Activity in the FID detection port: a big problem if underestimated

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Summary

It is commonly known in gas chromatography, that many problems can be traced to the injection system (e.g. sample, syringe, inlet), which is often a primary place to look at possible issues. This is a valid statement, as 90% of "trouble" is related to injection conditions.
One must also be aware that activity may be caused by other contributions. Especially if we look at non-symmetrical peaks, there are more important area's to look at.
Not only the columns used can be overloaded or poorly deactivated, also the contribution of the detector has a huge impact on peak shape and response. Here it is shown that flame tips can adsorb up to 90% of component and cause tailing on polar as well as base/acidic components. Though it looks columns are not performing, it's the detector that is the problem.

Introduction

There is an ongoing need to measure lower levels of components in different kind of matrices. Often the troublesome components are also more polar in nature, which challenges the analysis even more, especially if lower concentrations are to be reported. On top of that, in most labs, the user is given less time to optimize systems. Chromatography knowledge is fading and this is becoming an increasing challenge.

It's all about eluting and measuring a correct chromatographic peak. Such a peak should look like a Gauss curve. Any deformation from this curve is caused by an anomaly in the sampling and separation process.

The peak shape for a component in a typical GC is mostly affected in 3 area's:

- Injection and focusing
- Separation
- Detection

Injection and focusing.

As stated before, 90% of “troubles” are caused by injection problems. Users need to understand the processes that are occurring in the injection port. These processes depend from the technique used.

Fig 1: Inert liners are essential for correct sample introduction: shown: skv-liners

In splitted injection, the sample evaporates fast and injection, evaporization, homogenization and splitting must be done in a fraction of a second. Any interaction with liners, glass wool or residual septum particles, will slow down the injection and peak shape will be affected. Special liners like the latest Skyliner, have been developed, to minimize those interactions. Split liners usually are narrow to get high speed and optimal splitting conditions. Because the injection is done as a narrow band, a focusing effect is not needed.

This is different when using the Splitless, Cold on-column or Large volume injection technique. As the injection takes a longer time to get the components onto the column, a focusing effect is required to reduce the initial bandwidth. Retention gaps work very nice as well as solvent focusing and cold trapping devices. A nice development here is that capillary columns with integrated retention gaps have become available, which made it possible to inject larger volumes without using column coupling devices. These columns are also commercialized as “Integra Guard” columns. Basically the retention gap also works as a guard and visa-versa.

Separation

The separation pathway is very long, depending on the column used. Within the column, any residual active site will deform the idea peak shape. Figure 2 shows what can happen when activity is present. Peaks start to become lower in height (lower sensitivity) and when they look like “shark-fins”, we can expect impact on retention also. The retention time for a strong tailing peak depends on 2 mechanisms:

1. Gas liquid interaction, which is responsible for the “normal” retention.
2. Activity interaction, which is a different retention mechanism, based on adsorption.

The degree of activity makes a peak elute at a “wrong” position. Example is shown in Fig. 3 where the same amount of alcohols injected on different PONA columns.

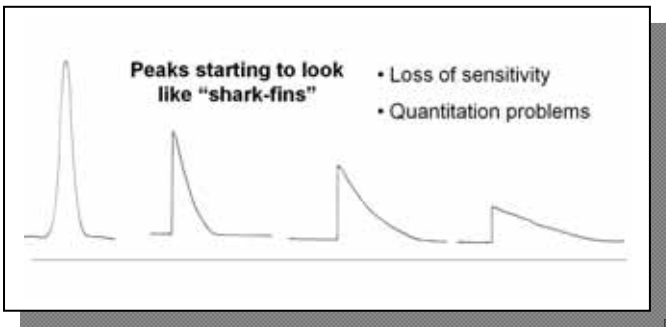


Fig.2 Impact of column activity on peak height

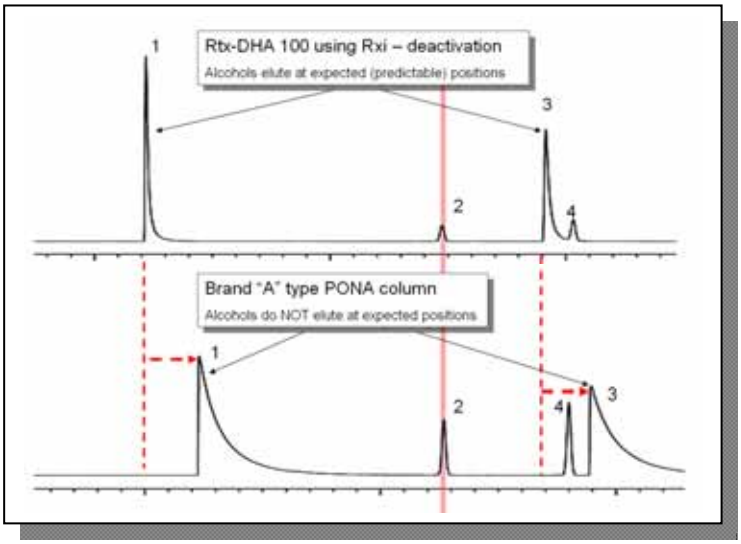


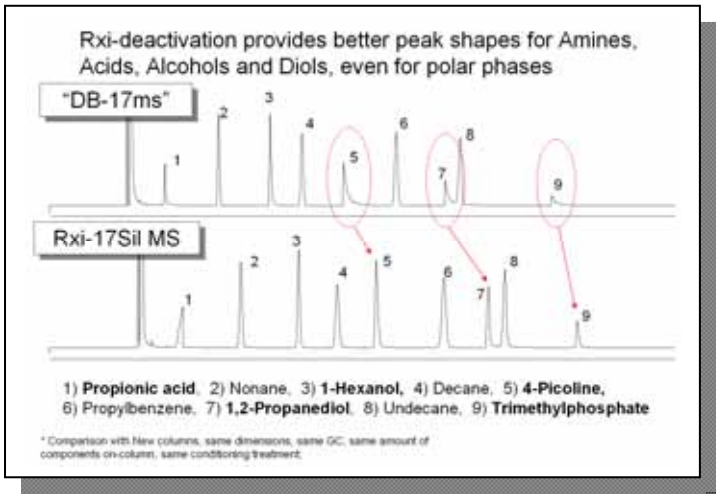
Fig.3 Impact of column activity on retention time of a polar analyte

On a poorly deactivated surface, the alcohols elute at complete different retention times, due to activity.
Only a proper deactivation, like used in the Rtx-DHA 100 columns, makes sure alcohols elute at expected positions. The other effect is that the retention time depends on the amount that is injected. Figure 4 shows an example what happens using an "active" commercial column, compared with an inert Rxi-5ms column. In this example we only looked at pyridine. The lower the amount, the more the peak shifts to the back.

The basis for the high inertness is the Rxi-deactivation [1]. This deactivation is applied with a large series of stationary phases, see table 1. The net result is low bleed and high inertness. Figure 5 and 6 show some comparisons with latest commercial phase technologies, clearly showing the unique qualities of the Rxi-deactivation.

Table 1 Next generation GC phases with successful application of the Rxi-deactivation

Non-polar	Rxi-1ms, Rxi-1HT	100% dimethylsiloxane
	Rxi-5ms , Rxi-5HT	5% diphenyl,95% dimethyl siloxane
	Rxi-5Sil MS	Sil-arylene stab equivalent of 5% diphenyl PDMS
	Rxi-XLB	Sil-arylene stab equivalent of DB-XLB
	Rxi-35Sil MS	Sil-arylene stab equivalent of 35% diphenyl PDMS
	Rxi-624Sil MS	Sil-arylene stab equivalent of 6%cyano/phenyl PDMS
	Rxi-17	50% diphenyl, 50% dimethyl siloxane
Polar	Rxi-17Sil MS	Sil-arylene stab equivalent of 50% diphenyl PDMS



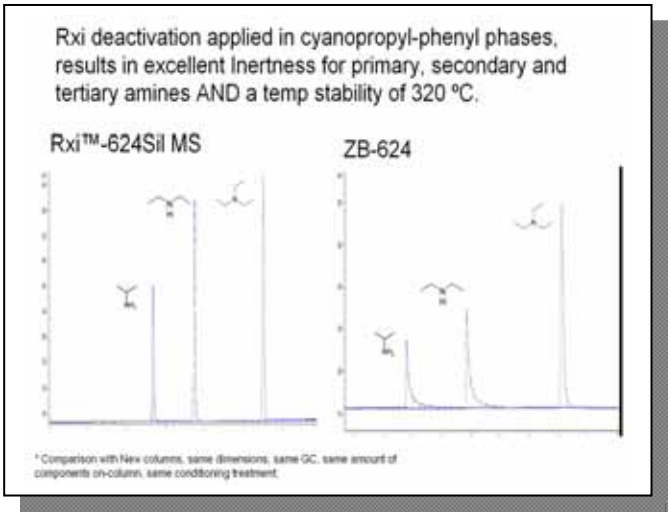


Fig. 5 and 6: Comparison of inertness of polar phase technologies with conventional available solutions. Rxi clearly shows improved peak shapes which helps securing the correctness of the data generated.

Correct column testing is a crucial part for measuring inertness. As columns become more and more inert, a “tough” test mixture must be used. Because of this, additional challenges will be put o the injection and detection operation

Detection

Purpose of a detector is to detect the components. Usually the detector is 10-20ºC above the highest oven-temperature we use to elute the analytes from the column. Sometimes detector temperatures are set above the maximum temperature of the stationary phase. For instance, polyethylene glycols will not appreciate to be at a temperature above 270ºC: they will decompose rapidly forming activity. One must be very careful with that especially after reading the next paragraphs. How important is correct installation at the detection port?

In the detector, there is always some distance between the end of the column and the actual detection. What can happen there? Looking in literature there is very little experimentation to find.
It seems that activity at the end of the GC system is often neglected. Here we discuss detector, but the same is true for transfer lines, valves, connectors, flow-switching devices etc. Columns and transfer lines can develop high activity, just in standby position. This happens with any detector, where the carrier pressure is stopped and the detector gas-flows and temperatures are still on.
For a FID, this is a big challenge and reason for doing some testing: What happens inside FID liner if you change column or when the pressure is stopped for some reason? Officially the detector should be cooled down when doing maintenance, and gases must be switched off. But is that always done in a routine laboratory? The FID usually is at high temperature, so if the column flow disappears, or the detector connection is opened, we can expect water/oxygen to enter this area. When air is on, there is always a little overpressure on top of the detector that will drive air into the jet. This is an ideal scenario to develop activity.

If a GC column is tested for inertness, it is a valid concern to be aware of the discussion above. Columns are tested with nano-grams of highly polar, base/acid analytes to verify its performance.

Experimental

A series of experiments was initiated to demonstrate if there is a detector contribution. A Rxi-5Sil MS column was installed in an Agilent 6890N GC and operated under normal column – performance test conditions as listed below:

GC	: Agilent 6890N
Column	: Rxi-5Sil MS, 30m x 0.25mm df = 0.25µm
Oven	: 135 ºC
Carrier gas	: He, 22.9 psi, constant flow
Injection	: split, 200 mL/min, 0.6 µl
Temp. Inj.	: 250ºC
Sample	: test mixture for Rxi column performance testing
Detector	: FID, temp. 300ºC

The column was installed according to the manual: the column end positioned 1-2 mm from the top of the flame tip. We analyzed the test mixture and obtained the chromatogram as shown in figure 7. Chromatogram looked as expected, good response and good peak shapes. This was our “baseline” chromatogram.

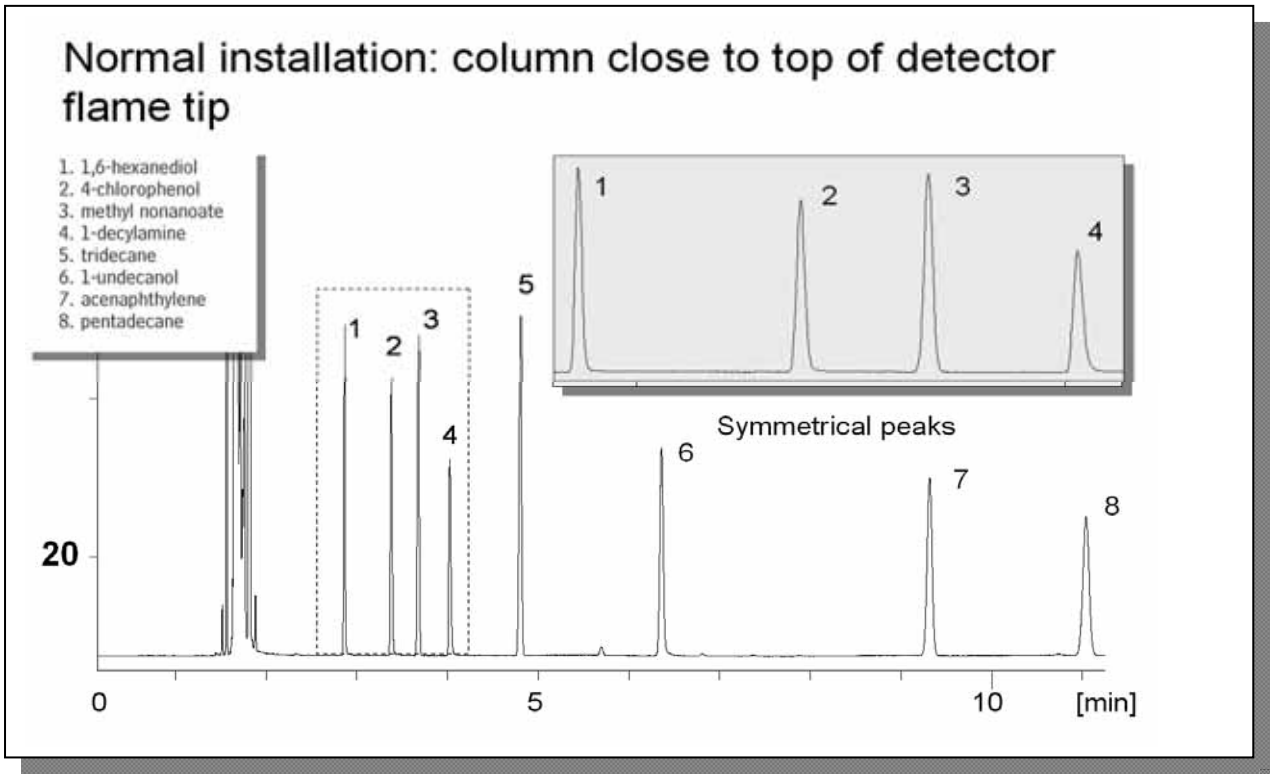


Fig. 7 Rxi-5Sil MS column installed in correct position in the detector. Peaks are symmetrical and show correct response.

Now we cooled the oven to 40ºC, slightly opened the detector connection and pulled the column back proximate 10mm. The connection was sealed again and oven temperature was restored. Figure 8 showed the impact of the 1 cm lower positioning of the column outlet in the FID.
The last 10mm of the FID caused a reduction in response for the polar analytes of almost a factor 2. Note the response relative to peak 5 (tridecane). Also significant tailing was developing on the polar compounds 2,6-hexane diol, 4-chlorophenol, 1-decylamine and undecanol. No column would pass QA if it showed this behavior. The last 10mm of the flame tip in the 6890 was highly activated causing huge adsorption and loss of many components.

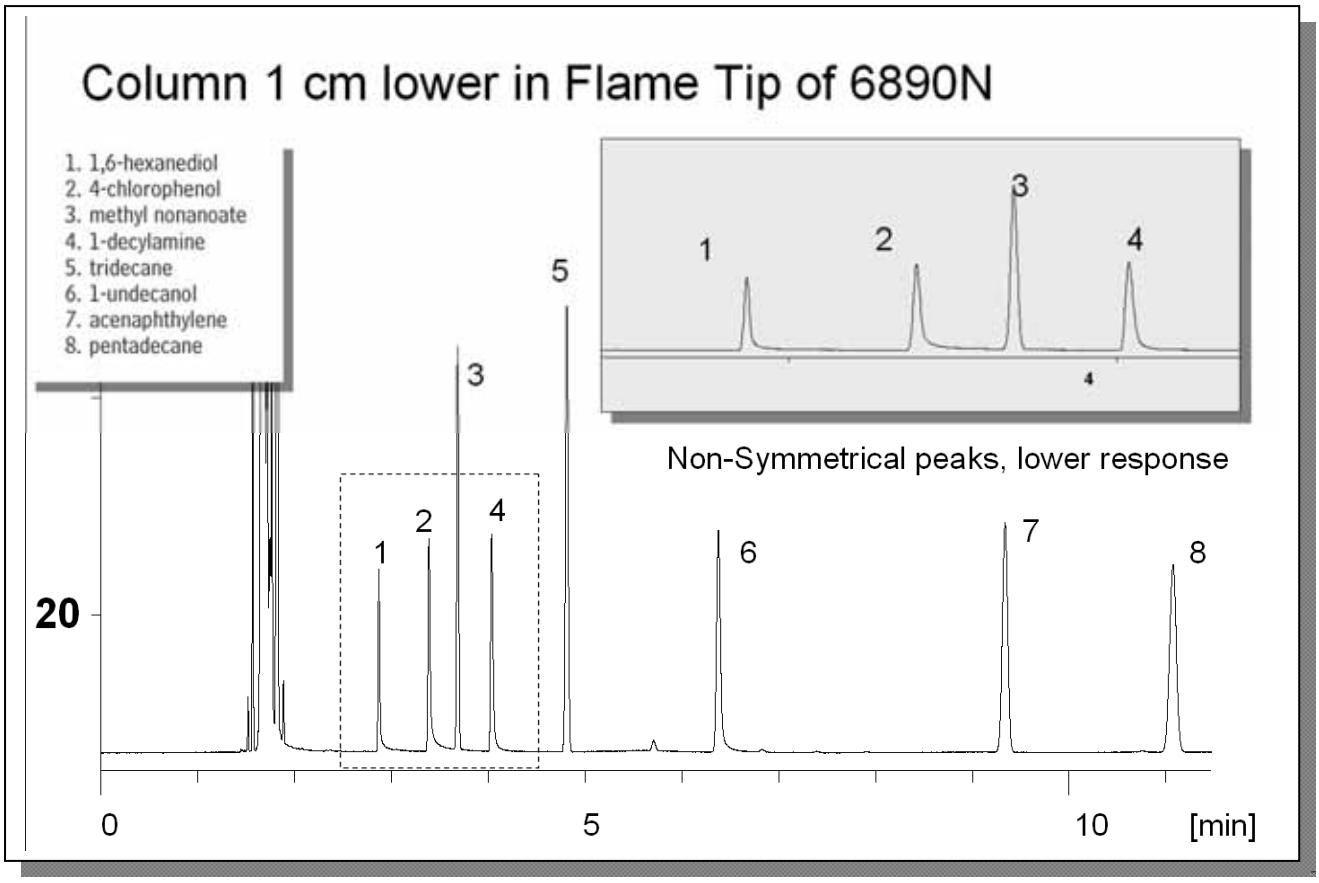


Fig. 8: Just 1 cm lower positioning in a 6890 FID, a big difference in response is observed. Also peak tailing starts to develop.

To maximize the impact of detector the column was put 4 cm lower in the detector. This would not be very realistic, but it surely makes a good point on what happens in the last 40mm of transport. The problems increased significantly, see fig.9. As many times detectors are used at lower temperatures, the temperature was lowered to 250ºC. Now we see almost a loss of 85-90% of response, see fig.10.

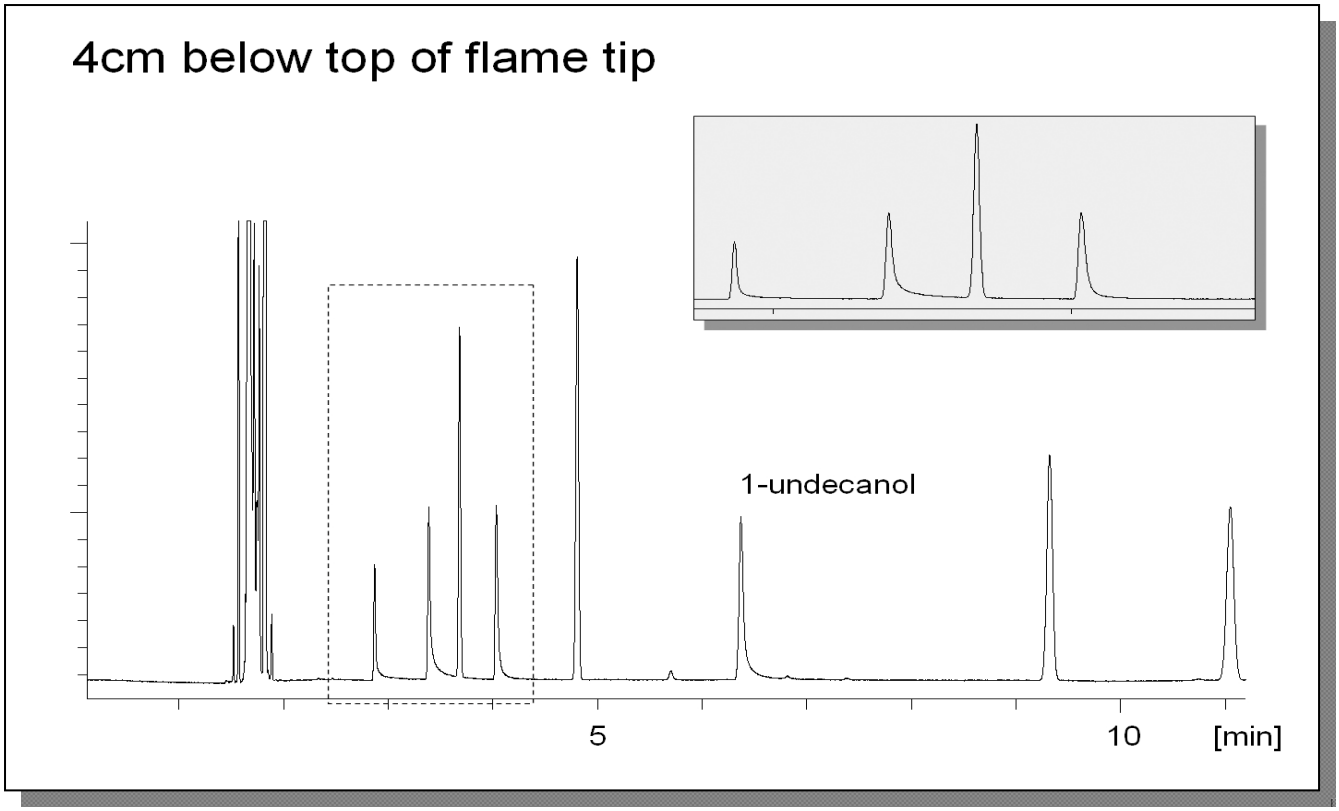


Fig 9: Column end 4 cm below top of flame-tip. Response of polar compounds diminishes even more

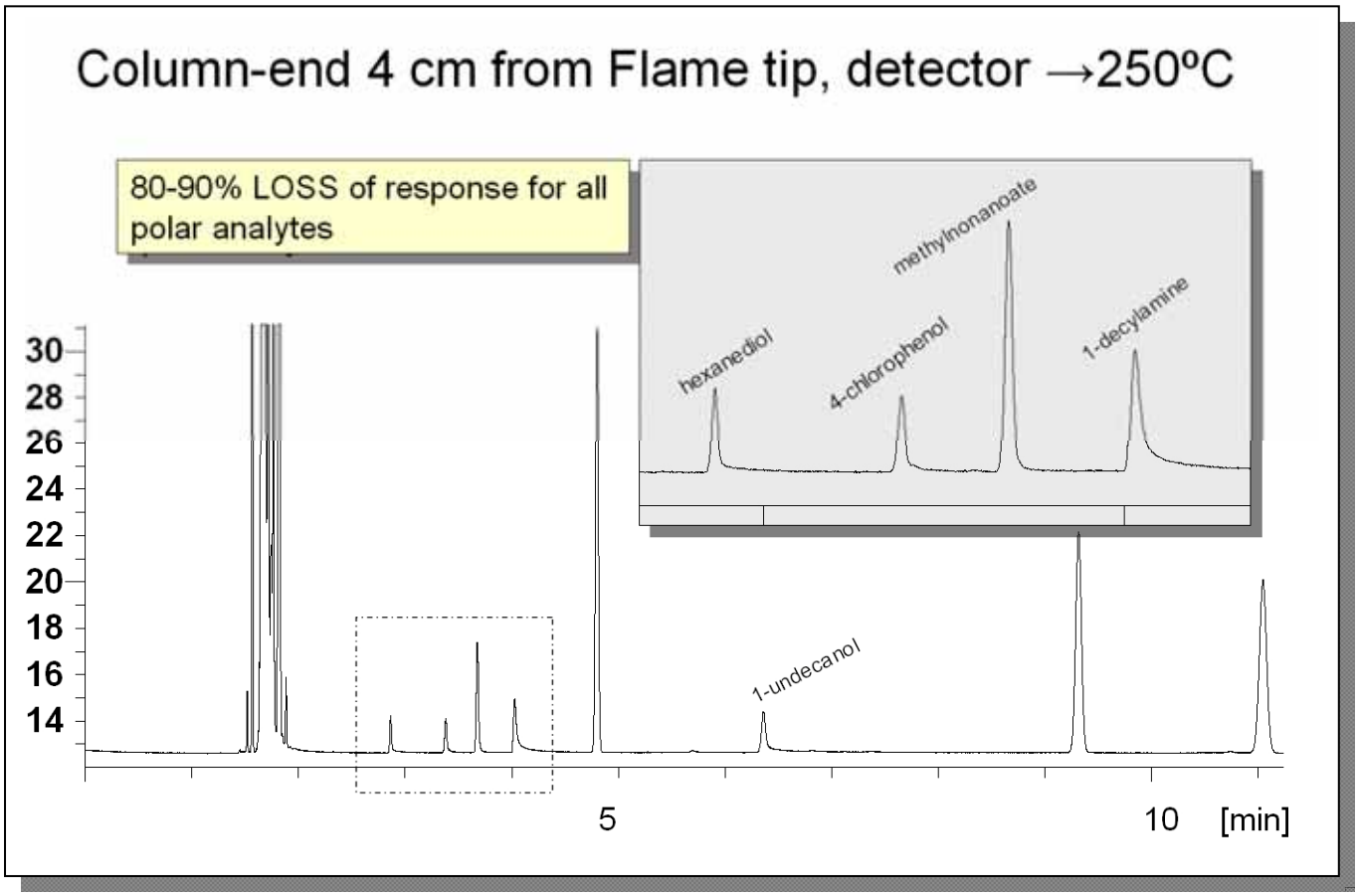


Fig. 10 FID- detector cooled down from 300 to 250ºC. Significant loss of response for polar compounds.

The next step was to reinstall the column again in the correct position. Fig.11 shows the chromatogram. The response was restored completely, demonstrating again the importance of correct position of the column outlet during installation.

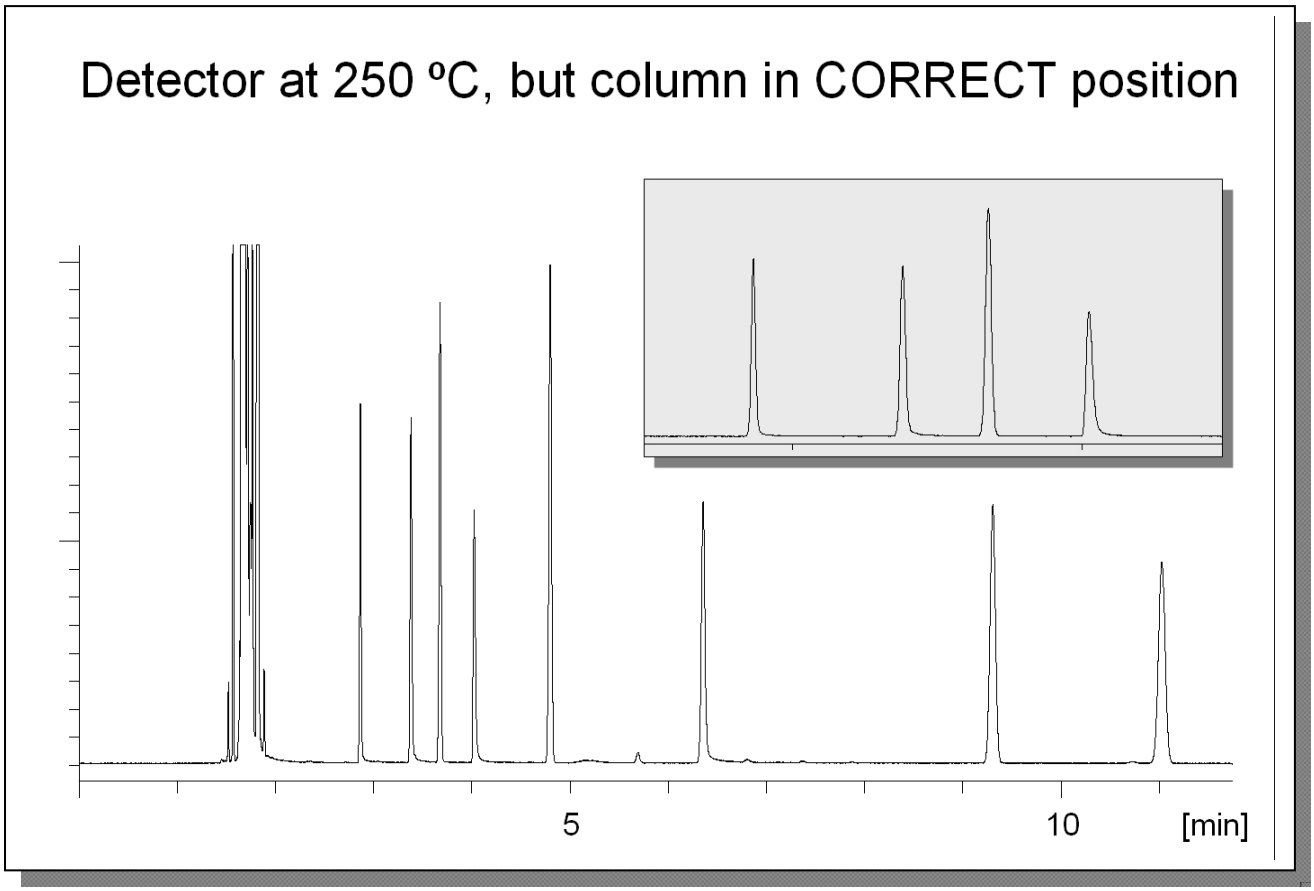


Fig. 11 Column positioned near flame tip when detector was at 250 C. System performance is completely restored

Other systems

We also checked an old HP-5890 system. Here another column was installed at different positions in the detector. Remarkable was that the position of the column in the detector did not make any difference in any position or temperature tested. Even when the column was cut 1 cm above the ferrule, the resulting chromatograms were very similar, see fig.12. The only difference with the newer systems, is the length of the FID-jet. The newer 6890 FIDs have a much shorter jet. This cannot explain the big differences observed.

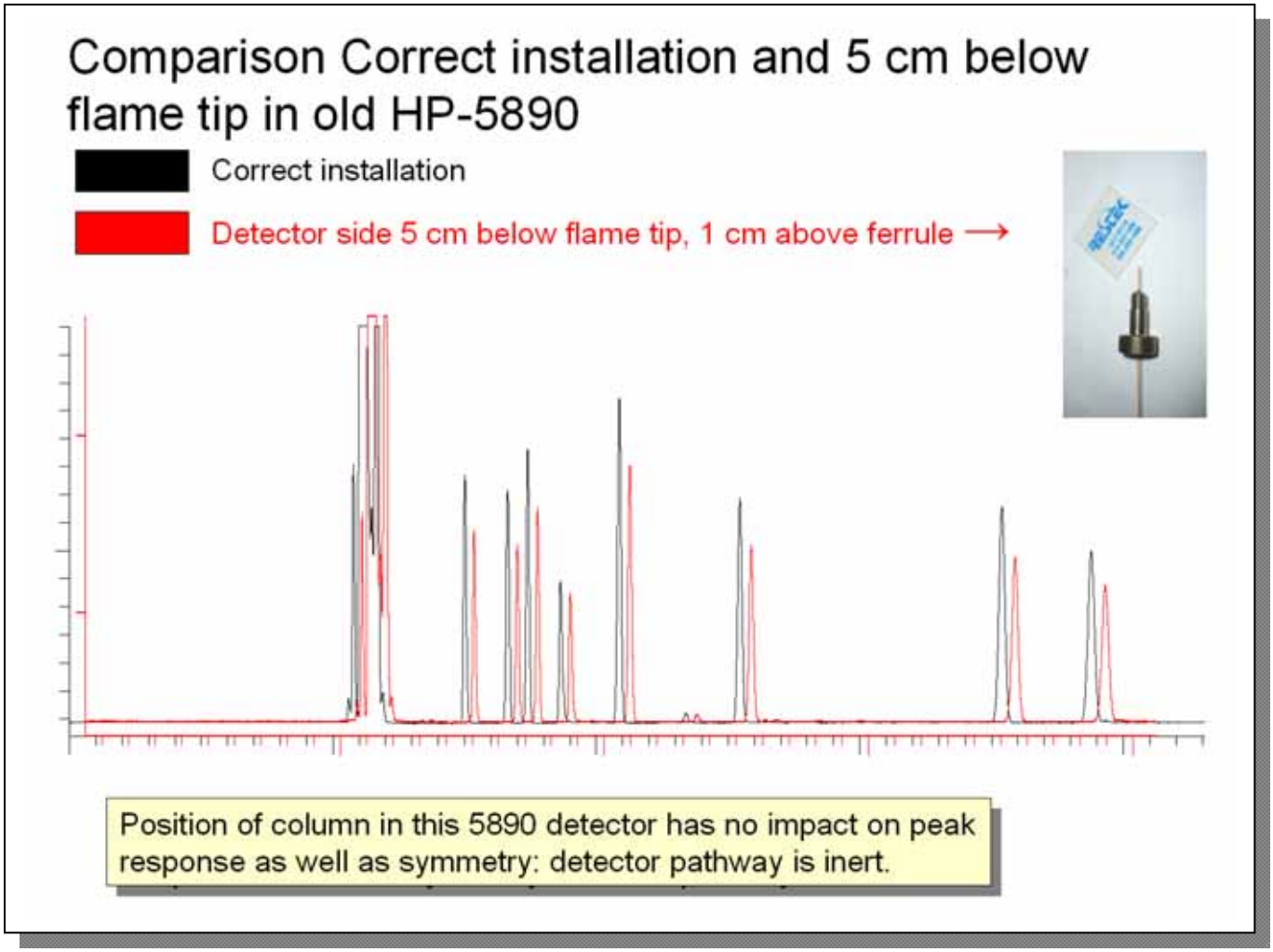


Fig. 12 Standard test in HP-5890 GC using correct (black) and challenging (red) positions for column outlet

The activity /reactivity of the flame tip in FID always depend on the moment. One can replace the flame tip for special deactivated ones (there are Siltek deactivated tips available), but activity in detection systems can also often be “masked” by conditioning columns at upper temperature and as some bleed products are formed.
Those bleed products can deactivate the detector, so it will perform OK. This “conditioning-deactivation” is a known method for deactivating transfer lines and traps f.i. in SCLD and MS systems.

Fig.13 SS and Siltek deactivated flame tips for agilent FID

Also one can assume when a GC is used with adsorption columns (alumina, silica, porous polymers, charcoal or molecular sieves), it can be very well possible that some ‘dust’ particles will be retained in the flame tip. Such particles are highly active.

Conclusion

For good GC we need a full inert gas path. Activity can be present not only in the injector and the column, but also in the detector. For many it may seem trivial to install columns the “correct” way, however, practically the importance of the position of column in a FID detector is underestimated. If detection ports are well deactivated, one will see no measurable impact. On the other hand, if there is activity developing, only a few millimeters of contact with the sample gas-path may lead to loss of components.
As a manufacturer of parts we can help with Inert liners (Sky-series) and Inert columns (Rxi-series), but for best results, one needs to be aware why columns are to be installed in certain positions in injection and detection systems.

References

1] J. de Zeeuw, R.Lautamo, G.Stidsen, C.English and S,Reese, American Lab, Vol. 40, nr.12, p.11-15.