Application Note No. 006

Direct thermal desorbtion using the OPTIC injector

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Introduction

In the past, thermal desorbers have been both complex and costly. This has stemmed from an assumption that the only way to achieve satisfactory peak shapes is to perform the transfer of the analytes from the air sample to the column in several stages, transferring the organic components into successively smaller volumes of gas, until the gas volume matched the input bandwidth required by the column. While generally effective, this approach suffers from a number of disadvantages, which in the main, arise from the complexity of the process employed:

1. Each concentration step involves a separate trap/desorb cycle offering an opportunity for the loss of analytes and for the introduction of impurities.

2. The number of parameters that require optimisation makes method development relatively complicated.

3. The amount of time taken to process a sample is often significant in comparison to the cycle time of the chromatographic separation.

4. Whole samples can be easily lost due to miss-operation or instrument malfunction. This is especially inconvenient as, (unlike liquid samples), gaseous samples acquired on adsorption tubes can only be analysed once.

5. Thermal desorbers are expensive, often costing more than the chromatograph that they serve.

Using OPTIC it is possible to transfer the sample to the capillary column in one step, with the sample being desorbed directly from the adsorption tube onto the head of the column.

In most cases, direct thermal desorption works extremely well, providing that care is taken to understand the principles involved. The purpose of this

Achieving acceptable input bandwidth

If the column is to perform an efficient separation of the sample, it is vital to devise a procedure which will ensure that the sample is deposited onto the column in the narrowest band possible. There are a number of different precautions that can be taken, some of which apply in all cases, others depend upon the hardware available or are only applicable to certain sample types.

General considerations

In virtually all cases, OPTIC should be set to its fastest program rate (16°C/s) in order to desorb the sample as quickly as possible. When sampling, it is advantageous to draw the air sample through the tube in the opposite direction to the gas flow during desorb, this, in effect, back flushes the adsorption tube offering a useful focusing effect. In addition, the adsorption tube should be packed with the smallest quantity of adsorbent required by the job in hand.

Cold trapping

If it is possible to desorb the sample onto a cold column, the organic compounds evolved, will partition strongly in favour of the stationary phase and remain at the head of the column in a narrow band until, as the temperature is increased, successive compound are transported down the column. Just what constitutes a cold column, depends upon the volatility of the compounds being determined. As a rule of thumb, compound which exist as liquids at room

temperature can be focused with the column at ambient temperature. In the case of compounds that are gaseous at room temperature, cold trapping necessarily involves the cryogenic cooling of that section of column which is just

below the injector, either by cooling the whole oven, or by installing a liquid CO_2 cryotrap. Cryogenic trapping has the virtue of working in all cases, acting to correct any band broadening generated during the process of desorption. However, the use of cryogenics is not always convenient, fortunately, careful optimisation of other parameters usually technical data sheet is to act as a guide to enable the best possible performance to be obtained from OPTIC in the direct thermal desorption role. renders the need for the use of cryogenic cooling unnecessary.

Phase trapping

When the sample enters the column, it begins to partition with the stationary phase, this causes its rate of transport to fall, giving rise to a focusing effect upon all components. The magnitude of this effect is governed by the phase ratio of the column, which is in turn dependant upon its film thickness. The use of a thick film column (3 micron or greater) will offer a significant benefit, with respect to early running peaks. The disadvantage of using such a column being that the separation may take longer to perform than with a thinner film column, and some trouble might be experienced with the elution of later running peaks.

Desorbing into a static gas stream

This is a very powerful technique, the only problem is that it is not always easy to implement with all OPTIC installations (GC/MS being a case in point).

When desorbing into a moving gas stream, the comparatively slow rate at which the sample is released means that the sample is desorbed in to a larger volume of gas than is ideal. If the carrier gas flow is halted for the few seconds that it takes to desorb the sample, then the sample is released into a very much smaller volume of gas. When the flow is resumed, the sample is swept onto the column in a tight band. In selecting the length of time for which the carrier gas is to be stopped, it must be kept in mind that there is a time lag between the outer temperature of the injector (which OPTIC displays) and the temperature inside the liner. As such the carrier flow should remain off, for at least 30 seconds after the final temperature is indicated, to ensure full benefit is gained.

Splitting of the sample

One additional source of band broadening can come from a disparity between the linear gas velocity in the liner and in the column. In the case of a 0.32mm i.d. column for example, when the split line is closed, the column carrier gas velocity of the gas in a standard injector liner. With the split line open, even at very low split ratios, a marked improvement in the shape of early running peaks is obtained.
Splitting also provides a means of matching the amount of each component transferred to the column, with the capacity of the column.

In most cases, it is possible to use a combination of the techniques listed above, coupled with sensible choice of adsorbent, to obtain excellent peak shapes for all peaks in the chromatogram - without recourse to cryofocusing.

Choice of adsorbent

Tenax TA is the most widely used adsorbent for air sampling applications. It has a high capacity for a wide range of organic at ambient temperature, while offering no significant adsorption of either water of CO_2. It is thermally stable and readily releases adsorbed compounds upon heating. Tenax is usually the best adsorbent to try first, although its desorption temperature should be limited to 225°C to avoid problems with the appearance of artefacts.

Active charcoal, despite its excellent adsorptive properties is a poor choice in this role, due to the difficulty of releasing compounds from it by heat alone. Its use tends to result in carryover and poor quantisation. There are other carbon based materials that have useful properties, in particular, carbosieve and the carbopacks. Carbopacks B and C have greater capacity than Tenax and can be taken to higher temperatures. Corbosieve is more adsorptive still.

The Porapaks are also used, and can be useful when Tenax proves unsuitable (in the trapping of CFCs for example).

It is possible to combine more than one packing in a adsorption tube in order to deal with situations where compounds of widely varying volatility need to be determined. In this case, a bed of weaker adsorbent (e.g. Tenax) is backed by a second bed of a stronger adsorbent (e.g. Corbosieve). The air sample is drawn through the weaker adsorbent first where the heavier compounds are retained, lighter compounds passing through it are trapped on the stronger adsorbent. If the trap is desorbed in the opposite direction the whole sample can be released without the problem of desorbing in volatile compounds from a strong adsorbent.

In order for an adsorption tube to be suitable for a given task, it is necessary to be sure that the volume of gas to be sampled can be passed through the tube without some of the lighter compounds breaking through. To be sure of this, it is necessary to determine the breakthrough volume of the lightest component to be measured.

Measuring breakthrough volume

The volume of sample that may be passed through an adsorption tube at ambient temperature, before the lightest compound passes the whole way through, is called the breakthrough volume. When sampling it is wise not to exceed a volume of half the breakthrough volume, in this way any changes in ambient temperature will not invalidate the result obtained. Published data is available of breakthrough volumes, usually expressing this parameter as a volume of gas per unit mass of adsorbent, however, breakthrough volumes are easy to establish experimentally.

If the OPTIC injector is connected to the detector with a length of uncoated silica column, the length of time taken for a component to pass through a packed liner at a near ambient can be measured directly. If the flowrate through the liner is known, then the breakthrough volume can be calculated.
In cases where compounds have large breakthrough volumes, it may be difficult to measure them directly due to the emerging peak being very broad. In such cases a better approach is to measure the breakthrough volume at several elevated temperatures, and to extrapolate back to ambient temperature.

Packing OPTIC Liners

When packing an OPTIC tube with adsorbent, it is important not to pack that section of the tube that is unheated. When placed in the injector, the top 16mm of the tube sits above the heated zone and as such any adsorbent material present in this section will not be desorbed when the remainder of the tube is heated.

Calibration

When making a quantitative determination, it is necessary to generate a standard by dosing an adsorption tube with a known amount of the compound to be determined. In order to achieve reliable results, the standard should be generated in a way that, as far as possible, duplicates the way in which the sample is taken.
The first step is to generate a gas phase standard. One way to do this is to use a 1 litre round bottomed flask fitted with a septum and containing a few glass beads. The flask should be warmed to around 80°C in an oven and flushed with clean helium. A known volume of liquid phase standard is then injected into the flask using a micro litre syringe and allowed to fully vaporise, the process can be assisted by gentle warmth and swirling the flask to allow the glass beads to mix the sample. A portion of the gas phase standard can then be withdrawn using a gas tight syringe.
The adsorption tube should be connected to a stream of clean gas flowing at a rate which matches the sampling rate. The gas phase standard can then be introduced into the flowing gas stream and swept onto the adsorption tube in a way which closely matches a real life sample is taken. This can be easily achieved by connecting the adsorption tube to a conventional packed column injector and introducing the standard via the septum, with the column oven at ambient temperature. Note that it is important to ensure the syringe needle doesn't enter the adsorbent bed.

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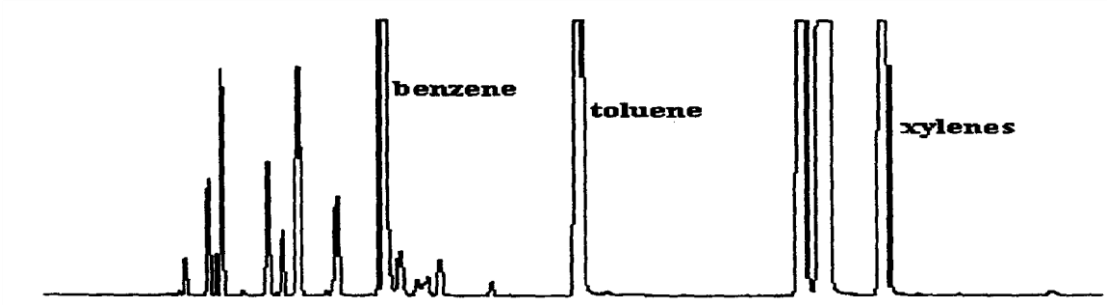
Conclusion

If attention is paid to the points covered it should be easy to obtain good quality results, using OPTIC in the direct thermal desorption role. If further advice or assistance is required, please feel free to contact either your local ATAS distributor or ATAS in The Netherlands.



Air sample desorbed using OPTIC, without cryogenics.

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