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# Benefits of Using Programmed Temperature Vaporizers (PTVs) instead of Hot Split/Splitless Inlets for Measurements of Volatiles by Liquid, Headspace, and Solid Phase MicroExtraction (SPME) Techniques


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## Keywords

Programmed Temperature Vaporizers, PTV, Split/Splitless Inlet, Septumless Sample Introduction, Oxidative Decomposition, Thermal Degradation



## Abstract

The benefits of using a Programmed Temperature Vaporizer (PTV) type inlets instead of hot split/splitless (S/SL) inlets for the liquid and headspace (HS) measurements of volatile compounds are shown. We used benzaldehyde as a model compound to show the possibility of oxidation or thermal decomposition of sample compounds in a hot S/SL inlet. Liquid and HS measurements of benzaldehyde in a standard sample as well as its determination in a cherry flavored cola by HS sampling show much higher recovery of the com-

pound when using the PTV. Although we believe that benzaldehyde is oxidized to benzoic acid, we were not able to detect the acid or other degradation products that would show direct evidence for the degradation of benzaldehyde using a HP 5 type column.

In addition we found better peak shapes (especially for the lower boiling compounds), better signal to noise ratios, and therefore better detection limits by using PTVs compared to results obtained for the sample introduced into a hot split/splitless inlet. Similar results are obtained by headspace sampling of volatile compounds from coffee.

The use of a PTV (GERSTEL CIS 4) for Solid Phase MicroExtraction (SPME) measurements has an advantage due to the use of a septumless head (SLH) instead of a septum for sealing the inlet. The significant accumulation of septum material inside the liner by SPME injections is demonstrated. This will lead to higher chromatographic background, restrictions in the flow through the inlet and in worst case to the loss of the fiber. This problem does not appear when using septumless sample introduction systems.

## Introduction

The analysis of volatiles in liquid or solid matrices is often performed by either Headspace (HS) or Solid Phase MicroExtraction (SPME) technique measurements. Most gas chromatographic systems are equipped with standard hot S/SL type inlets. Programmed Temperature Vaporizers (PTVs, Fig. 1) that are common for Large Volume Injection (LVI) are rarely used for HS and SPME applications. Here we present data on the benefits of using PTV type inlets for Liquid Injections (LI), HS, and SPME.

One main advantage of PTVs for HS applications is that the sample is not introduced into a hot oxidative environment but into a cold system. To demonstrate the benefit of the PTVs, volatile compounds and compounds that may be oxidized are used to compare results obtained for sample introduced into a hot S/SL inlet and a PTV.

For HS measurements the PTV gains importance because it allows injections of large volumes (up to 2.5 mL or even more by Multiple Headspace Sample Enrichment MHSE) by using a venting mode where the liner of the PTV is used as a cold trap and the split vent is open to eliminate the excess carrier gas. When injections into hot S/SL inlets are done a small split of at least 5:1 is typically necessary to be able to inject the sample fast enough onto the column. In addition, the PTV measurements show much better peak shapes and therefore better signal to noise ratios especially for low boiling compounds which improves detection limits.

For SPME measurements the best analyte peak shapes are obtained by inserting the fiber into a hot inlet, therefore the PTV inlet has to be set to the hot inlet mode. Although the tem-perature program function of the PTV is not used for SPME, the GERSTEL PTV (CIS) has the advantage of using a Septumless Head (SLH, Fig. 2) instead of a septum for sealing the inlet. SPME fibers are widely offered in 24 ga. (0.56 mm) and 23 ga. (0.64 mm) needle design. To allow easier exposure and withdrawal of the fiber the needles that are used with SPME fibers have a blunt tip. This tip type is not ideal when working with inlets sealed by septa because this will result in coring of the septum material. In many automated SPME samplers more stable 23 ga. SPME fibers are used since these systems work with agitation of the sample instead of stirring. The 23 ga. SPME needles are more stable during this agitation process but of course the protective sleeve with the large outer diameter can result in significant coring of the septum of traditional S/SL inlets. Especially in combi-nation with small ID liners (1 mm or less) that are typical for SPME applications the accumulation of septum material inside the liner causes higher chromatographic background and

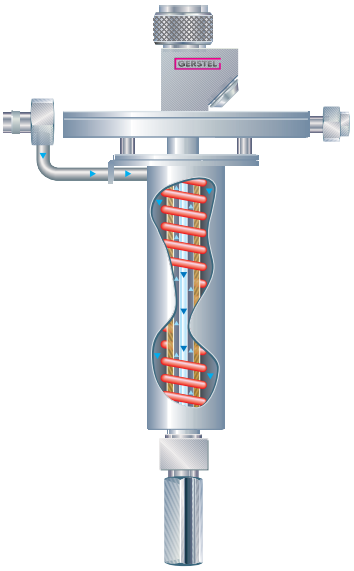


**Figure 1.** Schematic representation of the GERSTEL CIS 4 PTV inlet.

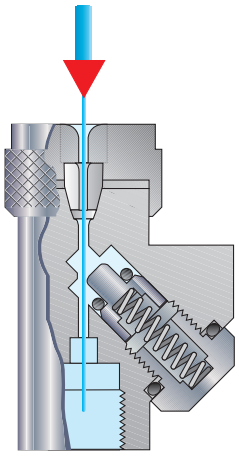

**Figure 2.** Schematic representation of the GERSTEL Septumless Head (SLH).

can also eventually lead to breakage of the fiber. This problem does not appear when SLHs are used that are available for PTV type inlets. For hot S/SL inlets septumless sample introduction systems like the Merlin Microseal® are offered.

## Programmed Temperature Sample Introduction

Combining a cool injection step with controlled vaporization eliminates a number of important disadvantages like discrimination and thermal degradation associated with the use of conventional hot sample inlets.

The primary difference between conventional hot S/SL and PTV inlets is temperature control. The liner of the PTV can be heated or cooled rapidly. In order to facilitate rapid heating and cooling the thermal mass of the liner is minimized.

## Experimental

*Instrumentation.* All analyses were performed on a GC (6890, Agilent) with a mass selective detector (5973N, Agilent), a PTV inlet (CIS 4, Gerstel), a split/splitless inlet (Agilent) and a MultiPurpose Sampler (MPS 2, Gerstel).

*Liquid injection.* A standard sample containing 1 ppm benzaldehyde in acetonitrile was injected into both the S/SL and PTV inlet.

*Headspace sampling (benzaldehyde standard sample).* Ten headspace samples from a standard mixture of 1 ppm benzaldehyde in water were injected into both the PTV and S/SL inlet.

*Headspace sampling (cherry flavored cola and coffee).* Ten HS samples of 5 mL cherry flavored cola and HS samples from 5 g of coffee grounds in 5 mL of distilled water were injected into both the PTV and S/SL inlet. Because of the complexity of the cherry flavored cola matrix, a slower oven program (40 °C, 5 °C/min, 200 °C) was used to resolve the benzaldehyde from other components.

*SPME experiment.* This experiment was setup to show that even a limited number of penetrations of the SPME fiber assembly results in significant coring of the inlet septum. To visualize the accumulation of septum material in the liner we used a liner filled with some glass wool. When using a straight and narrow-bore liner as normally used for SPME, the septum material will fall down and stay inside the inlet body. To show this effect we placed a 23 ga. SPME fiber assembly into the MPS 2 autosampler for injection into the hot S/SL inlet (300 °C) and after 10 injections we found an increased background in the chromatogram. The liner was taken out and evaluated.

*Analysis Conditions.*

| | |
|---|---|
| PTV: | glass wool insert |
| | solvent vent (50 mL/min) at |
| | pi = 0 kPa; split 20:1 |
| | 20°C; 12°C/s; 300°C (5 min) |
| S/SL: | glass wool insert |
| | split 20:1 |
| | 300°C |
| Column: | 30 m HP-5MS (Agilent) |
| | $d_i$ = 0.25 mm $d_f$ = 0.25 µm |
| Pneumatics: | He, constant flow = 1.0 mL/min |
| Oven: | 40°C; 10°C/min; 150°C |
| MSD: | Scan; 30-200 amu |

*Liquid injection.*

| | |
|---|---|
| Injection: | 1 µL (50 µL/sec) |
| Air volume: | 1 µL or 0 µL |

*Headspace sampling.*

| | |
|---|---|
| Injection: | 2 mL (500 µL/s); 90°C |
| Incubation: | 85°C (10 min) |

## Results and Discussion

*Liquid injection.* Figure 3A shows a comparison of the results of the measurements of benzaldehyde by liquid injection. The bar graphs give the average of ten measurements and the error bars indicate the reproducibilities. Reproducibilities are comparable for both inlet types. As shown, the chromatographic peak areas obtained by injections in the PTV are 51 % larger than those obtained with the S/SL. We believe the reason for the lower peak area obtained for the S/SL measurements is the degradation of benzaldehyde in the hot S/SL inlet. Although benzaldehyde should be oxidized to form benzoic acid, unfortunately we were not able to detect this compound directly nor did we find any other degradation products that would show direct evidence for oxidative degradation of benzaldehyde. On the other hand benzoic acid is a very polar compound and using an non polar column as we did in

our experiment, might lead to a very broad peak that cannot be detected. It is possible that simple thermal decomposition of benzaldehyde due to active spots in the liner of the S/SL inlet as well as oxidative decomposition contribute to the loss of benzaldehyde.

It appeared to us that the air volume that is often used when injecting liquids with an autosampler plays a role in the oxidation of compounds like benzaldehyde in hot environments like in the S/SL inlet. We therefore set the air volume to zero and reanalyzed the benzaldehyde sample with the S/SL inlet. This parameter change does not lead to an increase in the benzaldehyde peak area compared to the 1 µL air volume (Fig. 3A). This suggests that thermal degradation rather than oxidative decomposition is the major cause of loss of benzaldehyde under these analysis conditions. We tried to decrease the temperature of the of the S/SL inlet to 200 °C but this deteriorates the reproducibility for the measurements of benzaldehyde. We therefore stopped this approach.

*Headspace sampling (Benzaldehyde standard sample).* Figure 3B shows the results of the measurements of benzaldehyde by HS sampling from a standard mixture. Reproducibilities are better for the PTV, especially in the cool venting mode. As shown, the chromatographic peak areas obtained by injections in the PTV are 116 % larger than those obtained by injections into the S/SL. Again, we were not able to directly detect benzoic acid but the higher loss of benzaldehyde in the HS mode gives evidence to our idea that we are partly dealing with an oxidative breakdown. One would expect the degradation of oxidable compounds like benzaldehyde to be more obvious in the HS sampling mode than from liquid injections since in the HS mode a large volume of air – typically 1 or 2.5 mL or even more – that contains oxygen is injected into the hot environment of the S/SL inlet. When the PTV is set to the cool venting mode the oxygen is flushed out of the inlet before heating. To clarify the issue of oxidative or thermal degradation we repeated the HS measurement and used the PTV in the hot split mode. Under hot conditions similar to those when using the S/SL inlet, we obtained benzaldehyde peak areas nearly identical to those when using the S/SL inlet (Fig. 3B). This finding gives further evidence to the idea of oxidative decomposition because in the cold venting mode the peak area was far higher. On the other hand, we still cannot exclude the possibility of simple thermal degradation contributing to the loss of benzaldehyde in the hot S/SL inlet.

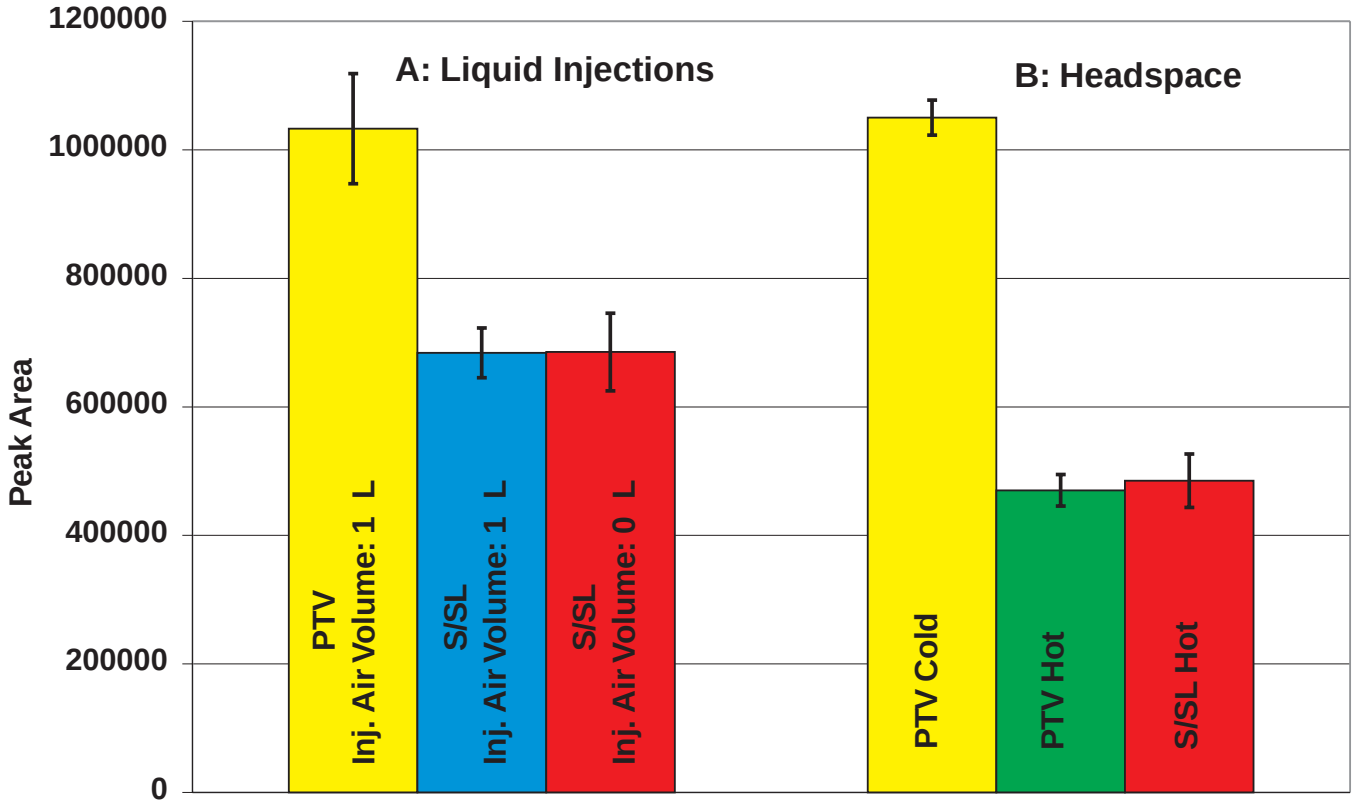


**Figure 3A and B.** Comparison of the results obtained with PTV and S/SL inlet for liquid injections of 1 ppm benzaldehyde in acetonitrile and HS sampling of 1 ppm benzaldehyde in water.

*Headspace sampling (Cherry flavored cola and Coffee).* These experiments were designed to show that the effect of oxidative degradation is also found with real life samples and is not only valid in our model system. Figure 4 shows the benzaldehyde peaks (m/z 77) in cherry flavored cola for measurements with the PTV and the S/SL inlet.

The shift to slightly longer (18 sec) retention times in the PTV is due to the slight delay as the inlet heats, compared to the direct introduction of the benzaldehyde into the column when using the S/SL inlet. This effect is most evident for low boiling compounds that are not refocussed on the head of the column. The improved peak shape and higher peak response of measurements with the PTV inlet results in higher signal to noise ratios and therefore lower detection limits even in the split mode as shown here.

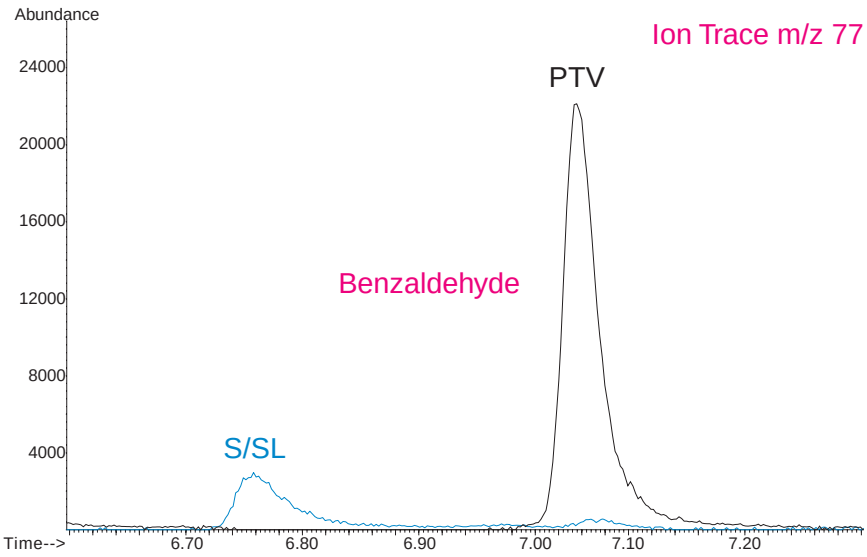


**Figure 4.** Comparison of the results obtained with PTV and S/SL for HS sampling of benzaldehyde in a cherry flavored cola.

Using coffee as a different sample type with other target compounds we were able to demonstrate that our results are not limited to our model compound benzaldehyde. Figure 5 shows a part of typical total ion chromatograms obtained for the coffee measurements with headspace injections in the PTV (black trace) and S/SL inlet (blue trace). From the overlay the shift in retention times due to the trapping of the compounds in the PTV is again obvious (see above). Only for higher boiling compounds that are focussed by cold trapping on the capillary column the shift in retention times becomes negligible. For the lower boiling compounds, far left in the chromatogram, the difference in peak shape is obvious. When looking in the retention time region at about 1 to 2 minutes there is one huge peak in the S/SL inlet chromatogram while there are several well separated peaks in the chromatogram obtained by the PTV. Since we are operating the PTV in the cold venting mode at 20 °C using a liner filled with silanized glass wool, very volatile compounds that will be detected using the S/SL inlet are probably not trapped in the PTV. When analyzing for low boiling compounds these will be trapped by using a liner filled with an adsorbent like Tenax at 5 or 10 °C. For the experiment performed here this was not necessary and we wanted to have comparable liner types in both inlets.

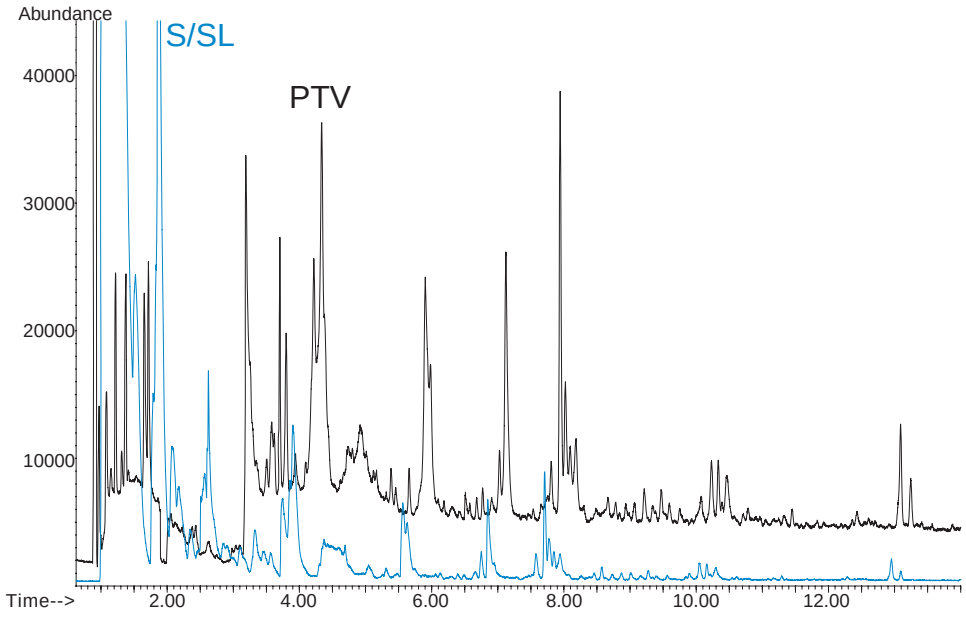


**Figure 5.** Total ion chromatograms of the coffee sample obtained with the PTV (black trace) and S/SL inlet (blue trace).

Figures 6 and 7 show two detailed views of ion traces 110 for dimethylpyrazine and methylfurfural an 81 for furfurylpyrrole. These compounds are volatile and will not be focussed by cold trapping on the column when a S/SL inlet is used. The PTV focusses all compounds and leads to a sharp injection profile. Besides the peak shape the peak areas determined by using the PTV inlet are much larger than that resulting from the S/SL measurements. This suggests that degradation can occur in any sample that contains oxidable compounds like flavors and fragrances.

When looking for measurements at low concentrations another benefit of the PTV type inlets gains importance. Using the venting mode and cold trapping of the analytes, rapid splitless injections are easily accomplished. When looking at S/SL inlets the injection speed for the injection of large volumes (2.5 mL) of HS is limited by the flow through the inlet which is then basically the column flow. At 1 mL/min column flow, it would take 2.5 minutes for a HS injection, far too slow to give sharp peaks. If injections are done faster than that this, loss of compounds through the septum purge line can result. That means that it is not that easy to do splitless HS injections with S/SL inlets. One can try to solve the problem by increasing the inlet flow during injection by techniques like the pulsed splitless injection but this requires further method development.

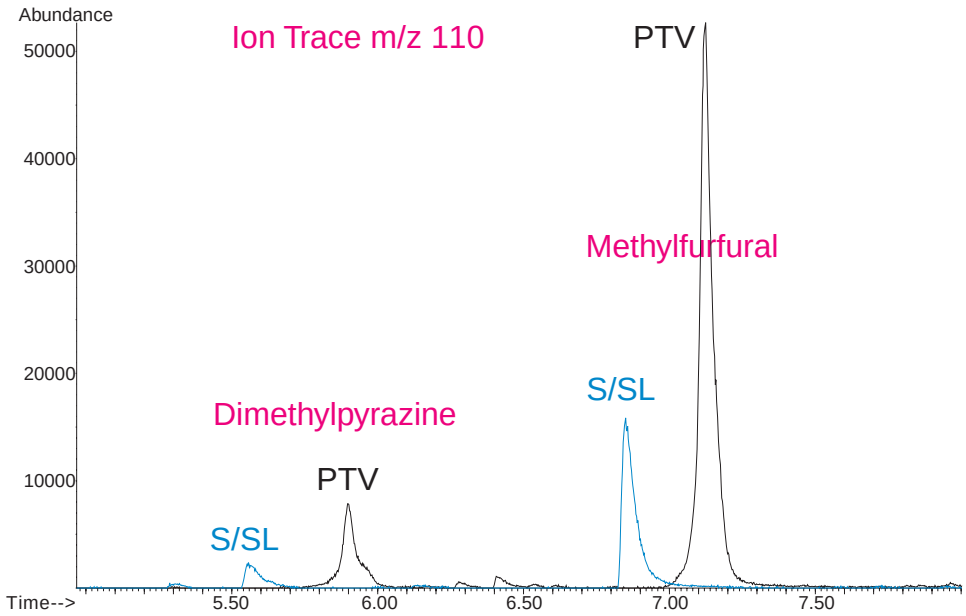


**Figure 6.** Comparison of the peak shapes and recovery for dimethylpyrazine and methylfurfural obtained with the PTV and S/SL inlet for HS sampling of volatiles in coffee.

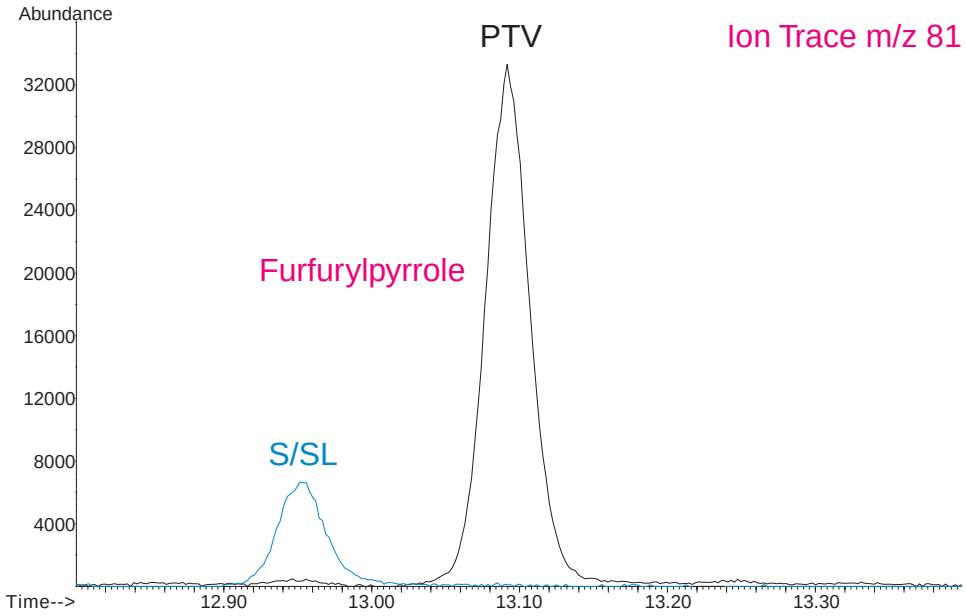


**Figure 7.** Comparison of the peak shapes and recovery of furfurylpyrrole obtained with the PTV and S/SL inlet for HS sampling of volatiles in coffee.

*SPME experiment.* Using the 23 ga. SPME fiber assembly we found a significant amount of septum material inside the liner with the glass wool plug even after only 10 injections using a pre-pierced septum. Figure 8 demonstrates this accumulation of septum material inside the liner of the S/SL inlet.

When using a standard straight liner this material will fall down in the inlet and accumulate there. This accumulated septum material can significantly increase the background of the chromatogram. Figure 9 shows an overlay of a chromatogram before (blank measurement) and after accumulation of septum material inside the liner after only 10 injections.

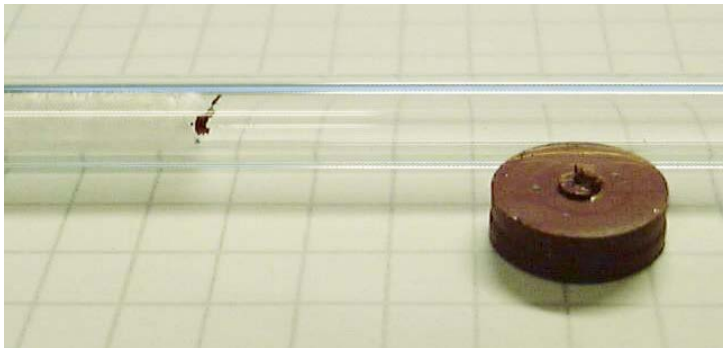

**Figure 8.** Accumulation of septum material inside the liner of the S/SL inlet after 10 injections.

## Conclusions

The results that were summarized in this paper indicate that there are benefits of using PTV inlets instead of hot S/SL inlets for the analysis of all three injection modes under consideration, i.e. liquid injections, headspace injections and SPME measurements.

For liquid and even more obvious for headspace injections we clearly demonstrated the effect of degradation of compounds by using benzaldehyde as a model compound. We were not able to completely clarify if we are dealing with oxidative degradation or simple thermal decomposition so far.

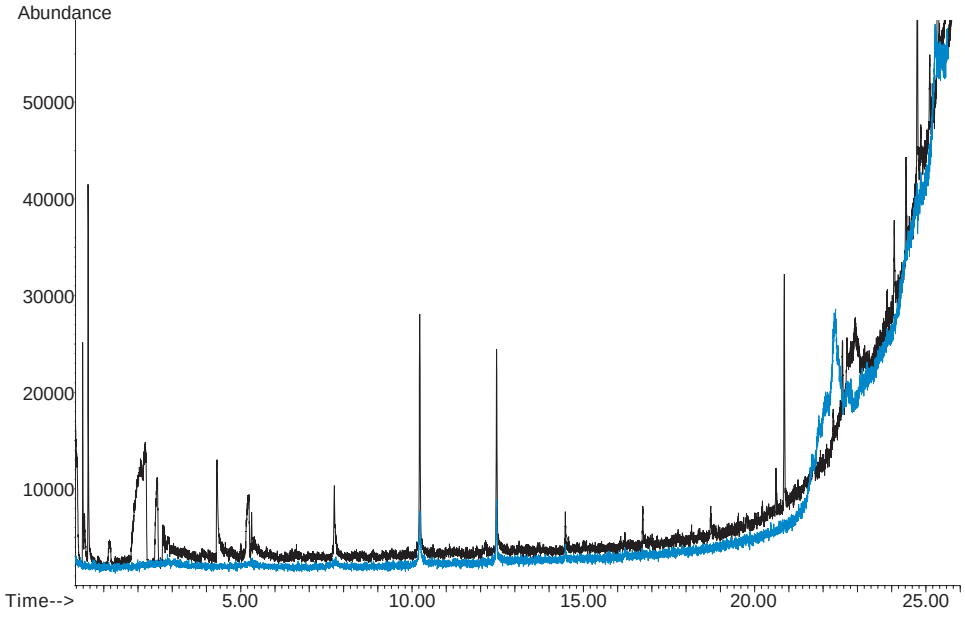


**Figure 9.** Overlay of the chromatograms obtained for the empty liner (blank, blue trace) and with septum material (black trace) accumulated in the liner. Most compounds were identified by library search results as siloxane type compounds which most likely originate from the silicone septum material.

Our studies confirmed the assumption that PTVs are better for the analysis of unstable compounds, irregardless of the mechanism of degradation. The degradation was also demonstrated in two real life samples (cherry flavored cola and coffee).

In addition to decreasing the amount of sample that decomposes in the inlet, the use of a PTV potentially lowers the detection limit by sharpening the peaks and thereby increasing the signal to noise ratio.

For SPME measurements the inlet is kept hot all the time. The septumless head (SLH) on the PTV inlet avoids the accumulation of septum material generated by coring of the S/SL inlet septum with the SPME fiber protective sleeve and the resulting increase in the chromatographic background. In the worst case the fiber can be broken by hitting the septum material that works as a restriction in the narrow-bore liner. This is particularly problematic for automated SPME analyses, where the broken fiber will not be discovered until the end of the sequence. When working with SPME and hot S/SL inlets we highly recommend using a septumless sample introduction system like the Merlin Microseal®.

There may be additional benefits like increased fiber life time if the PTV inlet is cooled after desorption of the SPME fiber. This idea needs to be further studied.

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