

Sample Enrichment and Selective Injection for Gas Chromatograph (Prototype-1)

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ABSTRACT: Resolution of the detected peaks in gas chromatogram can be improved by enriching the sample before injecting. This provides sharp peaks and higher capacity. Cryo-focusing is very effective mode for sample separation at initial stage but requires bulky cryogenic system to sustain liquid nitrogen at such temperatures. Existing Sample preparation mechanism have a loop in sub-zero temperatures and they are subjected to flash heating to inject samples into GC. This is combined with Headspace at prior and fed to GC later. Controlled elution of volatiles from sample, controlled adsorption on the surface and controlled elution for injection to GC can prove better results. An attempt is made to construct a device for the same purpose in a crude way. Further, Digital interface and control would provide precise control over process parameters.

KEYWORDS: Gas Chromatographer, adsorption, elution, Flash heating, resolution.

I.INTRODUCTION

Many studies in the field of biology as well as in chemistry require identifying the components present in the obtained sample, which are not generally of same composition. Analytical Chemistry is the branch in chemistry which deals with the study of separation, identification and quantification of the chemical components of natural and artificial materials. Qualitative analysis determines the component in the sample but doesn't comment on its concentration; rather Quantitative analysis determines the amount of the component in the given sample. The separation of the sample components can be achieved by Chromatographer, Field flow fraction or Electrophoresis. Chromatography is an analytical study in which the constituents of the sample are determined depending upon the Chroma (colour) the separated compounds. Mikhail Tswett is the father of chromatography. He first separated the contents of the plants chlorophyll by using Calcium Carbonate powder, Petroleum Ether and the plant extract i.e. chlorophyll, and found that the then known single compound chlorophyll contains more than 5 constituents. This experiment was then taken further and studied and many electronic Chromatographers were developed.

An instrument called as Gas chromatographer is used to identify the number of the components present in the sample with their respective concentration. This is achieved by relative comparison with the known samples which are again evaluated by the same instrument under same operating conditions. Once the sample, which is specifically in liquid form, is given through the injector of the instrument it is evaporated in the injector port and then further propagated via carrier gas in the stationary phase of the capillary column. Here in this column which may be polar, mid-polar or non-polar in nature provides the interaction between the volatile molecules and the liquid applied inside the capillary column. The interaction depends on number of factors, and this interaction creates the groups of the volatile molecules inside the column which are simultaneously propagated further by the carrier gas call as the mobile phase. This group of molecules are then detected by detectors attached to the instrumentation circuit. Generally inert gases like nitrogen, helium etc. are used to just drift the molecules further. Fig. 1 classifies the various methods in chromatography. We focus our research in Gas chromatography and develop means to improve its performance in terms of better detection and increased resolution of peaks detected.



Fig. 1 Classification of Chromatography.^[10]

II. RELATED WORK

More long is the column in size more is the interaction with the volatiles molecules and hence more is the group formation of the same molecules. These groups of same molecules are then taken out if the stationary phase and given to the injector. The detector is the device which detects the groups of molecules. There are various types of GC detectors available. Once the group leaves the column and enters the detector chamber it is the detected and a real time indication is given on the computer screen showing the current peaks which is measured across time the more the molecules in the group the more is the area under the current pulse. The concentrations of the components are estimated in terms of percentage and the numbers of components are measured by its resolution i.e. the number of perfectly separated peaks.

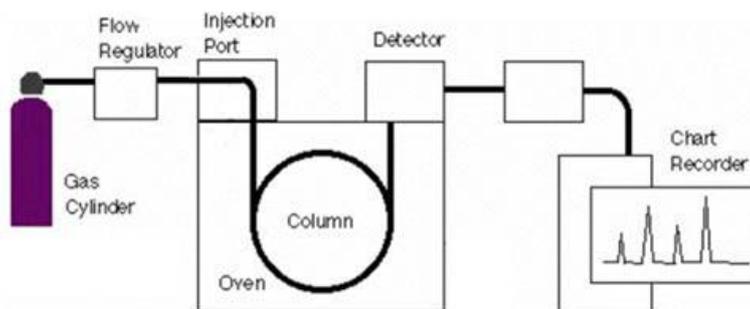


Fig. 2 Basic Gas Chromatography process.

Moreover this method is just a separation process for injected sample, no enrichment or sample separation at initial stage is done. Fig. 2 shows the basic technique employed in a gas chromatograph. Various components of GC are assembled as shown in fig. 2 and the process is commenced with isothermal temperature programming. This method proves very effective in detecting the volatiles from gaseous as well as liquid samples. Gas cylinder consist of the

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drifting inert gas mostly nitrogen or helium, injection port is preheated to evaporate the sample compounds and given to capillary column which is then fed to detector which detects the group of compounds reaching at successive time intervals called as retention time. Cryo-focusing, Adsorbent trap for gas chromatography along with headspace proves better results in terms of sample enrichment, its capacity, sharp peaks and partially controlled separation detection. Adsorbent trap for GC, consist of vacuum pump 46, which vents all the un-necessary volatiles above trapping temperature set by cryogenic system controller 32.

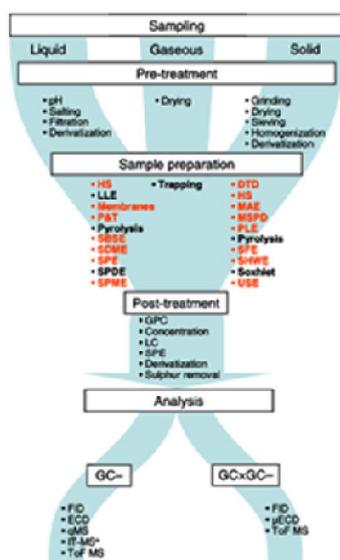


Fig. 3 Typical Strategy for GC Sample procedure [6].

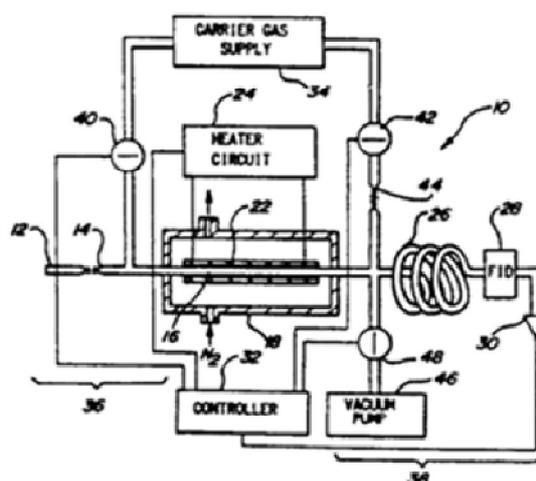


Fig. 4 Adsorbent trap for Gas Chromatography [7].

Fig. 3 shows the sampling strategy used for sample preparation for GC. Different phases of samples are treated with different methods before injecting, called as pre-treatment. Once it is trapped then subjected to post treatment for selective extraction of compound to be injected in GC. Fig. 4 shows a patented design for effectively trapping volatiles for GC. The inlet is flooded with the volatiles generated by headspace at a predetermined temperature of interest and kept recorded for further iterations. During trapping mode valves and vacuum pump are made on and the trapping chamber is kept at a trapping temperature. Trapping chamber adsorbs only those volatiles which have boiling point below trapping temperature. Rest of the volatiles with high boiling point is vented out by the vacuum pump; this is called as Trapping Mode. Now the chamber temperature is raised to a fixed value and all the volatiles elute and are fed to the analytical column of GC, called as injection mode. This helps to selectively adsorb and analyse the volatiles having boiling point lower to the trapping temperature. This somehow provides a partial selectivity. Moreover this mechanism can be modified and selective trapping along with selective injection can be incorporated for better results. Volatile Sample separation device aims at providing selective injection to the GC column by controlling the injection temperature, hence better selectivity. A solid or semi-solid sample is heated to desired temperature and nitrogen gas is inlet gushing through the sample holding chamber eluting the volatiles having boiling point lower than the desorptor temperature. Here desorptor temperature is controlled by external PID controller. The eluted volatiles travel along the line and is brought to the adsorbent chamber where they get adsorbed. For their injection into GC, the condenser mechanism is directly flash heated so as to dump all volatiles into the GC analytical column.

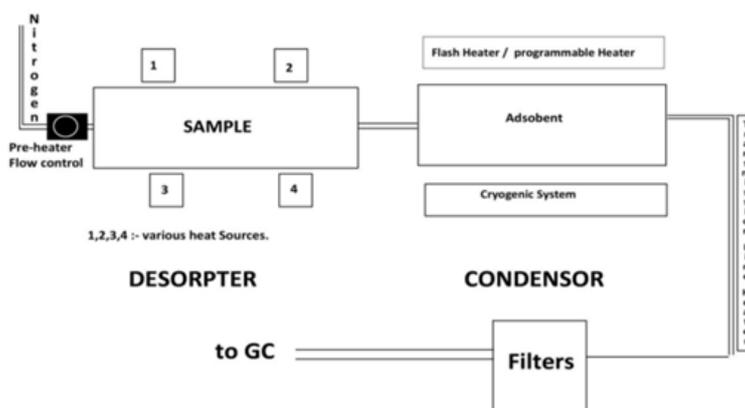


Fig. 5 Concept of Thermo-kinetic desorptor^[7].

This however faces a problem of decomposing the volatiles within the condenser at higher flash heating rates. Prototype on the same work is been made with modification so as to get better results. CFD analysis proves turbulent gas inlet elutes more volatiles from the mother matrix and the same is transferred further.^[1] The Desorptor and condenser is modified and made efficient according to CAD-CFD analysis.^[4]

III. VOLATILE SAMPLE SEPARATION DEVICE

Prior studies on the heating process of thermo-kinetic desorptor by CFD analysis^[3], creates a suitable platform to build a prototype that with efficiency in fluid dynamics. Fabrication of desorptor device and condenser device is done in Stainless Steel (SS316), food grade steel so as to avoid any chemical reaction of volatiles with the device metal^[4] Fig. 6 shows the components manufactured completely in SS316.



Fig. 6 Desorptor and Condenser in SS316

Preliminary investigation concluded that SS being bad conductor of Heat energy, resulted in very sluggish rise in temperatures, as well as inherited high heat storing capacity. This raised concerns for high time requirements for experimental iterations, being unacceptable since condenser is to be brought to cryogenic temperatures for adsorption. Figure 7 shows heating effect in desorptor cavity by 2nos. 125w heaters, with rise time equal to 10mins, and cool down time is 60mins @50°C. Fig. 8 shows the heating effect in condenser mass with approximately same ratings. Here 2 heaters of 175W each are employed so as to have high temperature rate.

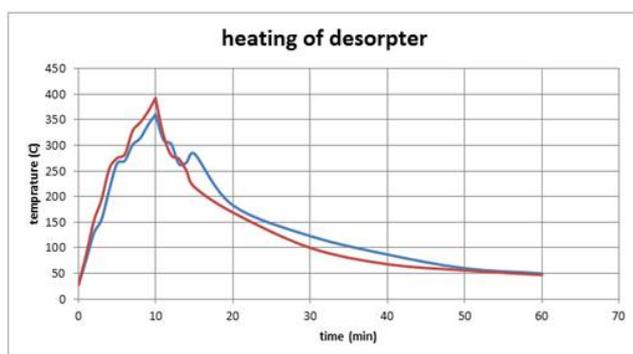


Fig. 7 Heating Curves for SS316 Desorpter

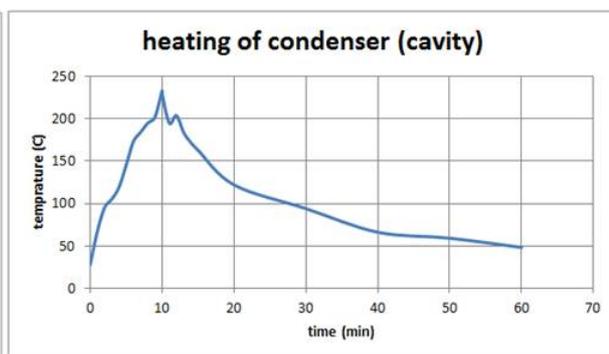


Fig. 8 SS316 Condenser Heating 2heater 175W

Low heating rate and high cool down period led us migrate to aluminium 3060 to be considered for condenser fabrication, since it experiences much extreme low and high temperatures during adsorption and flash heating. Figure 8 showcases the rise in rate of temperature in aluminium condenser here the rise is brought down to 3min, under same environmental and excitation conditions. Cool down rate is improved by employing 35CFM CPU cooling fan.

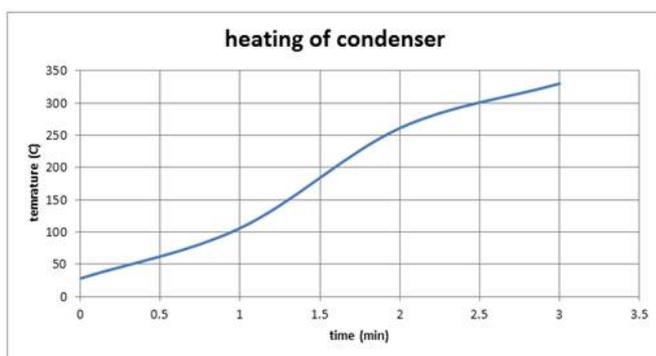
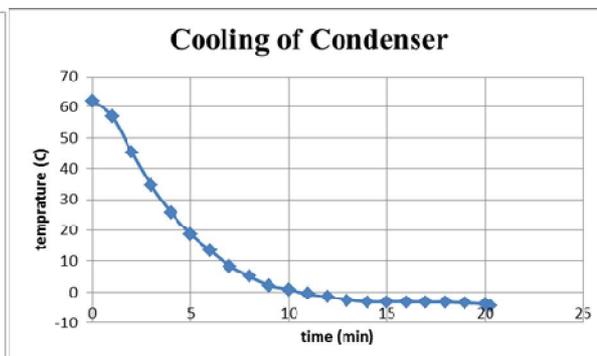


Figure 9: Heating curve for Aluminium Condenser. Fig. 10 Sub-zero cooling in condenser by 100W Peltier, Water cooled @0°C.



Adsorption in condenser takes place at cryogenic temperatures. Bringing aluminium mass to cryogenic temperatures can be done in various ways. Using nitrogen liquid is exhaustive mode and needs to be refilled each time, rather using solid state heat pumps like Peltier with water cooling proves good option at cost of increased power consumption. Peltier are enhanced versions of thermocouple and uses the reverse thermoelectric effect to reach at cryogenic temperatures. Experimentation resulted subzero temperatures of about -7°C with single Peltier of 100W/12V, water cooling and water at temperature of 0°C , achieved using ice bath. However the volatiles eluted at room temperature can be trapped if adsorbent temperature is well below their boiling temperature, hence selection of three Peltier devices with water cooling is selected and the result is as show in Fig. 10.

These remains un-exhaustive mode for attaining cryogenic temperatures as compared to liquid nitrogen. The same is employed in the system. Figure 11 shows the cooling curve by three Peltier. Fig. 12 and Fig. 13 show the pictorial view of actual cooling of the condenser component. These condenser and desorpter are connected by SS316 connecting rod with internal tapering^[4]. SS is chosen in order to allow the formation of temperature gradient during cooling of condenser and heating of desorpter simultaneously. For heating of condenser the Peltier are required to be disengaged so that they do not get damaged due to flash heating mode of operation.

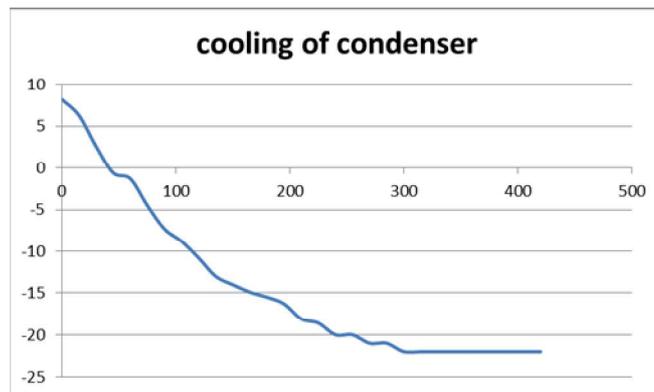


Figure 11: Cryogenic cooling by three peltiers 100W each, water cooling @0°C

Fig. 11, 12, 13 shows the solid state heat pumps in action with water cooling as primary cooling. This temperature is maintained till the entire system is kept ON. However it is found that if the humidity content is more than the formation of ice on the surface further helps to achieve and maintain the cryogenic temperature value.



Fig. 12 Sub-zero(-6.8°C) Temperature by one Peltier.



Fig. 13 Cryogenic Temperature (-24°C) by three Peltier.

Figure 15 below shows the connection of desorptor and condenser heated up to 268°C and cooled down to -19.6°C simultaneously. Electrical Network is setup with SMPS as primary power supplies and heaters are powered by 230VAC/50Hz mains power. Toggle switches are interfaced in series to control the Peltier and heaters as shown in figure 14. These are made to work for extreme temperatures in ON-OFF modes. Sequence of the same is as described in the Figure 15. SS tubing of 1/16” is employed for the flow of gas of nitrogen. Loader cap is beneath the desorptor and is used to load the sample. Solenoid valves are connected in series to the inlet of desorptor and outlet of the condenser so as to inject into the GC.

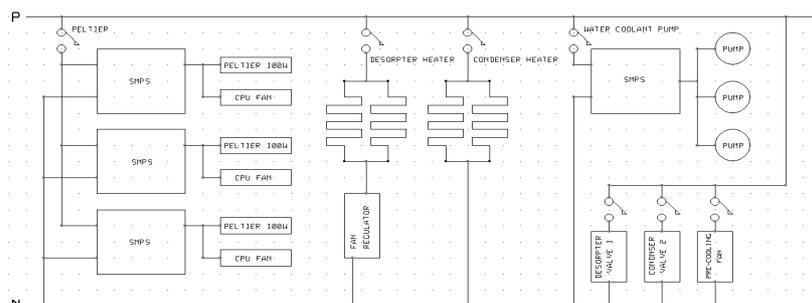


Fig. 14 Schematic for electrical connections

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Fig. 15 Simultaneous operation of Desorptor and Condenser. (@-19.6°C & +268°C)

Simultaneous heating of desorptor at 268°C and cooling of condenser at -19.6°C is achieved under normal room conditions. This experimental condition was found to be repeatable and can be maintained for longer time. Hence the simultaneous heating of volatiles and their trapping is possible. The successive flash heating and cryo-cooling of aluminium condenser made it necessary for the Peltier's to be physically disengaged for this temperature cycles. Overheating the Peltier surface may damage the PN chips inside leading permanent damage.

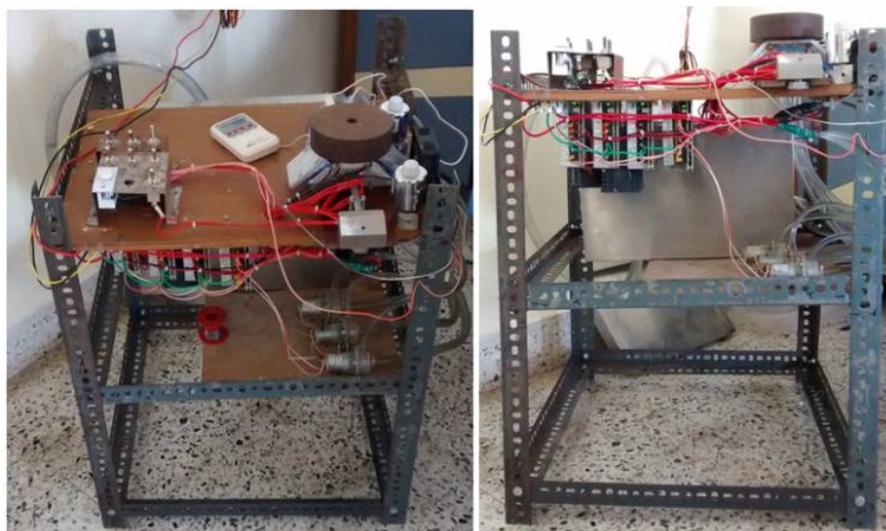


Fig. 16 Prototype-1, Complete System

Complete prototype-1 is as shown in fig. 16. Hardwiring is done for the heating and cooling process. Temperature is controlled by a solid state power regulator. And SMPS are employed for DC power conversion. Ice bath is accommodated with water circulating pumps. The entire assembly can be further ascetically designed for proper use with GC.

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| Steps | Step1 | Step2 | Step3 | Step4 | Step5 |
|---------------------------|---|------------------------------------|--------------------------------|-------------------------------|------------------------|
| Process | Device preparation | Sample loading | Process start | Condensation | Flash heating |
| Actuators | | | | | |
| Desorptor N2 Valve | ON | OFF | ON | ON | ON |
| Desorptor Heaters | ON | OFF | ON | ON | ON |
| Pre-cooling | OFF | ON | OFF | OFF | OFF |
| Peltier | OFF | ON | ON | ON | OFF |
| Condenser Heaters | ON | OFF | OFF | OFF | ON |
| Condenser Valve | ON | OFF | ON | ON | ON |
| Comments | Air purging, cleaning the equipment for 2 min | Sample Loading, Condenser to -25°C | Sampling And Separation starts | Volatile accumulation process | GC injection procedure |

Fig. 17 Steps & modes of operation for Prototype-1

Fig. 16 shows the complete setup of the prototype. This consists of power supplies and desorptor and condenser assemblies. Ice bath, Peltier assembly, pump, SMPS and injection pipe to GC along with switching interface is one the same platform.

IV.CONCLUSION

Achieving extreme temperatures is possible simultaneously with SS316 connecting rod. Non-Exhaustive Cryogenic system using Peltier proves application specific though high power consumption but imposes one time cost. Further, Desorptor and condenser both can be fabricated in aluminium alloy to ease high temperature rates and avoid any volatile reaction with material. Digitally controlled environment can be interfaced so that precise control over process parameters like temperature and gas pressure can be controlled.

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