HIGHLY INERT GLASS INJECTION PORT LINERS FOR SEMI-VOLATILES ANALYSIS

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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, in as narrow a band as is possible. Passivation of glass surfaces and inlet liner design are both important in controlling sample discrimination and band broadening.

Experimental

All experiments used a Hewlett-Packard 5890 GC, fitted with a single standard split/splitless inlet, electron capture (ECD) detector and a 7673 autoinjector. Analysis was performed in a BPX5 column (15 m x 0.25 mm x 0.25 µm). Probe compounds for the analysis were DDT and endrin in hexane at a concentration of 10 µg/ml. At this concentration the ECD was overloaded, a simple stream splitter (1:10) was assembled between the column outlet and the ECD to ensure adequate response. For injection comparison an SGE on-column injector (OCI) was mounted on the oven of the GC. For this inlet sample introduction into the column was by manual injection with an SGE on-column syringe.

In addition to the straight glass liner, comparison studies were carried out using a tapered open liner, the SGE FocusLiner and an inverted cup liner (Figure 1). Deactivation treatments used either a thick film coating or SGE's proprietary deactivation methods. Comparison to untreated glass was made in some cases.

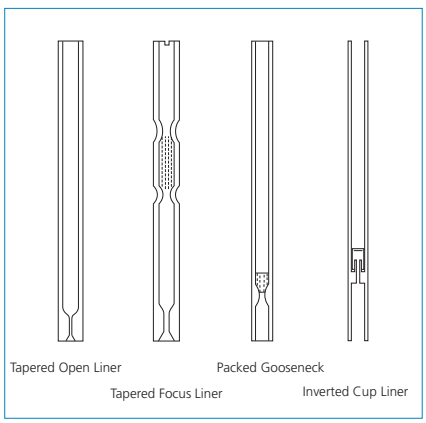

Figure 1. *Liner types considered for evaluation.*

Which Probe?

The endrin and DDT breakdown tests are widely accepted performance indicators for injection port liners. Because both compounds are labile, a number of variables influence the result of the extent of analyte breakdown and therefore the results of the test. Both compounds are sensitive to thermal and catalytic degradation and it is reasonable to conclude that the residence time in the injection port and concentration of analyte must be constant and meaningful to achieve a valid test result. The analyte concentration must be such that the rate equation remains first order with respect to both analyte and active sites.

$$\text{Rate of degradation} = k_{catalytic}\,[\text{endrin or DDT}] \times [\text{active sites}] + k_{thermal}\,[\text{endrin or DDT}] = [\text{endrin or DDT}] \times (k_{catalytic}\,[\text{active sites}] + k_{thermal})$$

The rate equation is more complex for mixed components or surfaces where each component can contribute to degradation proportionately to the concentration of analyte to which it exposed:

$$k_{catalytic}\,[\text{endrin or DDT}] \times [\text{active sites}] = \Sigma\,(k_{catalytic})_a\,[\text{endrin or DDT}]_a \times [\text{active sites}]_a$$

For a glass injection port liner, the most likely source of alternative active sites comes from analyte contacting the base seal or metal components of the injector body. Figure 2 shows the effect of allowing interaction between labile compounds and hot metal parts. Although this is an extreme example (325°C) it indicates the degradation possible when metal is allowed to contact the vaporized analytes. DDT/internal standard ratio is graphed rather than % degradation of USA EPA 8081A footnote 1, to show the real effect of hot metal contact.

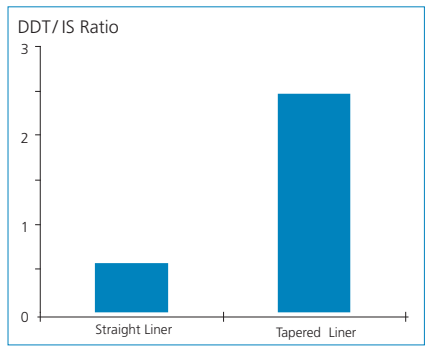

Figure 2. *Remaining DDT after injection through Focusliner onto a copper base seal. Inlet Temperature 325°C. Helium carrier.*

What About the Solvent?

In use, a large volume of solvent is co-injected into the flash vaporizer inlet with the analyte. Depending on the nature of analytes and solvent, under the hot conditions present, chemical reaction or adsorption is possible. The masking of active sites on the liner by solvent vapor can alter the degradation mechanisms for the probe compounds. The influence of different solvents (350°C) on analyte degradation is shown in Figure 3.

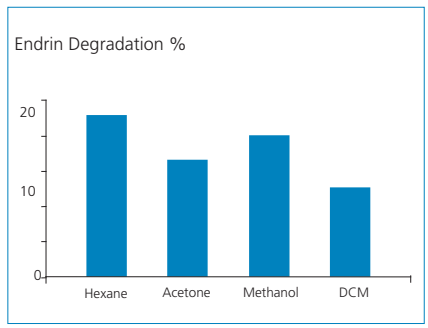

Figure 3. *Endrin degradation (%) in a coated single tapered liner at 350°C. Reaction with different solvents (n=3).*

Is it the Liner or the Deactivation?

The most significant causes of analyte degradation in the flash vaporizing injector are direct thermal reaction and catalytic breakdown through contact with inlet hardware. The former is related to the vaporization temperature and can only be reduced by changes in experimental conditions.

Catalytic activity, a surface contact effect, can be minimized by careful control of the inlet component surfaces. The simplest is the installation of an inlet liner that provides minimal reaction sites. For splitless or low split injections, this is effected by the use of a liner that encloses the region around the capillary column inlet, one with a bottom taper. The liner construction that best effects minimal degradation is best chosen by comparison on a reactive probe. Two probes were used in this study on the same types of liners. The probes used were the thermally labile pesticides endrin and DDT (Figure 4). Degradation was calculated by the method and formulae given in USA EPA 8081A.

As would be expected the on-column injection gave the least degradation, as it is an injection made directly onto the column at low temperature. The presence of degradation products following on column injection may be attributed to systematic effects on the introduced sample and this technique provides a measured baseline from which the further generation of degradants can be measured.

The effects of surface deactivation are obvious when the single tapered liner with differing deactivation coatings are compared. It is particularly noteworthy that the uncoated tapered open liner shows a significantly greater reactivity than the silica wool filled FocusLiner. The lower degradation values for the latter are partially due to the cold solvent effect. As the solution is injected into the hot liner the evaporating solvent cools the silica wool around the analytes. After the solvent has evaporated and as the wool reheats, the analytes dissolve in the gas phase as they reach volatility. They then pass in laminar flow down to the column inlet with minimal contact with the liner wall. Cold solvent effect is analogous to the cool injection techniques of the programmable temperature vapourizer (PTV) Footnote2. Deactivating the silica wool further decreases the extent of analyte degradation. The inverted cup liner, through its convoluted gas flow path exposes the analytes to a higher surface area of hot glass and so increases the extent of thermal degradation caused by the high temperature of the flash vaporizing inlet. Consequently high degradation values are obtained despite the use of an effective surface deactivation technique.

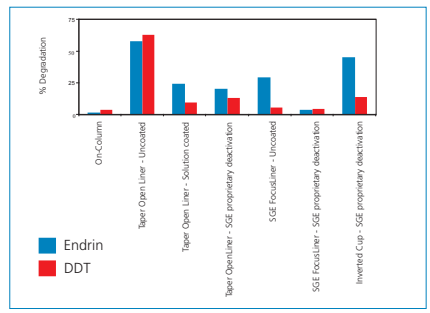

Figure 4. *Endrin and DDT degradation on different liner construction and deactivation.*

Conclusion

A tapered, necked liner packed with correctly deactivated silica wool provides the best method for introducing vaporized analytes onto the capillary column head. The liner provides a cooler entry through the flash vaporizer and, as a consequence of effective surface passivation, the minimal amount of catalytic degradation.

Footnotes

1. www.epa.gov/epaoswer/hazwaste/test/pdfs/8081a.pdf [Section 8.4.6.1]
2. http://www.sge.com/pdfs_local/posters/TP-0130-A_ElucidationGCSampleIntroProcesses.pdf

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