ELUCIDATION OF GAS CHROMATOGRAPHIC SAMPLE INTRODUCTION PROCESSES

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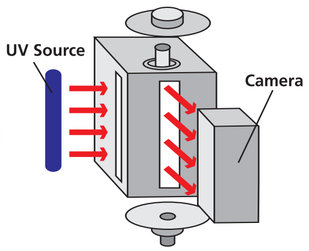
INTRODUCTION

The primary function of a gas chromatographic inlet system is to present the gas chromatographic column head with all, or a representative sample of, the vapor or gas to be analyzed without degradation or mass discrimination. The groundbreaking work by K. Grob and M. Biedermann[1-3] indicated the potential of visual imaging for evaluation of the gas chromatographic inlet vapourization process. Mechanical and thermal limitations of their apparatus however, prevented its use in the evaluation of commercial injector liners.

VISUAL EQUIPMENT

Two parallel slots were cut longitudinally nearly the full length of an aluminum injector block, both intruding into the liner cavity at right angles to one another. One of these supplied UV light from a cold cathode discharge lamp to provide fluorescence excitation of injected solution, and the other slot to allow the resultant visible light emission to be recorded on a miniature CCTV camera. Two white light beams illuminate the syringe needle tip and another the head of the column. In operation the liner was sealed with a septum cap at one end, and a fitting which supported a column and exit vent at the other. The injected solution was perylene in ethyl acetate.



QUANTITATIVE ANALYSIS

Comparison of the observed results with chromatographic evaluations was carried out with a solution containing acid, base and neutral probes, injected to evaluate the transfer efficiency and reproducibility of the liner designs. Direct contact of some solutes with a hot surface may cause thermal or catalytic degradation.

REPEATABILITY TESTS

Test solution of neutral, acidic and basic compounds. One microliter split (1:50) injections, using an Agilent 7673 Autoinjector. Injector and detector at 200°C, oven isothermal at 140°C. Results (n=10) in ***Figures 1 & 2***.

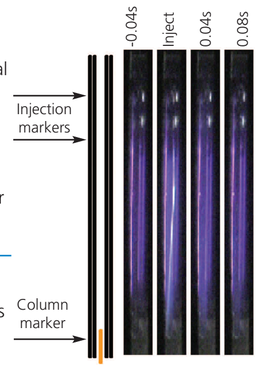
PASSIVITY TEST

Liner/injector activity was determined by injecting a mixture of thermally unstable endrin and tetrachloroxylene (50ppm) into a splitless injector heated to 350°C. The detector was at 200°C and oven isothermal at 190°C. Helium carrier. Ratio (n=10) of endrin/IS chromatographic peak areas. Results in ***Figure 3***.

Straight liner

Traditional protective barrier between analyte vapor and metal walls of injector. Poor heat transfer into injected liquid stream. Liquid solvent jet may extend to walls or base of injector, causing analyte degradation. Droplets may enter column head. Highly injection dependent.

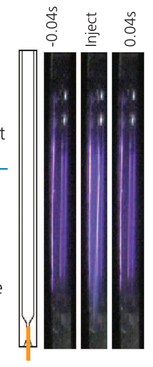
Sample reaches column inlet region not fully vaporized. Detector response to compounds low ***(Figure 1)*** and inconsistent ***(Figure 2)***.



Bottom Taper

Used for splitless injections where the solutes may be kept in the injector for tens of seconds, to minimize solute contact to hot metal surfaces at the bottom of the injector. Acts as a restrictor for high split injections but may be used for low split applications.

Sample retained in liner for longer. Better chance of full vaporization. Outlet restriction caused by taper, solvent vapor viscosity preferentially forcing more solute onto the column head ***(Figure 1)***, increasing response. This effect may cause mass discrimination. Results more consistent ***(Figure 2)***. Less contact with injector walls, indicated by low endrin degradation ***(Figure 3)***.

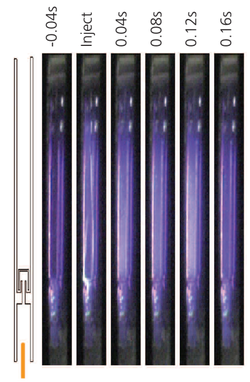


Jennings Cup

Developed, in part, to overcome the incomplete evaporation of the solution stream by providing a convoluted path. Ensures all analytes are exposed to hot glass surface to maximize vaporization.

Performed well, solutes vaporized before reaching column head. Reproducible results with no observable rise in injector pressure forcing excessive solutes onto column head ***(Figures 1 & 2)***.

Contact with glass components of injector caused endrin thermal degradation ***(Figure 3)***.



Gooseneck

Liquid jet evaporates through contact with glass walls of liner. Small gooseneck orifice minimizes liquid penetrating into lower chamber and contacting column head. Droplets may be swept through orifice during solvent expansion pressure pulse.

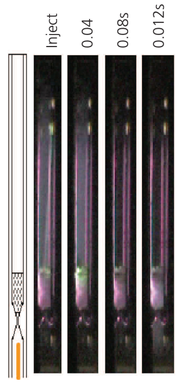
Solvent stream sprayed directly onto restrictor in some cases. Hot sputter of solvent evident causing droplet formation. Lower transfer of solutes onto column head ***(Figure 1)***. Fair reproducibility ***(Figure 2)***.

Gooseneck and Wool

Silica wool ensures mixing of liquid solution jet. Gooseneck expansion then provides expanding laminar flow past column head.

Solvent sprayed off liner wall, settling on silica wool before transferring through to the column head region. Slow evaporation of solvent off wool delayed solute evaporation. Results show similar solute transfer ***(Figure 1)*** onto the column as FocusLiner although the results were less reproducible ***(Figure 2)***.

Contact of solvent onto hot glass causes less degradation than spraying solution onto hot glass ***(Figure 3)***. Lower ratio Endrin/IS value may be partly caused by non-tapered bottom allowing analyte contact with base of metal injector.



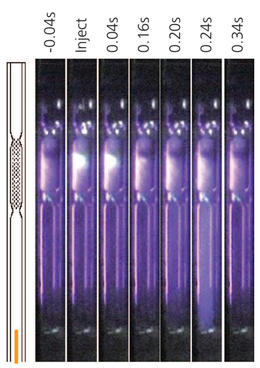
FocusLiner™

Universal split liner. Syringe needle wicks solution onto wool. Solvent evaporation minimizes solute temperature exposure, concentrates solutes into center of wool. Slower heat transfer creates fast, homogeneous, cool vapor evolution onto column head and split vent.

Syringe tip contacted the top of the silica wool, aiding transfer of solution. As solvent evaporated from the outside the solutes moved inward with the solvent (white fluorescence), concentrating to a solid plug on the liner center line, maintained at the boiling temperature of the solvent. When all solvent had evaporated, the solutes misted out of the silica wool at their vaporization temperatures (violet mist fluorescence), filling the lower liner chamber.

Reproducibility was significantly improved over other liners ***(Figures 1 & 2)***.

When tapered FocusLiner was used, minimal endrin degradation was apparent ***(Figure 3)***.



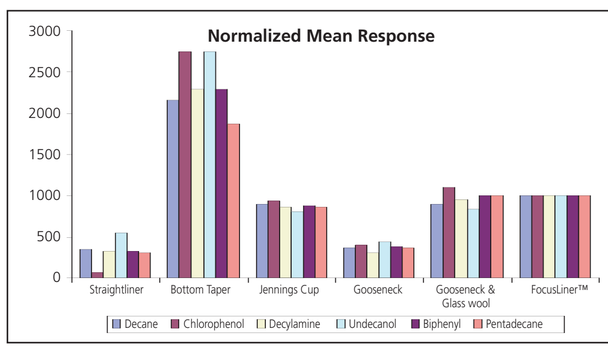


Figure 1. *Mean (n=10) of detector response to compound normalized to FocusLiner response (most reproducable results - Figure 2)*

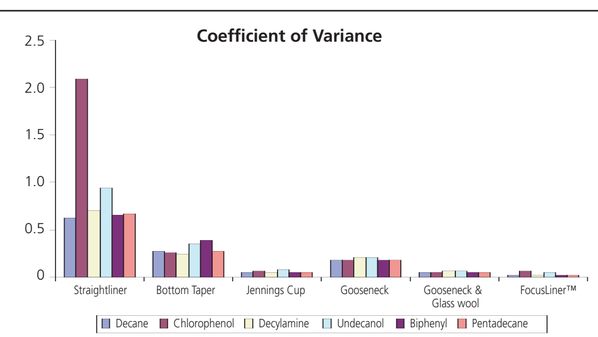


Figure 2. *Coefficient of variance of results from Figure 1.*

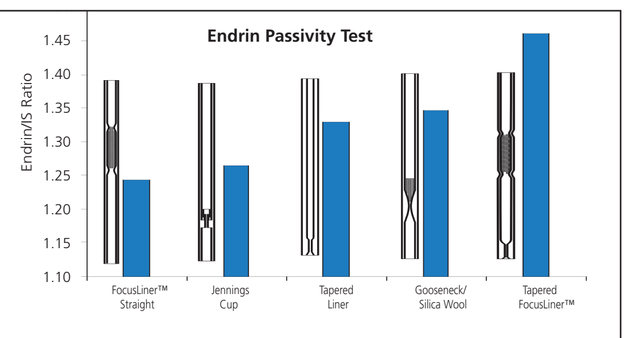


Figure 3. *Average (n=10) Endrin/IS peak area ratio.*

CONCLUSION

FocusLiner shows considerable advantage over other injector liners. Using a combination of direct syringe to silica wool transfer of solution and controlled heat transfer into the deactivated silica wool mass, a high, reproducible amount of solute is transferred onto the column head at the minimum possible temperature. For high split applications the non-tapered FocusLiner is suggested as it maximizes representative mass transfer, while for low split or splitless applications the tapered FocusLiner is recommended to eliminate contact with metal parts of the hot injector.

References

1. *K. Grob, M.Biedermann, J.Chromatogr A. 897 (2000), 237-246*
2. *K. Grob, M.Biedermann, J.Chromatogr A. 897 (2000), 247-258*
3. *M. Biedermann, A. Fiscalini, "Large volume CSR splitless injection: a look inside the injector and experimental data", 27th ISCC, Riva del Garda, Italy, 2004.*

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