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Review Paper for Sample Separation and Preparation for Gas Chromatography

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Abstract: ***Sample directly introduced into the injector port of the Gas Chromatographer (GC) is subjected to the programmed thermal environment in response to which the adsorption and elution of the compounds takes place internally of the capillary column and physical separation of individual compound takes place. Since the mobile phase is gas, a limitation on the type of sample introduced is abided. If the sample is conditioned to proper needs and a required amount is inserted, then better resolution of peaks as a result is encountered. This paper showcases the technologies and novel approaches towards the sample separation and preparation to make the GC instrument better in its performance.***

Keywords: Gas Chromatographer, adsorption, elution, capillary column, resolution.

1. Introduction

Organic samples are generally conditioned and converted into liquid form if not so as to be inserted into the GC. If the sample is gaseous then dissolved into suitable solvent or if in solid form then diluted with the same and a small portion is inserted into GC, in the range of microliters. This inserted sample is heated within the injector port to a predetermined set value and the sample gets vaporized. This vapor is then swept by the mobile phase gaseous carrier generally nitrogen or helium, to the heart of the GC system i.e. a capillary column. Being more selective in its performance capillary column provides more interaction with the vaporized sample and hence the separation. The vapor entering the capillary column undergoes successive adsorption and elution inside the hollow column, since the carrier gas drifts the compound molecules. The inside of the column is coated with the fused silicate or similar adsorbent material which leads to the molecules of the compound to adhere, at the next instant the carrier gas removes the compound due to its pressure and velocity, hence elution occurs from the column internal wall and thus this successive interaction takes place to the entire length of the wall. The length of the wall is proportional to the amount and degree of separation. Each group of same organic compound gets separated depending upon its respective boiling point. Hence physical parameter is used in this separation process. Temperature programing is done with help of electronic control circuitry and a method development is carried out for proper separation and high resolution of peaks. The separated organic compounds exit the capillary column in sequential way where they are subjected for measurement by either invasive or non-invasive type detectors. These detectors are electronics transducers and they measure actual concentration of each organic compound giving peaks on the graphs of the data acquisition system. This is the general operating system of the GC system widely used. The compound within the sample takes different time to reach the detector port due to its nature and interaction with column also called as affinity towards the column. Hence compound having more affinity with the column tend to remain inside the capillary and their retention time will be more as compared to other compounds. As the number of compound increases in the given sample it is more likely that more than one compound will have same affinity with the column and will arrive the detector port almost same time and hence resulting to the overlap of detected peaks at the output. However it has been evident that if the sample is pre-conditioned and then inserted into GC, the results are effective and performance of GC is also enhanced. Many researches have been published and patents are filed claiming the necessity for the sample separation and sample preparation for its enrichment and proper injection into GC. Mainly improvement in the resulted resolution, longer and indirectly selectable retention times with respect to chromatogram have been obtained.

2. 'Modern' Sample Preparation Techniques – Thermal Desorption

In order to improve the results of GC, many practices have been carried out on the sample itself. Sample preparation is necessary for following believed reasons[6]:

- Improvement of the chromatographic behavior of the analyte(s).
- Improvement of the Detectability of the analyte(s), or
- Isolation of the analyte(s) from the matrix.

Traditionally and widely used sample preparation mechanism using thermal desorption is headspace technique. A vial half filled with the liquid form of sample is heated at a predetermined temperature of the required volatiles. The volatile compound having boiling point below the vial temperature gets collected in the upper open space called as the headspace, and is then directly inserted into the GC either by using dummy loop or by syringe injection.

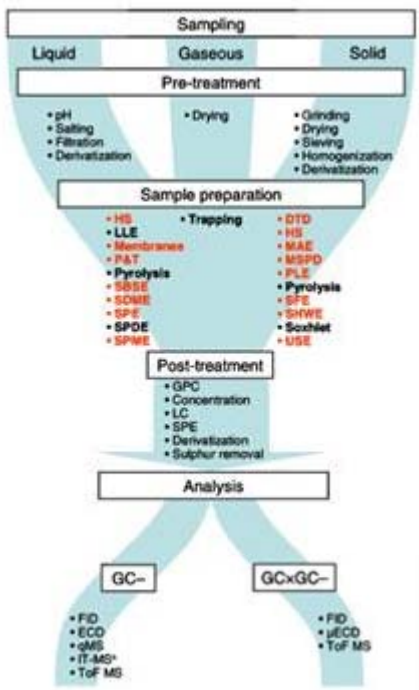

Figure 1: Typical Strategy for GC Sample procedure [6].

Thermal desorption is another valuable method and alternative to headspace method. It can be regarded as the advanced method of headspace [6]. The sample in solid or semi-solid form is first pre-heated to a set temperature value. Volatile compounds get desorbed and are transferred to a cool trap, wherein they are adsorbed by some means. Then for its analysis, they are heated at rapid rate resulting for its fast passage to the GC injector port [6]. One such adaptation is done in so called cryo-focusing. The volatiles are trapped under cryogenic conditions and then eluted when necessary.

3. Cryo-Focusing

One of the most effective methods for sample separation at very initial stage is the cryo-focusing. This aims at trapping the sample volatiles itself into the capillary column of the GC. But this puts a limitation and requires that the GC should be equipped with the cryogenic temperature sustaining unit to preserve the liquid nitrogen. As well as it take a longer time to bring down the temperature of the whole column itself. Another method to carry out cryo-focusing is to divide the capillary column in two parts initial subjected to the cryogenic temperature helping the enrichment of the sample and then feeding the latter capillary to carry out separation. The enrichment effect is same as before and also has low cool-down period. This enhanced technique is also known as Capillary head trapping.[5]At first stage the initial part of the column generally 50% of the total column is taken as cryogenic trap. It is then enclosed in a PTFE insulating tube. Nitrogen gas at room temperature is passed through liquefied nitrogen bath kept at 77ºK or below. This is then made to pass through cooling the capillary as shown in Figure 2. This is done for approximately 10mins. Once the column is cooled down then the sample volatiles are inserted by headspace or any method by heating the sample.

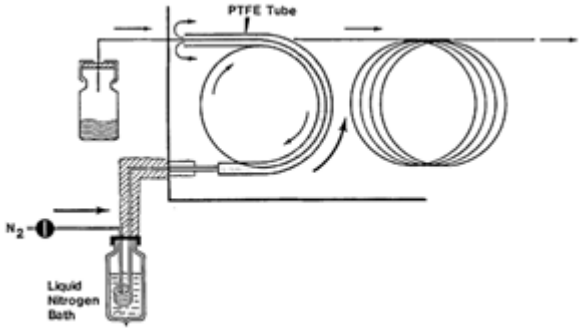

Figure 2: Cryo-Focusing in Gas Chromatography by Capillary head trapping [5].

These volatiles from the sample don't really get trapped into the column but they have low migration into it. The relative migration rate R_F of the sample can be expressed in the following way :

$RF = 1/(1+k) = uS/uC.$

Where k is the capacity factor of the solute; uS and uC are the respective velocities of the sample vapor and the carrier gas.[5]

Now when the volatiles are trapped within the column the nitrogen supply is literally cutoff and the column temperature rises to room temperature or can be controlled externally. This allows the elution of the only required volatiles sequentially. Hence the sample enrichment and sharper peaks are obtained. Variations in the volatiles trapping mechanism are made in the patent for 'Adsorbent Trap for Gas Chromatography' by Peters et al.[7]

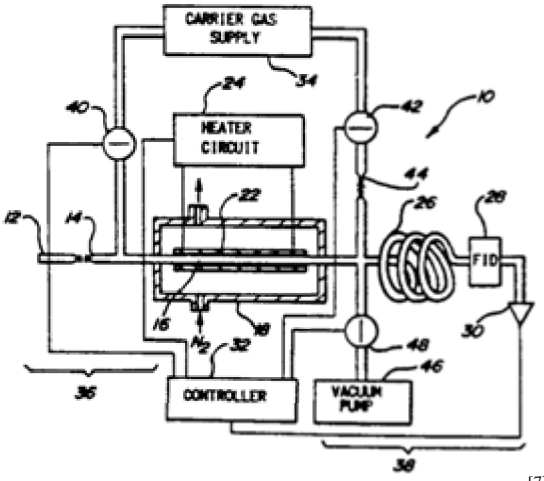

Figure 3: Adsorbent trap for Gas Chromatography[7]

Modifications to the cryo-focusing setup and adding some adsorbent like AL2O3 into trapping chamber named porous layer open tubular (PLOT), gave better volatiles selection for GC detection. The sample is inlet from port 12, and is passed through silica fused valve 14 into the trapping chamber 18. Trapping chamber consist of N2 hollow chamber along with PLOT the trapping chamber is active when N2 is kept as the required trapping temperature and is continuously flow through the chamber 18, so that the PLOT is at trapping temperature. Trapping temperature is that value of low/sub-zero temperature at which the group of volatiles gets adsorbed onto the trapping chamber. Once the trapping temperature is set then the volatiles having higher boiling point then this gets adsorbed within the trapping chamber. When sample needs to

be evaluated by GC the temperature of the chamber is raised by the temperature controller 32, heater circuit 24 so that the desorption of only that volatiles take place which have boiling points lower than the same. Below diagrams shows the chromatograph of five volatile compounds.

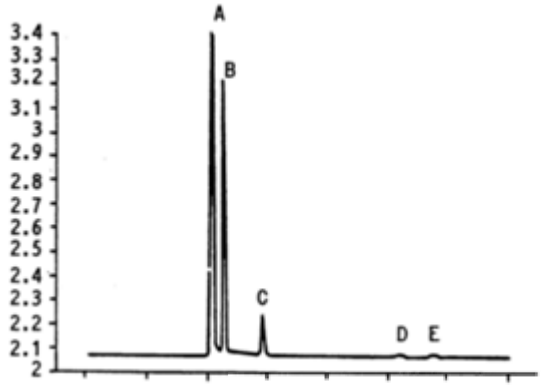

Figure 4: Natural sample chromatogram @-130 ºC [7]

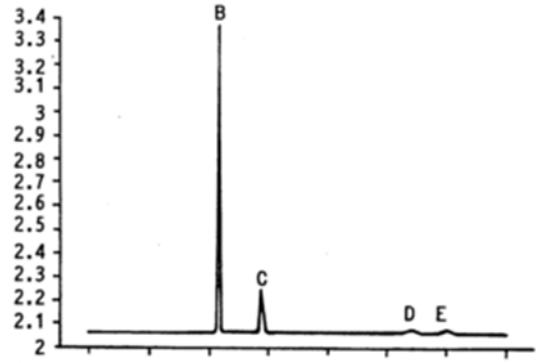

Figure 5: Trapping temperature @-70ºC[7]

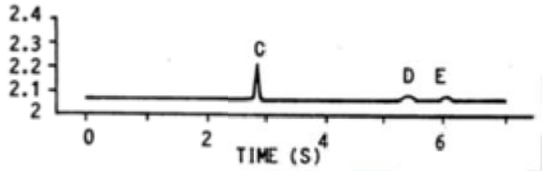

Figure 6: Trapping temperature @-30ºC[7]

Figure 4 shows a simple chromatogram in isothermal temperature procedure, and has five volatile compounds i.e. A, B, C, D, E; with their boiling points at AºC, BºC, CºC, DºC, EºC such that A<B<C<D<E. The sample is initially heated to desired temperature so as to elute its volatiles and then applied to the adsorption trap for gas chromatographer. At first the trapping temperature is kept -130ºC and valves are opened so as to create vacuum by a vacuum pump. All the volatiles gets adsorbed at this cryogenic temperature and remaining gets vented by the pump, this is the adsorbing stage. The next is the injection mode, wherein the heater is made on and is kept at an injection temperature of 100ºC. All the trapped volatiles gets eluted at same time and is directly applied to the analytical column, which in turn generates the chromatogram of five peaks. Later, in the second iteration the sample is heated but the trapping temperature is kept -70ºC. Now the volatile A which has boiling point higher than -70ºC remains un-trapped and gets flushed via vacuum pump. And now the trap consist only four compounds, which is then applied to the column in the injection mode. The chromatogram is as shown in Figure 5. In the third iteration the trapping temperature is raised to -30ºC. now two compounds namely A & B gets flushed out by vacuum pump and remaining three gets trapped inside the adsorbent column, since the boiling point of B is higher than -30ºC. Figure 6 shows the chromatogram with trapped three peaks when eluted in injection mode. This is a novel method and good modification to the cryo-focusing technique. This allows selective analysis of closely packed compounds, along with sample enrichment in terms of its capacity and detection.

4. Volatile Separating and Sampling Device Based On Thermo-Kinetic Principle

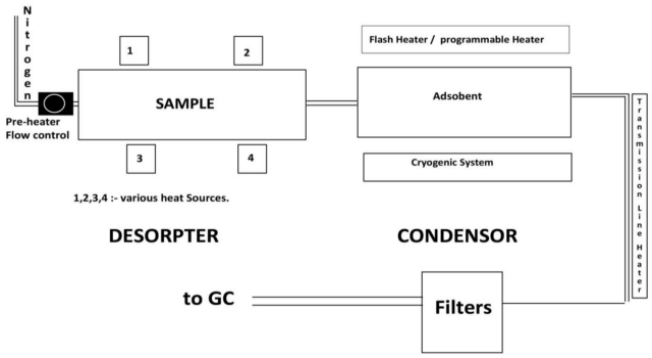

Figure 7: Thermo-kinetic Desorpter[1]

Controlled adsorption and flash or uncontrolled desorption was the technique utilized in the previous work. Here this thermo-kinetic desorpter exhibits control over both desorption and condenser temperatures there by providing controlled injection or controlled desorption of volatiles and thereby give better control over the sampling process. The desorpter device is believed be loaded with any kind of the sample whether solid, liquid, gaseous. It is then heated to a specific temperature so that the volatiles elute and gets into the adsorbent chamber also called as condenser, since it is at very low temperature (sub-zero). This condenser is internally coated with adsorbent material to trap the eluted compounds and the condensation temperature can be set by temperature controller. Here the advantage is that selectable amount of volatiles are eluted from the sample through desorpter and is condensed at condenser. Later this condenser is subjected to either flash heating so as to inject all volatiles into the analytical column, or condenser is heated in steps to elute the volatiles of desired choice so the GC separates it with better resolution. Since these volatiles are eluted upon heating they are thermally generated and gains kinetic energy while their travel hence called as thermo-kinetic desorption. Its practical implementation and incorporation of study of CFD analysis proved an increase of 25% in detection of peaks by GC.

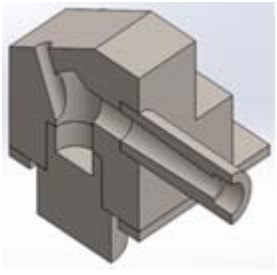

Figure 8: Desorpter Model[1]

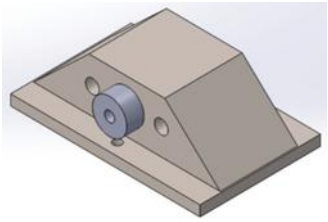

Figure 9: Condenser Model[1]

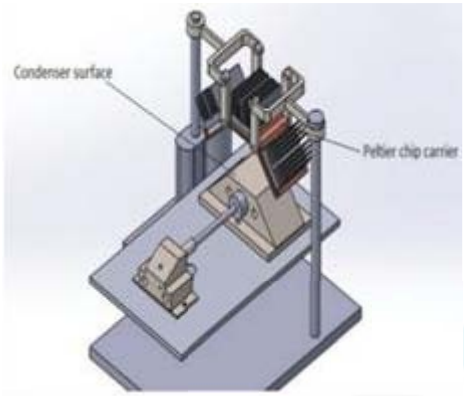

Figure 10: Complete Device Design[1]

Greater advantage is achieved in this design, since solid state heat-pumps i.e. Peltier are utilized. They form a non-exhaustive source for cryogenic cooling required for adsorption in the condenser.

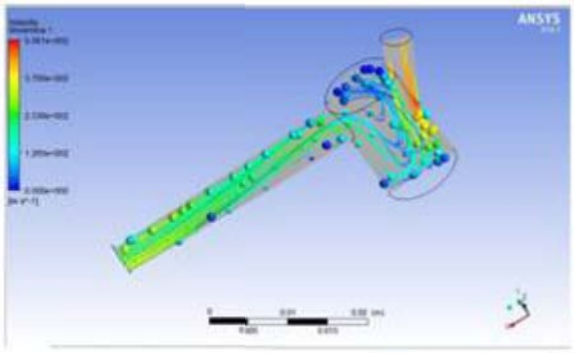

Figure 11: CAD CFD Analysis of Desorpter[1]

CFD analysis of the same proved better performance if turbulent flow of nitrogen was accepted as the inlet flow. Giving a digital platform improves the controllability of the system.

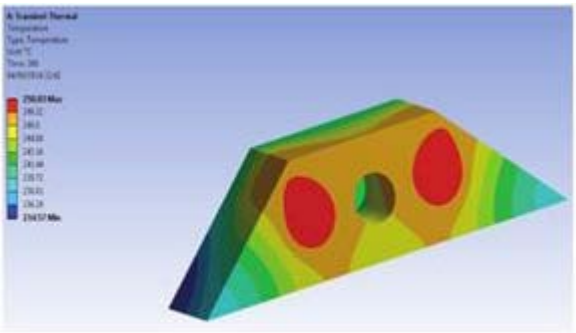

Figure 12: Condenser Heating Contour [1]

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Author Profile

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