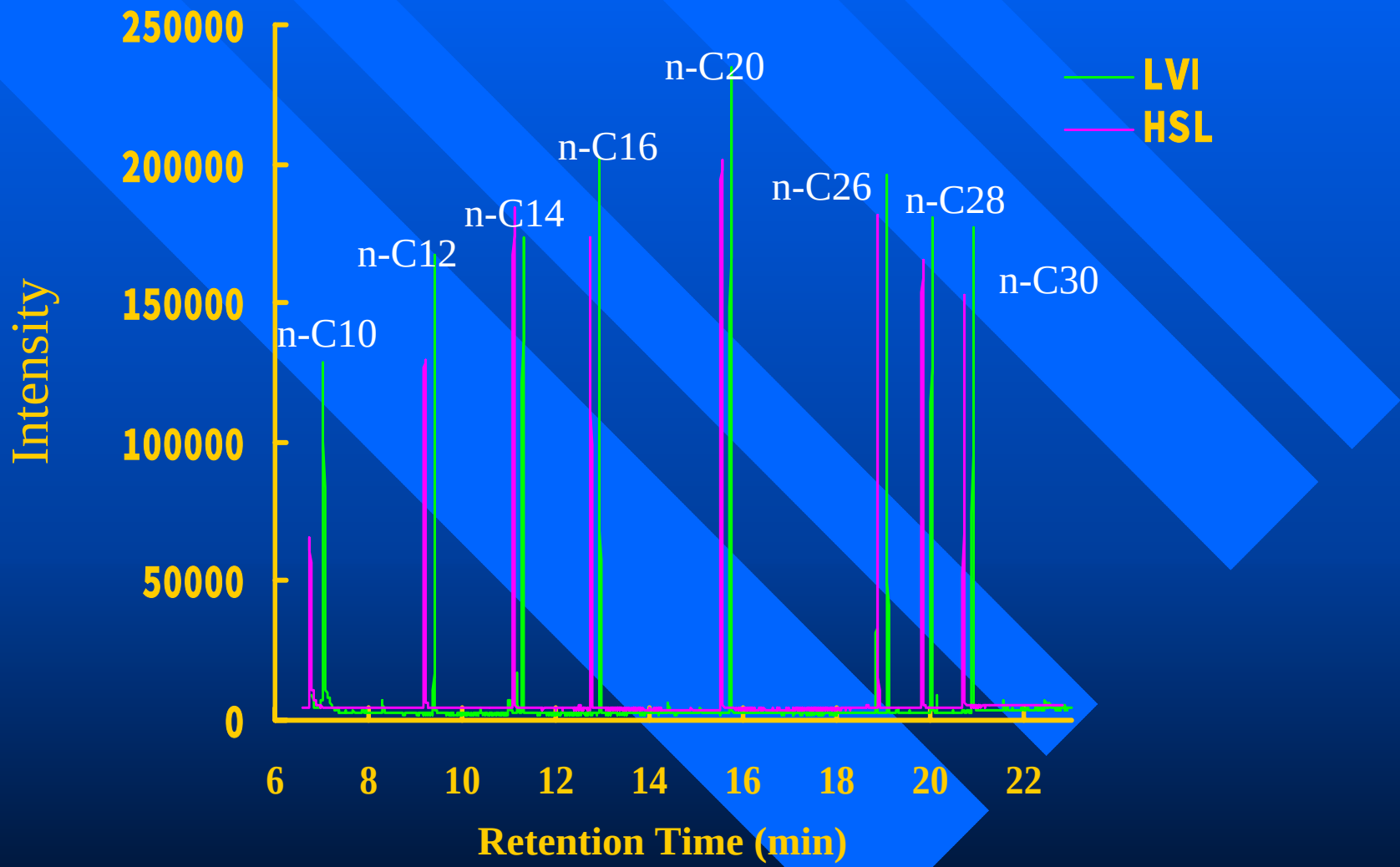


Fig. Chromatograms obtained by injecting

40 μl (LVI) of n-alkane **in hexane** (**0.005ng/μl**) and

2 μl (HSL) of n-alkane **in hexane** (**0.1ng/μl**)

Linearity (1)

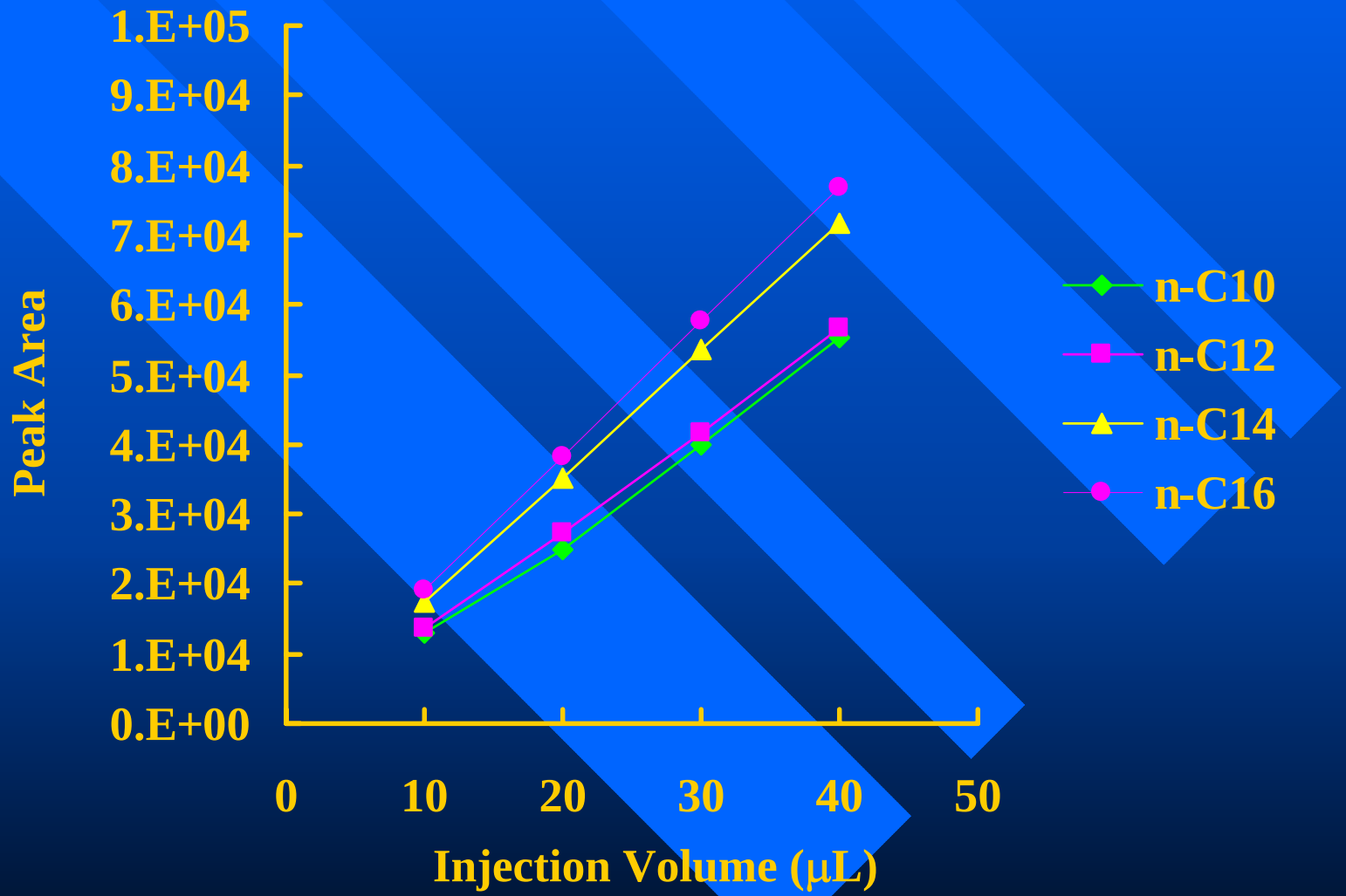


Fig. The relationship between the peak areas and injection volumes (10, 20, 30, 40 μl).

Linearity (2)

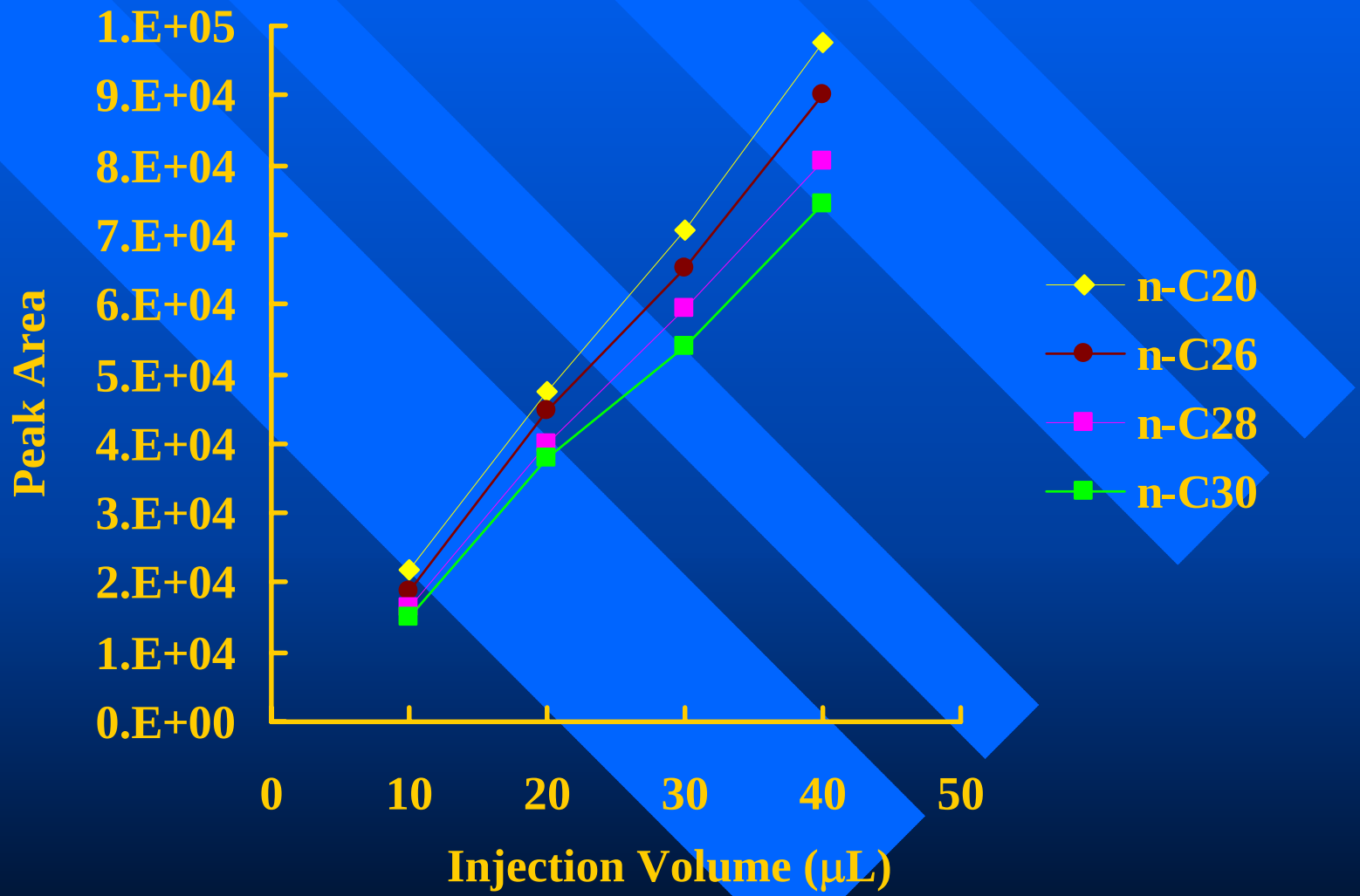


Fig. The relationship between the peak areas and injection volumes (10, 20, 30, 40 μl).

Reproducibility

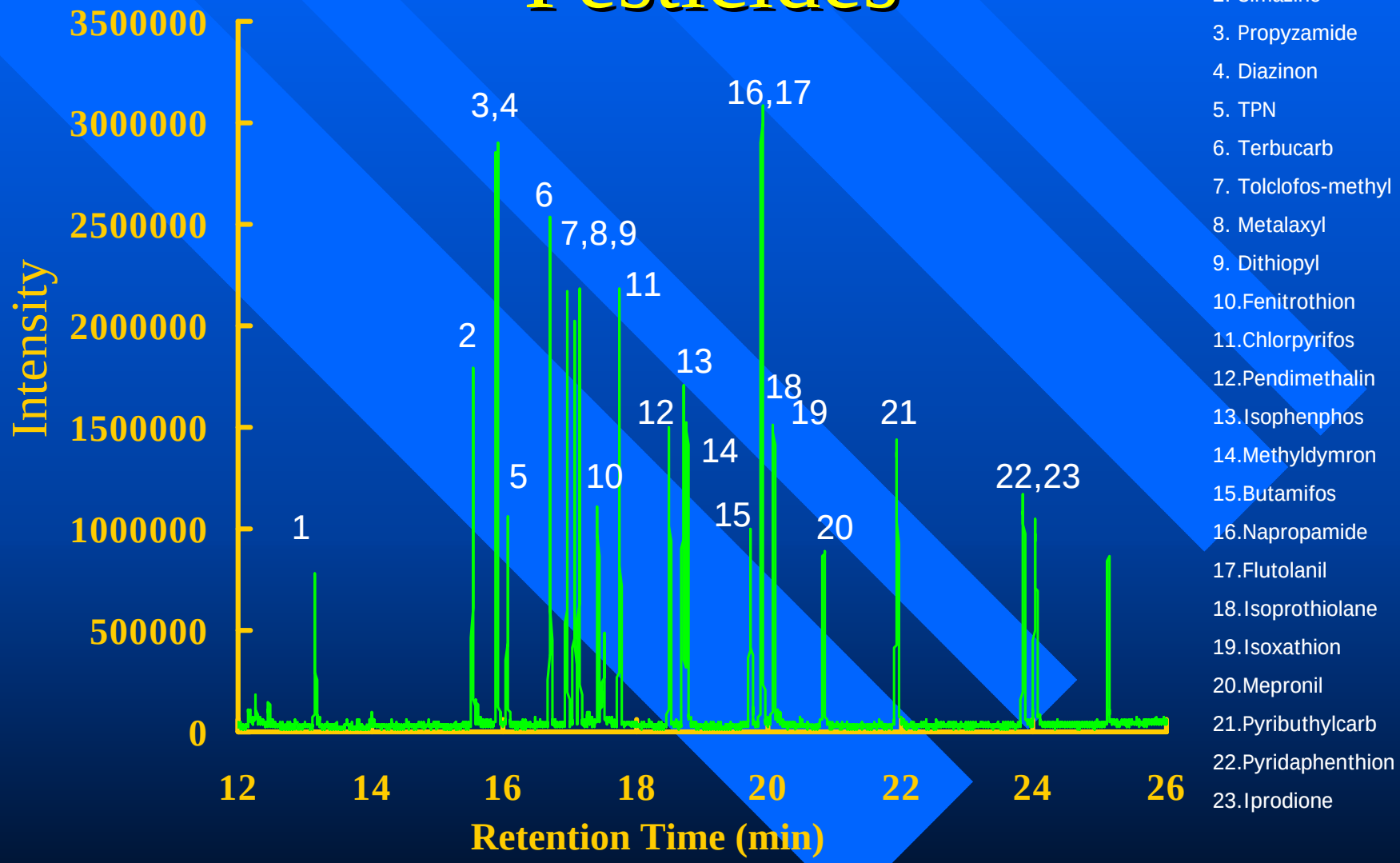
Table Peak areas of the n-alkanes, average areas and relative standard deviations (R.S.D.).

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	51233	**5.69**
n-C12	54558	53766	56513	56928	55022	55649	55608	55216	**2.13**
n-C14	68280	66573	70789	70938	68802	69554	69727	68949	**2.36**
n-C16	73940	71708	76300	76578	74089	76538	75586	74762	**1.63**
n-C20	95321	94970	98971	98405	96841	97975	97946	95994	**1.13**
n-C26	91589	92683	95061	95372	93360	94678	94747	89547	**1.76**
n-C28	80805	82380	85617	85720	82771	85824	85186	80177	**1.80**
n-C30	77339	78448	79743	79869	79956	80383	79710	74771	**1.41**

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

Pesticides



1. Etridiazole
2. Simazine
3. Propyzamide
4. Diazinon
5. TPN
6. Terbucarb
7. Tolclofos-methyl
8. Metalaxyl
9. Dithiopyl
10. Fenitrothion
11. Chlorpyrifos
12. Pendimethalin
13. Isophenphos
14. Methyldymron
15. Butamifos
16. Napropamide
17. Flutolanil
18. Isoprothiolane
19. Isoxathion
20. Mepronil
21. Pyributhylcarb
22. Pyridaphenthion
23. Iprodione

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

PCBs

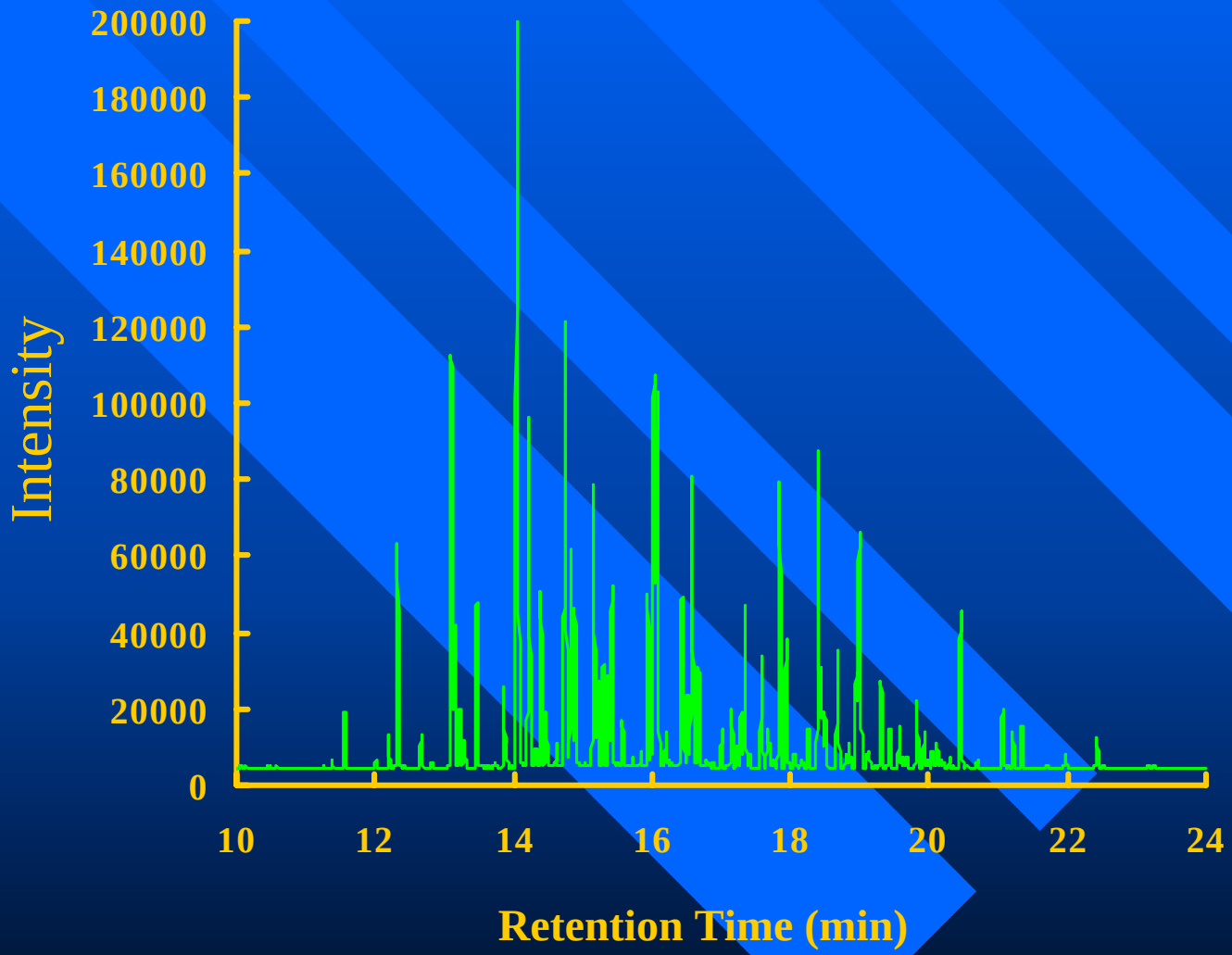


Fig. Total ion chromatogram obtained by injecting **20 µl** (LVI) of PCBs **in toluene**

PAHs

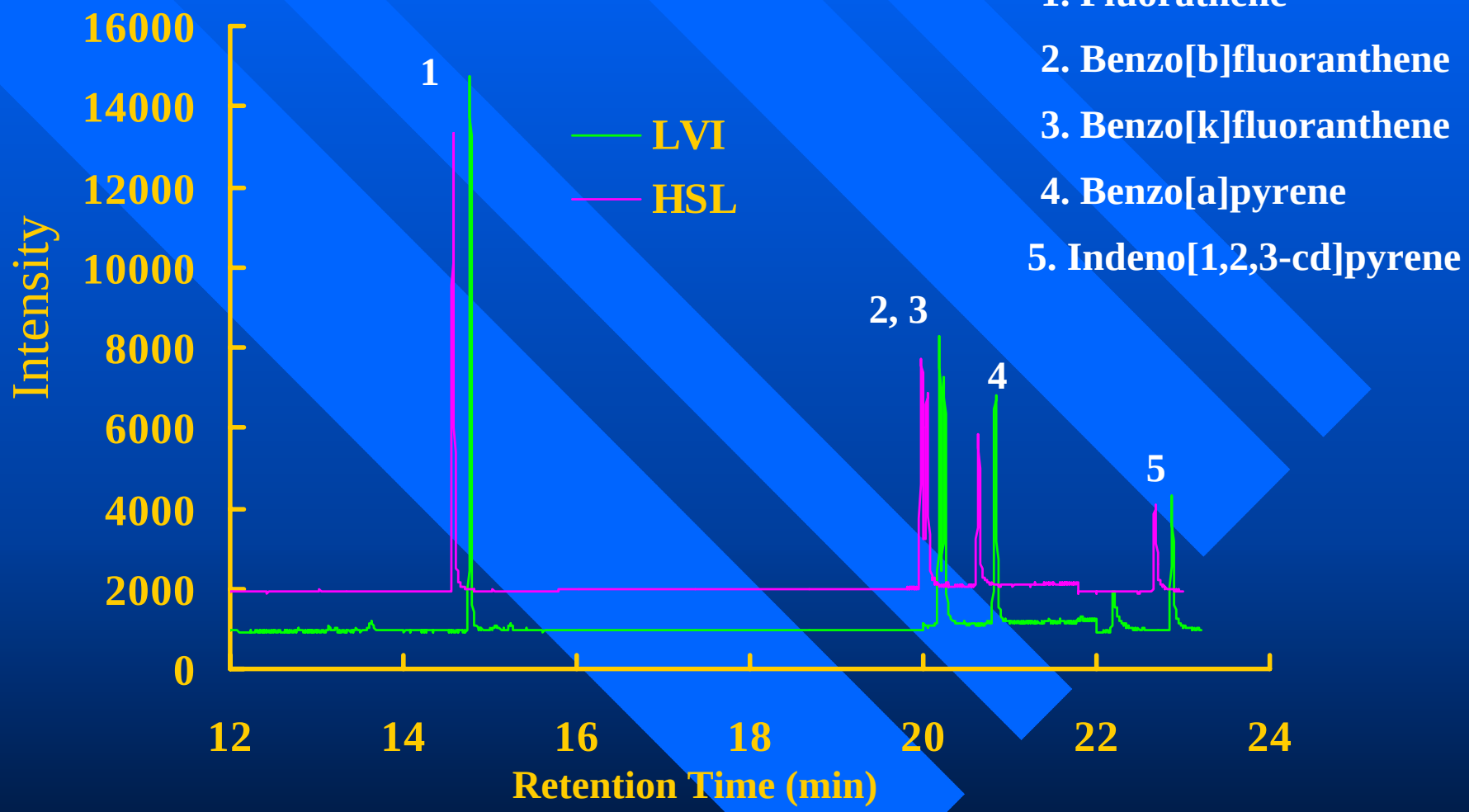
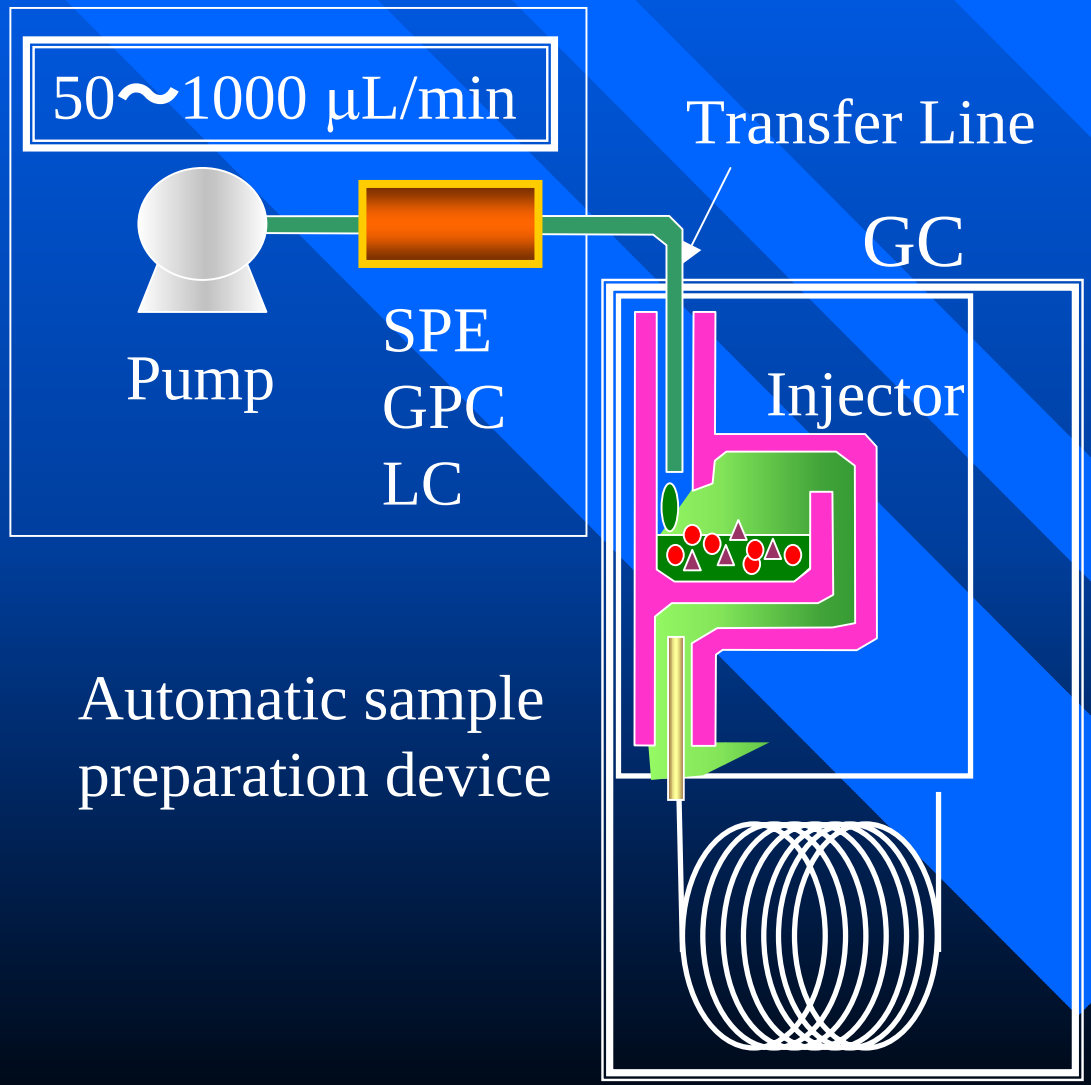


Fig. Total ion chromatogram obtained by injecting
200 μl (LVI) of PAHs **in hexane** (**0.1pg/μl**) and
2 μl (HSL) of PAHs **in hexane** (**10pg/μl**)

Interface of On-Line GC



Automatic sample preparation device

This large volume injection method was employed for an interface to connect automatic sample preparation device (SPE, GPC, LC) to GC as an automatic on-line operation system.

On-Line SPE-GC

On-Line GPC-GC

On-Line LC-GC