

Optimized Automatic Sample Injection and Vaporization in Capillary GC

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OVERVIEW

The performance capabilities of the new AI/AS autosampler Finnigan AI/AS3000, designed to achieve automatic liquid injection in capillary GC, are illustrated and discussed, using both cold needle and hot needle SSL injection techniques. These very different injection methods involve independent mechanisms of sample vaporization: liquid band formation and thermospray respectively. Depending on the injection conditions selected, one of these two mechanisms will strongly influence the sample evaporation process and the sample transfer to the separation column. The new AI/AS3000 is designed to permit easy, appropriate selection of the operating conditions in order to avoid mixed vaporization mechanisms which are the main source for lack of repeatability.

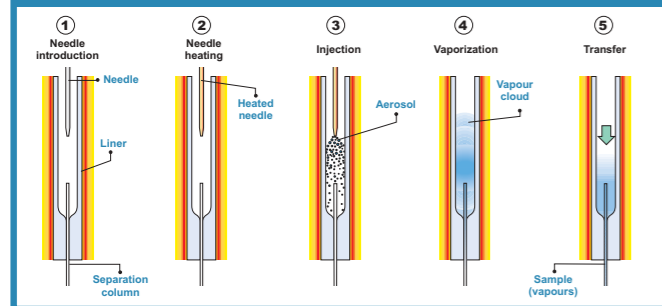
SSL recovers compared to ON Column results are complete for both techniques indicating a non-discriminating transfer. Cold needle technique prevents sample distillation out of the needle before the injection. It requires the use of a small amount of packing material (e.g. a glass wool plug) in the liner to stop and collect the liquid band. The hot needle technique does not require packing material at all and it should be preferred when analysing labile compounds.

On the other hand the cold needle technique should be the method of choice in split mode while analyzing highly concentrated samples in order to avoid dilution because it allows small sample volumes (up to 0.1 µl) with accurate results.

- References
- [1] F. Munari, S. Trestianu in Proc. 4th Int. Symp. Capillary Chromatography, Hindelang Germany, R. E. Kaiser (ed), Hüthig, Heidelberg, 1991, p. 349
 - [2] K. Grob, M. Biedermann, J. Chromatogr. A., 897(2000), 237-246
 - [3] K. Grob, M. Biedermann, J. Chromatogr. A., 897(2000), 247-258

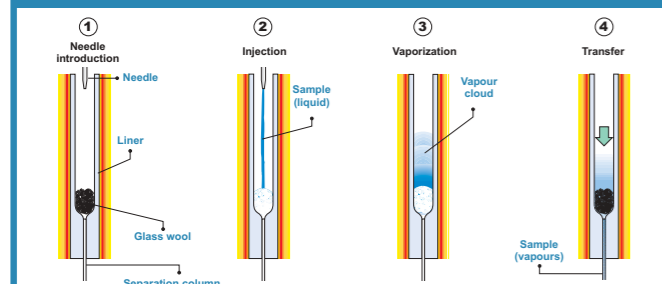
SAMPLE INJECTION AND EVAPORATION MECHANISMS INTO HOT SPLIT/SPLITLESS INJECTOR

FIGURE 1. Thermospray formation (hot needle injection)



Experiments performed with a transparent SSL injector [1-3] showed that a solvent expelled from the hot needle of a syringe forms an aerosol. Heating above the boiling point, produces bubbles of solvent vapour inside the needle. This makes the internal pressure of the needle increase, limiting further vaporization. The solvent becomes a propellant causing the "explosive" expelling of the liquid in form of droplets scattered in the carrier.

FIGURE 2. Liquid band formation (cold needle injection)

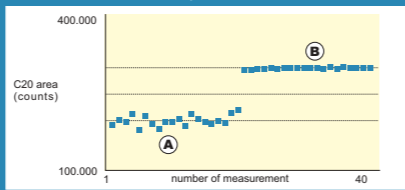


If heating of the needle is minimized, the solvent expelled from the needle tip forms a liquid band [1-3]. This band may reach the bottom of the liner even with low-boiling solvents, thanks to a vapour cushion that immediately surrounds liquid. Use of glass wool as packing material traps the liquid. The experiments conducted in the SSL transparent injector [3] indicate that sample leaves the wool only after the solvent vaporization.

FIGURE 3. (A) The AS3000 autosampler version installed on the Finnigan Trace™ GC ULTRA (B) The AI3000 autosampler version installed on the Finnigan Focus™ GC



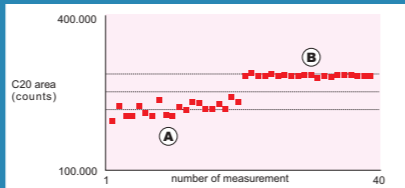
FIGURE 4. Optimisation of cold needle injections C20 area in a sequence of 40 splitless cold needle injections without (A) and with (B) glass wool. RSD% is 4-5% for (A) and less than 0.4% for (B)



The optimal conditions found for cold needle injection can be summarised as follows:

- liner partially packed with glass wool
- minimum needle depth into the injector (short needle insertion injection mode)
- no dwell times (minimum warming and boil-out)

FIGURE 5. Optimisation of hot needle injections C20 area in a sequence of 40 splitless hot needle injections. Dwell time is (A) 0.1 sec. and (B) 5.0 sec. RSD% is 6% for (A) and less than 0.8 % for (B)



The optimal conditions found for hot needle injection can be summarised as follows:

- 5 seconds pre injection dwell time (warming of the needle above the solvent b.p.)
- whole needle insertion into the injector (standard needle insertion mode)
- empty liners

PROOF OF PERFORMANCE: SPLIT INJECTION

FIGURE 6. Cold needle (left) and hot needle (right) split injections of a standard hydrocarbon mix (see conditions in the box)

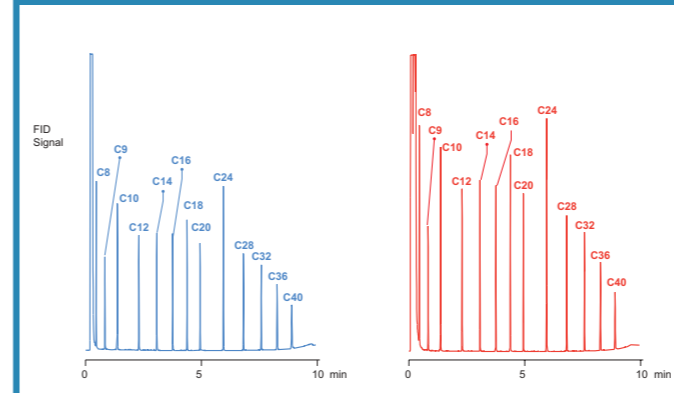
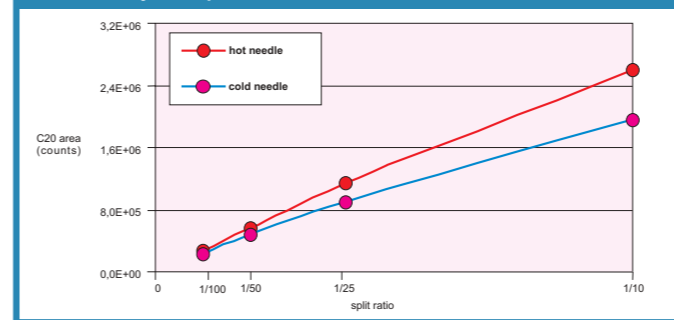


TABLE 1. Split peak areas repeatability and recoveries (on ten consecutive measurements)

Component	Cold needle injection			Hot needle injection		
	Average (counts)	RSD%	R _{SS/OC}	Average (counts)	RSD%	R _{SS/OC}
C9	4.63E+05	0.31	1.04	7.29E+05	0.31	0.98
C12	4.97E+05	0.34	1.01	8.37E+05	0.40	1.02
C16	5.01E+05	0.82	0.98	8.63E+05	0.53	1.02
C20	5.32E+05	1.18	1.00	8.84E+05	0.48	1.00
C24	8.78E+05	1.16	1.02	1.41E+06	0.60	0.99
C32	5.52E+05	1.21	1.05	8.39E+05	0.46	0.96
C36	5.15E+05	1.07	1.06	7.57E+05	0.48	0.93
C40	4.37E+05	1.75	1.08	6.31E+05	0.48	0.94

Sample: n-alkanes in n-hexane, 100-200 ng/µl
 Sample volume: 1 µl (split ratio 1:30)
 Instrument: Finnigan Focus GC
 SSL injector (300°C),
 FID detector (345°C)
 Column: RTX-1 30 m, 0.32 mm i.d., 0.10 µm
 Carrier: helium, 2.5 ml/min
 Oven method: 90°C (1') to 340 (2') @ 30°C/min.
 Sample method: cold needle — hot needle —

FIGURE 7. Linearity of the split ratio



C20 peak areas versus the nominal split ratio (column flow divided by the split flow). Split ratio of 1:10, 1:20, 1:50, 1:100 correspond to split flow rates of 25, 50, 125, and 250 ml/min respectively. The difference in the two lines is still related to the needle volume.

PROOF OF PERFORMANCE: SPLITLESS INJECTION

FIGURE 8. Cold needle (left) and hot needle (right) splitless injections of a standard hydrocarbon mix (see condition in the box)

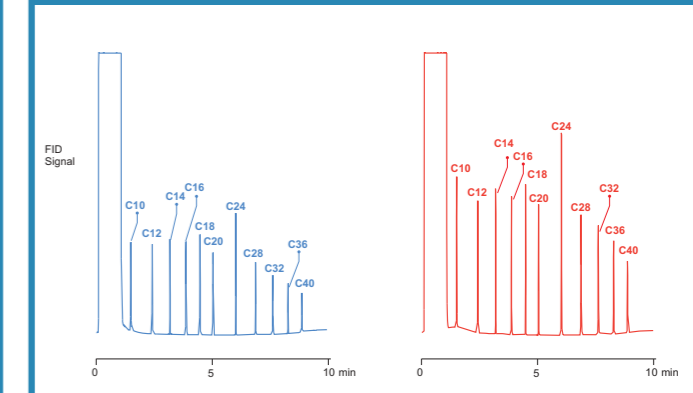
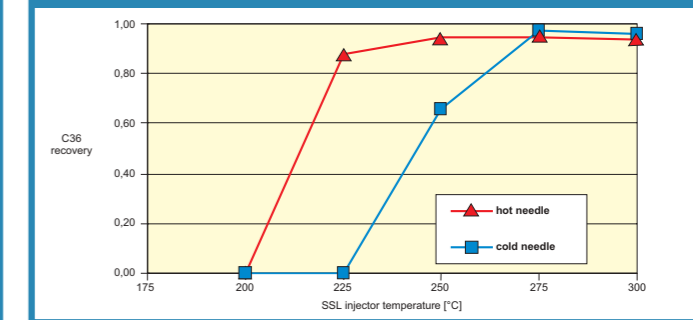


TABLE 2. Splitless peak areas repeatability and recoveries (on ten consecutive measurements)

Component	Cold needle injection			Hot needle injection		
	Average (counts)	RSD%	R _{SS/OC}	Average (counts)	RSD%	R _{SS/OC}
C12	2.34E+05	1.38	0.93	3.89E+05	0.34	0.98
C16	2.61E+05	0.63	1.01	4.03E+05	0.71	0.98
C20	2.72E+05	0.63	1.00	4.29E+05	0.56	1.00
C24	4.44E+05	0.71	1.01	7.03E+05	0.63	1.01
C32	2.69E+05	0.86	1.00	4.15E+05	0.75	0.97
C36	2.48E+05	0.83	1.00	3.97E+05	0.85	1.01
C40	2.04E+05	0.69	0.99	3.06E+05	0.90	0.94

Sample: n-alkanes in n-hexane, 2-4 ng/µl
 Sample volume: 1 µl
 Instrument: Finnigan Focus GC
 SSL injector (300°C),
 FID detector (345°C)
 Column: RTX-1 30 m, 0.32 mm i.d., 0.10 µm
 Carrier: helium, 2.5 ml/min
 Oven method: 50°C (1') to 340 (2') @ 30°C/min.
 Sampler method: cold needle — hot needle —

FIGURE 9. Effect of glass wool



C36 recovery at increasing injector temperature. At 225°C recovery in hot needle is almost complete while cold needle achieves a complete recovery at a temperature about 50°C higher. TRACE and Focus are trademarks of Thermo Finnigan LLC.