Review Paper for Sample Preparation Methods for Gas Chromatographer

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***Abstract*- Gas Chromatographer has been used over the year to identify and differentiate constitutes of a volatile chemical. It has been limited in way of operation to only volatile chemicals. Chemist and scientist over the years have repeatedly tried different methods to make a chemical sample Gas Chromatographer friendly. In this paper some of the techniques that are used to enable make Gas Chromatographer a more versatile Laboratory equipment are explored.**

***Index Terms*- Gas Chromatographer, Sampling, Headspace, Sample preperation**

1. GAS CHROMATOGRAPHY

A. *Chromatography*

There are currently many diverse techniques that can be used for the separating solutes from mixtures. These are used in the analysis of constitutes of a mixture organic or inorganic in nature. Chromatograph is a chemical analytical instrument used for extraction of various constituents from a complex entity. The chromatograph uses a packed narrow column, in this column the complex entity which is to be extracted is entered from one end. Then due to adsorption and desorption phenomenon the various constituents of the entity travel at different velocities through the column. The constituents are then separated and differently collected.

In gas chromatography, the components of a sample are dissolved in a solvent and vaporized in order to separate the analytes by distributing the sample between two phases: a stationary phase and a mobile phase. The mobile phase is a chemically inert gas that serves to carry the molecules of the analyte through the heated column. To separate the compounds a solution sample that contains organic compounds of interest is injected into the sample port where it will be vaporized. The vaporized samples that are injected are then carried by an inert gas, which is often used by helium or nitrogen. This inert gas goes through a glass column packed with silica that is coated with a liquid. Materials that are less soluble in the liquid will increase the result faster than the material with greater solubility. The purpose of this module is to provide a better understanding on its separation and measurement techniques and its application.

B. Micheal Tswett's Experiement

Michael Tsweett was a Russian Botanist, who was mainly interested in the composition of chlorophyll. His initial assumption, contradictory to the popular belief, was that chlorophyll consisted of mixture of different solutes. Initially, accidentally there was chalk on which an ink and water was dropped. Having remained there for some time, he observed that the ink had been split into multiple colours. On further investigation, it was understood that the multiple colours where nothing but its primary constituents. This was basis on which his further experiment set up. After this an experimental setup shown below was assembled.

The experimental setup consists of a glass column with a stop cork at one end and open at the other end. At the bottom was a cotton plug. The complete column was packed with slurry of finely powdered CaCO3 mixed in Petroleum ether. This was to ensure that the CaCO3 was evenly distributed over the Column. Then a concentrated solution of chlorophyll dissolved in petroleum ether was then evenly distributed on the cotton plug at the top. This setup was allowed to remain for certain time before the results were taken.

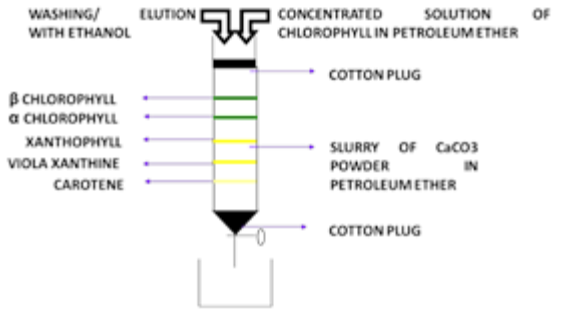

Figure 1: Micheal Tswett's Experiment

After certain time it was observed that the chlorophyll was travelling downward direction. And after sometime different colour bands were observed in the Glass Column. These bands were later identified as β-chlorophyll, α-chlorophyll, Xanthophyll, Viola Xanthine, Carotene. These are the constituents of the chlorophyll.

The phenomenon of formation of different colour bands was attributed to the principle of Adsorption and Desorption. Wherein the Chlorophyll would be adsorbed on the CaCO3 surface and correspondingly desorbed. Different constituents would require different amount of time to adsorption and desorption. Hence the basic constituents would be separated in different colour bands. When Petroleum ether was changed and an alcohol was used in its place. It was observed that the colour bands were inverted in their order. The conclusion was then made that the carrier phase, the mobile phase, and the compound properties are dependent on each other as to how the constituents are separated and observed.

C. *Gas Chromatography*

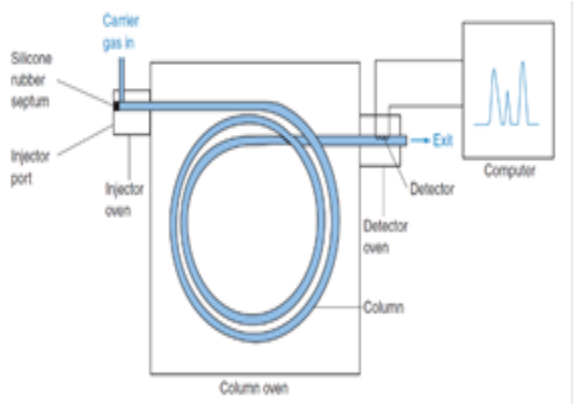

Figure 1: Typical Gas Chromatography Block diagram

The basic Operating Principle of a GC involves evaporation of the sample in a heated inlet port(Injector), separation of the components of the mixture in a specially prepared column and detection of each component by a detector. At the end of the process, the amplified detector signal is often recorded and evaluated by an integrator calculating the analytical results.

D.*Column*

The heart of the Gas Chromatograph is the Column. There are multiple types of columns available for variety of applications depending on the nature of the molecule matrix. In the column, the molecules due to different rates of adsorption and desorption separate out and at the end of the column, due to the behaviour of the molecules they are spaced out. Columns used in Chromatography can be up to 1 meter in diameter. In the case of Gas Chromatograph the two popularly use columns are mentioned below.

E.*Carrier Gas*

Helium is the most common carrier gas and is compatible with most detectors. For a flame ionization detector, N2 gives a lower detection limit than He. H2, He, and N2 give essentially the same optimal plate height (0.3 mm) at significantly different flow rates. Optimal flow rate increases in the order. Fastest separations can be achieved with H2 as carrier gas, and H2 can be run much faster than its optimal velocity with little penalty in resolution. There are drawbacks to using H2. It can catalytically react with unsaturated compounds on metal surfaces, and it cannot be used with a mass spectrometric detector, because H2 breaks down vacuum pump oil in the detector. The main reason why H2 was not used more often in the past is that it forms explosive mixtures in air when H2 is greater than 4%. Flow rates in capillary chromatography are unlikely to create a dangerous concentration of H2. Electrolytic generators produce high-purity H2 and eliminate the need for tanks of compressed H2. H2 and He give better resolution than N2 at high flow rate because solutes diffuse more rapidly through H2 and He then through N2.

F.*Injector*

After cleaning the syringe several times with solvent, take up air, then solvent, then air, then sample, and then more air. When the needle is inserted through the rubber septum into the heated injection port of the chromatograph, sample does not immediately evaporate, because there is no sample in the needle. If there were sample in the needle, the most volatile components would begin to evaporate and would be depleted before the sample is injected. The air bubble behind the sample plug prevents sample and solvent from mixing. The solvent plug washes sample out of the needle, and the final air plug expels solvent from the needle. Many auto-samplers are capable of this "sandwich" injection. Carrier gas sweeps vaporized sample from the port into the chromatography column. For analytical chromatography, the injected volume is typically of liquid sample. Gases are injected by a gas-tight syringe into the same kind of sample loop used in liquid chromatography. Decomposed sample, non-volatile components, and septum debris accumulate in the glass liner, which is periodically replaced. The liner must seal properly or carrier gas will bypass the liner.

G.*Detector*

The detector is the device located at the end of the column which provides a quantitative measurement of the components of the mixture as they elute in combination with the carrier gas. In theory, any property of the gaseous mixture that is different from the carrier gas can be used as a detection method. These detection properties fall into two categories: bulk properties and specific properties. Bulk properties, which are also known as general properties, are properties that both the carrier gas and analyte possess but to different degrees. Specific properties, such as detectors that measure nitrogen-phosphorous content, have limited applications but compensate by their increased sensitivity.

H.*Uses*

Gas chromatography is a unique and versatile technique. In its initial stages of development, it was applied to the analysis of gases and vapors from very volatile components. As an analytical tool, GC can be used for the direct separation and analysis of gaseous samples, liquid solutions, and volatile solids.

Drugs and Pharmaceuticals: Gas chromatography is used not only in the quality control of products of this field but also in the analysis of new products and the monitoring of metabolites in biological systems.

Environmental Studies: Many chronic respiratory diseases (asthma, lung cancer, emphysema, and bronchitis) could result from air pollution or be directly influenced by air pollution. Air samples can be very complex mixtures, and GC is easily adapted to the separation and analysis of such mixtures.

Petroleum Industry: The petroleum companies were among the first to make widespread use of GC. The technique was successfully used to separate and determine the many components in petroleum products.

Clinical Chemistry: Gas chromatography is adaptable to such samples as blood, urine, and other biological fluids. Compounds such as proteins, carbohydrates, amino acids, fatty acids, steroids, triglycerides, vitamins, and barbiturates are handled by this technique directly or after preparation of appropriate volatile derivatives.

Pesticides and Their Residues: Gas chromatography in combination with selective detectors such as electron capture, phosphorus, and electrolytic conductivity detectors have made the detection of such components and their measurement relatively simple.

Foods: The determination of antioxidants and food preservatives is an active part of the gas chromatographic field. Adaptations and sample types are almost limitless, and include analysis of fruit juices, wines, beers, syrups, cheeses, beverages, food aromas, oils, dairy products, decomposition products, contaminants, and adulterants.

I.*Advantages*

1.An Analytical Technique. This is used not only for the qualitative identification of components in a sample, but also for quantitative measurements.

2.A Physical Research Technique. This may be used to investigate various parameters of a system, such as determination of partition coefficients, thermodynamic functions, and adsorption isotherms

3.A Preparative Technique. Once the analytical conditions have been determined, the system may be

scaled up to separate and collect gram amounts of components.

4.An Online Monitoring Probe. A gas chromatograph can be locked into a process line so that the process stream may be monitored on a 24-h basis.

5.An Automated System. A gas chromatograph may be interfaced to a computer with an automatic sampler so that routine analyses can be run overnight.

6.Resolution. The technique is applicable to systems containing components with very similar boiling points. By choosing a selective liquid phase or the proper adsorbent, one can separate molecules that are very similar physically and chemically. Components that form azeotropic mixtures in ordinary distillation techniques may be separated by GC.

7.Sensitivity. This property of the gas chromatographic system largely accounts for its extensive use. The simplest thermal conductivity detector cells can detect a few parts per million; with an electron capture detector or phosphorous detector, parts per billion or picograms of solute can easily be measured. This level of sensitivity is more impressive when one considers that the sample size used is of the order of 1 μL or less.

8.Analysis Time. Separation of all the components in a sample may take from several seconds up to 30 min. Analyses that routinely take an hour or more may be reduced to a matter of minutes, because of the high diffusion rate in the gas phase and the rapid equilibrium between the moving and stationary phases.

9.Convenience. The operation of GC is a relatively straightforward procedure. It is not difficult to train nontechnical personnel to carry out routine separations.

10.Costs. Compared with many analytical instruments available today, gas chromatographs represent an excellent value.

11.Versatility. Gas chromatography is easily adapted for analysis of samples of permanent gases as well as high-boiling liquids or volatile solids.

12.High Separating Power. Since the mobile phase has a low degree of viscosity, very long columns with excellent separating power can be employed.

13.Assortment of Sensitive Detecting Systems. Gas chromatographic detectors are relatively simple and highly sensitive, and possess rapid response rates.

14.Ease of Recording Data. Detector output from gas chromatographs can be conveniently interfaced with recording potentiometers, integrating systems, computers, and a wide variety of automatic data storing modules

J.*Limitations*

1.Sampling in Gas Chromatograph is limited only to Volatile sample, any sample include non-volatiles, semi-solids, solids cannot be processed in Gas Chromatograph

2.Thermally unstable samples are labile in a Gas Chromatograph due the temperature gradients and variations. Such sample break down producing a unexpected outcome this makes it difficult in identifying the sample injected. Also, hyphenated techniques cannot be used on such samples

3.Fairly difficult for application of large preparative samples.

4.Gas Chromatography will provide only detection of sample, but identification of samples is not possible with Gas Chromatography. For identification of the sample have to be sent from Gas Chromatographer to Mass Spectrometer. Hyphenated techniques like GC-MS, GC-LC are expensive for operation.

II.SAMPLE PREPARATION

Modern gas chromatography cannot be fully treated without also discussing sample preparation. Unlike most other instrumental techniques, gas chromatography requires many specialized sample preparation techniques, due to the requirement that samples for GC be vaporized in the inlet. Further, in most cases, the analytes must be distributed in an organic liquid or a vapor phase prior to injection. The myriad sample matrices and interferences that may be present further complicate this. As a result, there are a tremendous variety of sample preparation techniques available for gas chromatographers. These range in complexity from simple dilutions and injection of “neat” samples, to sophisticated fully on-line instruments such as supercritical fluid extractors.

The sample that is injected into the gas chromatograph following sample preparation must be either a liquid or a gas, the analytes must be volatile enough under the conditions of the inlet and column to traverse the instrument, and, ideally, the matrix interferences must also be volatile, so as not to contaminate the instrument or column. In most cases,

liquid samples must be dissolved in a volatile organic solvent. The basic goal of sample preparation is to ensure that these conditions are met, with additional goals that the preparation be reproducible to meet quantitative analysis requirements and straightforward to perform, if the analysis is to be performed routinely, as in quality assurance and in other routine testing laboratories. Very few native analytical samples, which may be solids, liquids, gases, or simple or complex mixtures and contain volatile and nonvolatile contaminants, meet these requirements. It is readily seen that there are numerous possibilities possible for a given sample type. This presents the choice of sample preparation technique as one of the most difficult choices in developing an analysis. Most interesting among these, is the possibility of changing the phase of the sample (by dissolving in a solvent or trapping on a sorbent, for example) to make the sample more amenable to available, sensitive, or selective instrumentation.

III.TYPES OF SAMPLE PREPARATION

A. *On Column Cryo-Focusing*

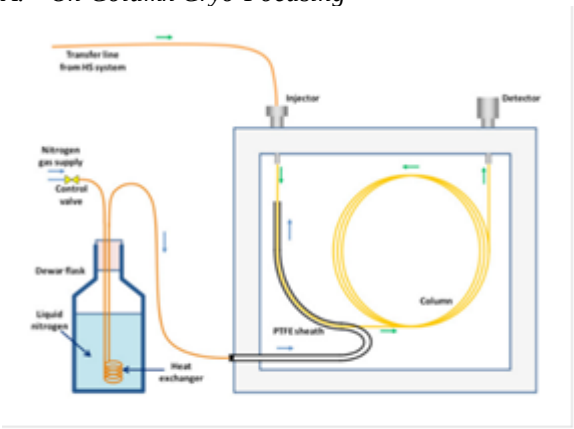

Figure 1: On Column Cryo Focusing

One technique that was successfully used for many years was to cool the GC column and so re-focus the compounds in a higher volume of injected vapor. By temperature programming the column once the injection was complete, peaks eluted that were narrow and higher thus retaining chromatographic resolution and significantly improving detection limits. The simplest means of achieving on-column re-focusing, would be to deploy a sub-ambient accessory for the GC oven that would use liquid nitrogen or liquid carbon dioxide to cool the whole oven. In practice, whole oven cooling is rather overkill. We don't want to perform chromatography at these temperatures but rather just focus the compounds in a few millilitres of vapor at the column inlet. The first loop of the GC column is threaded through a length of thin-walled PTFE tubing through which a stream of cooled nitrogen gas is flowing. This creates a very effective cooling sheath around this section of the column and is able to re-focus almost all organic compounds at the column inlet. The nitrogen gas is cooled by passing it through a heat exchanger made from a coil of copper tubing which is submerged in liquid nitrogen held inside an insulated Dewar flask. The flow of gas is turned on and off by a solenoid valve under the control of the GC method. Using cooled gas in this way enables the cooling process to be rapidly applied and when turned off, the GC column quickly returns to the oven temperature. Cooling temperatures of -150 °C or even below are easily achieved. The relationship between sampling time and amount injected will remain the same for regular pressure balanced sampling. Note that although the system is very effective in improving detection limits, there are a few caveats that must be considered. The main issue is the presence of water in the headspace vapor. This water will condense and freeze inside the section of cooled column and will easily block the flow of vapor through it thus effectively ruining the analysis. To address this issue, a water abstractor device containing a desiccant such as lithium chloride or potassium carbonate may be inserted into the sample vapor stream. This removes the moisture at lower temperatures and is reactivated by the heat of the GC oven when temperature programmed.

B. *Dynamic Head Space Sampling*

Figure 1: Dynamic Head Space Sampling

Dynamic headspace is a technique very similar to equilibrium (static) headspace sampling but is intended to direct most, if not all, of the headspace vapor into the GC column. It is also very similar to the purge and trap technique except that the incoming gas supply is introduced into the headspace rather than made to bubble through the sample. Two needles are used to puncture the vial seal: one to introduce carrier gas and the other to provide an outlet. Normally the two needles are combined into a concentric arrangement for mechanical simplicity. Some form of trap is located in the outlet path. A schematic diagram of a typical dynamic headspace setup using a stream of carrier gas to drive the headspace vapor into a suitable trap. The trap normally comprises a series of adsorbent beds that will retain the analytes. The sample is prepared and equilibrated in the same way as for regular equilibration headspace. The trapping device may be a cold spot in a tube or column or may be a purpose-designed adsorbent trap. After the vial has been swept and the sample vapors have been collected in the trap, the trap is heated to vaporize the collected compounds and valve changes are made so that carrier gas carries the compounds into the GC and column for analysis. This technique is able to

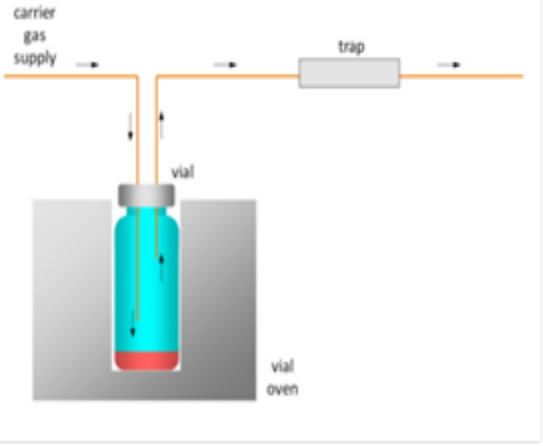

Figure 1: Dynamic Head Space Sampling

improve detection limits for analytes in samples by a factor of 100x or even more.

C.*Head Space Trap Sampling*

Headspace trap sampling uses equilibrium headspace to produce a stable headspace vapor. The sample vial

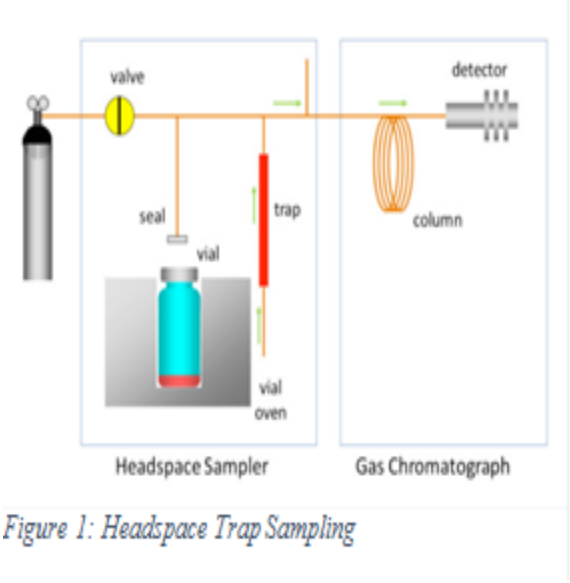

Figure 1: Headspace Trap Sampling

is pressurized to a high pressure and then the pressure is allowed to decay by allowing the vapor to flow through an adsorbent trap to vent. In this way, most of the headspace vapor may be extracted and the compounds in it are retained on the trap. Extraction will eventually stop once the pressure inside the vial is the same as ambient pressure; thus, some vapor is left in the vial at the end of this process. A schematic diagram of a HS Trap system in the trap load mode. In this instance, the vial has been thermally equilibrated and pressurized with carrier gas in the same way as for the standard pressure balanced sampling technique. The pressurized headspace vapor inside the vial is allowed to vent through an adsorbent trap which retains the analytes. An isolating flow of carrier gas keeps the headspace vapor out of the GC column during this step. Once the analytes are in the trap, the isolating flow is turned off, the flow of carrier gas is reversed and the trap is heated. The thermally desorbed analytes are carried by the carrier gas into the GC column where they are separated and detected. The act of pressurizing the sample vial and venting it through a trap will not extract the entire vapor from the vial – after venting, vapor is still left in the vial at atmospheric pressure.

D. Solid Phase Micro extraction

SPME is another technique that can be used to extract and concentrate compounds from headspace vapor. Instead of using carrier gas to sweep or pulse the

headspace vapor out of the sample vial into some sort of trapping device, SPME essentially inserts a 'trap' into the headspace vapor inside the vial. This 'trap' is normally implemented in the form of a retentive coating applied to a narrow fused silica fiber which is located within the needle of a special syringe. This syringe is normally operated by an autosampler but the whole process may be performed manually if required. The needle pierces the seal of a vial containing the sample and the coated fiber extends down into the headspace and starts to absorb or adsorb compounds from the vapor. The system is left to stabilize or equilibrate for a period of time. The fiber is drawn back into the syringe needle which itself is withdrawn from the vial and inserted into a heated GC inlet. The fiber is extended and absorbs heat from the injector liner which desorbs the extracted analytes and carrier gas transfers them to the GC column for analysis. SPME considerably simplifies the extraction technique – no gases or plumbing are required. It provides a good degree of analyte pre-concentration for many analytes and is very effective at eliminating the effects of water, etc. which may enter the trap and column with other techniques. However in terms of the theory behind the extraction process, things are significantly more complex. Essentially, HS sampling by SPME is a 3-phase system. The headspace vapor phase will interact with the sample phase and with the SPME fiber coating. Two thermodynamic systems are at work simultaneously: analytes will seek to achieve an equilibration between the sample and the headspace vapor with a concurrent equilibration taking place between the headspace vapor and the fiber coating. Thus two partition coefficients are involved to achieve a final equilibration in the system. SPME is still going to retain only a small fraction of the total compound present in the headspace and in the original sample. The other potential issue with SPME concerns the kinetics in achieving equilibration. The presence of the additional phase will add to the equilibration time. Fortunately, molecular diffusion in the headspace phase is fast and the thickness of the coating on the fibre is thin – both of these will help accelerate this equilibration process. The area of this phase interface, however, is very low which will slow it down. One of the difficulties in SPME is that overlapped thermostatting is not possible with the

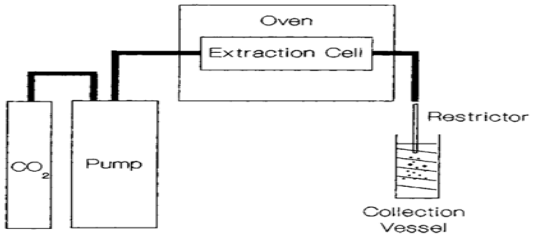

Figure 7: Super Critical Fluid Extraction

fibre in the vial. The samples must first be thermostatted for a period of time to achieve equilibration between sample and the headspace phase and then an additional equilibration period would be required once the fibre is inserted into the sample vial. This additional step significantly reduces sample throughput. To improve sample throughput, many SPME methods, do not wait for the system to achieve equilibration but rather sample the headspace for a fixed period which occurs in advance of equilibrium. Of course, this technique is going to be most suitable to certain types of sample – those in which the compounds of interest migrate first into the headspace and sorb onto the fibre coating. Regarding detection limits, typical extracts injected into the GC column will be in the range of 0.1 to 1% of the compounds in the original sample. Thus SPME will offer a slight improvement in detection limits over conventional (equilibrium) headspace but will not approach the detection limits offered by dynamic headspace or HS trap.

E.*Super Critical Fluid Extraction*

Supercritical fluids (SFs) are dense gases above their critical temperature and pressure, possessing gaslike viscosities and diffusivities, and having densities and solvating properties that approach those of a liquid. A A typical phase diagram representing the three different phases of a pure compound, with the shaded area representing the supercritical fluid region. Above the critical temperature, an increase in pressure will not drive the fluid into the liquid phase . The properties of SFs make them ideal for extracting analytes from solid matrices such as soils, agricultural products, foods, and solid sorbents. Supercritical fluids have the ability to maximize the extraction selectivity by controlling the temperature and pressure of the supercritical fluid. Initially, the solubility of an analyte in a supercritical gas is

dependent on solute vapor pressure; thus the solubility of the analyte in the gas first decreases with a rise in pressure reaching a point of minimum solubility. As the gas is compressed into the critical phase, there is a rapid increase in analyte solubility, which ends at a maximum pressure that is determined by the extraction temperature. Any additional increase in pressure will only slightly increase analyte solubility. Also, in some cases a higher extraction temperature will result in an increase in analyte solubility. At least two factors play a role in the extractability of an analyte from a solid matrix by SFE: (1) the analyte must by soluble in the supercritical fluid and (2) the analyte solvent interactions must be more energetically favorable than those of the analyte and the matrix. To determine whether the analyte is soluble in the SF, knowledge of the physical properties of the analyte is helpful. The melting point of the solid can be vital, since analytes tend to be more soluble in SFs in their liquid states. Above the melting point, the mass transfer of the analyte into the SF is improved along with analyte solubility because the cohesive forces of the liquid are less than those of the solid. In addition, the vapor pressure can play a role in the solubility of an analyte, especially for multicomponent systems. Information on analysis of the analytes by supercritical-fluid chromatography may be helpful in determining the analyte solubility in a supercritical fluid. If the analyte is soluble in a SF yet cannot be extracted from the matrix, the analyte matrix interactions may be too strong. The problem may be overcome by the addition of modifiers to the

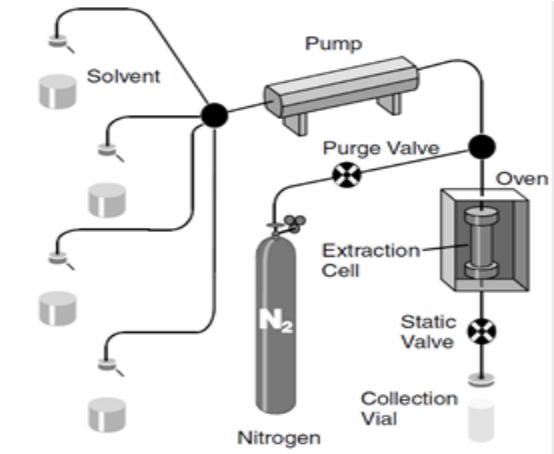

Figure 1: Accelerated Solvent Extraction

Supercritical fluid, or by the direct addition of a modifier to the extraction vessel. Modifiers have two basic effects on the SFE of analytes from a matrix. They can interact with the surface of the matrix displacing the analyte into the SF. To distinguish between the two types of modifiers, they are commonly termed solvent modifiers and matrix modifiers, respectively.

F. *Accelerated Solvent Extraction*

This technique is very similar to SFE in that the analytes are extracted from the sample using a heated organic solvent at relatively high pressures. The solvents are typically the ones that were commonly used as additives in SFE. However, the solvents are not under supercritical-fluid conditions. This method of sample extraction is rapid and automated, which is useful to labs that perform numerous analyses of solid samples. ASE instrumentation is very similar to that used for SFE, a high-pressure pump is used to deliver the extraction fluid to a vessel that can with stand high pressures and temperatures. The vessel is heated and has an automated sealing mechanism, which controls the pressure and solvent flowrate, and the extract is collected in collection vessels. ASE has the advantage of being able to use traditionally employed organic solvents to elute analytes from a sample matrix. By heating the solvents to a higher temperature, the extraction efficiency is improved. The elevated temperatures increase the solvents extraction efficiency, which accelerates the rate of extraction and reduces solvent volumes and elution times. The operation of the instrumentation and the extraction process is also similar to that of SFE. The sample vessel is loaded, then placed in the ASE instrument where the extraction process is automated. The solvent is introduced to the vessel where it is heated and pressurized. The system is allowed to stand (static extraction), and after a period of time, a nitrogen purge of the vessel flushes the solvent to a sealed vial. These parameters can be optimized to influence the solubility, mass transfer, and desorption of the analytes from the sample matrix. Since the extraction solvents are organic, they are compatible with gas chromatographic analysis.

G. *Pyrolysis*

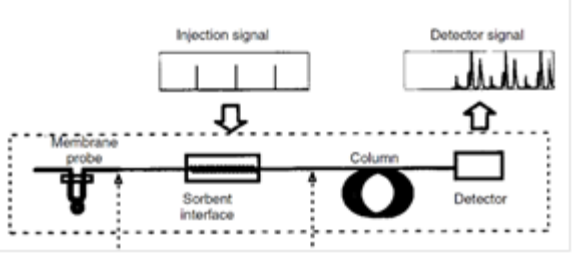

Figure 1: Pyroysis Block Diagram

Pyrolysis, the breaking apart of larger molecules into smaller ones using only thermal energy, is commonly interfaced to gas chromatography for the analysis of large molecules by thermal degradation. For example, polymers may undergo chain scission, in which the backbone of the polymer is broken up, resulting in smaller oligomers; sidegroup scission, in which the sidegroups are broken off; and unzipping, in which the polymer reverts almost entirely to monomer. The pyrolysis conditions must be adjusted so that these processes can occur rapidly enough to be analytically useful. Generally, this is done by increasing the temperature, with pyrolyzers capable of heating to 1400◦C common. Typical temperatures are on the order of 500–800◦C. A diagram of the connection of a typical pyrolyzer to a gas chromatograph. The carrier gas is routed through an eight-port valve to pass it through the pyrolysis chamber, hich sits directly on top of the inlet. The eight-port valve allows the pyrolysis chamber to be isolated for inserting and removing samples and to introduce a purge flow to remove air prior to heating. Applications of pyrolysis include art materials, biological samples, environmental samples, food and agriculture, forensic analysis, geochemistry, and fuels and synthetic polymers. An example illustrating the pyrolysis of isoprene-butadiene rubber.

H. *Volatile Separating Device*

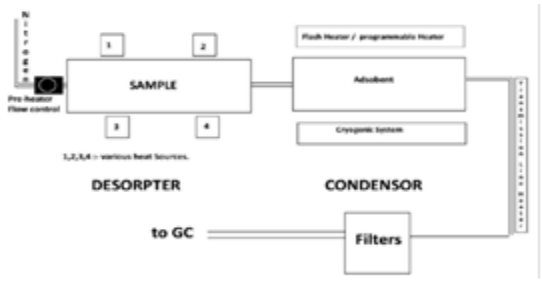

Figure 1: Volatile Sampling Device

Volatiles in the current context are molecules with boiling point up to 200 0C. Conventional methods for separating volatiles are biased towards one of the physical or chemical properties of the molecule and hence are not complete. So volatiles separated from the mother matrix will contain fewer molecules and even the most precise instruments can resolve only fewer molecules. On the other hand a better sampling device utilising thermal desorption, kinetic desorption, solubility in steam, desorption by microwave , desorption by magnetic induction or laser can separate larger number of molecules and hence can enhance the efficiency of instruments like MS. A sampler using thermo-kinetic desorption was fabricated in house and comparative study was conducted against conventional techniques. A 25% increase in peaks was observed when analysed with GC. The possibility of thermal decomposition was ruled out by conducting GC- MS studies. The aim of the current study is to develop a highly precise sampling device with global standards and has wide applications in the field of aromatic, analytical, biological and medical fields. The conventional methods used to separate volatiles from materials from plants or animal origin are biased to any single physico-chemical properties of the volatile. These methods are efficient to separate low boiling fractions only. As the development of modern technology; better heating methods, ability to maintain inert environment and controlled adsorption-desorption are evolved and hence a better method can be developed to separate volatiles from the mother matrix completely. Volatile is a substance which is capable of readily changing from a solid or liquid form to a vapour; having a high vapour pressure and a low boiling point. This classic definition of volatiles is vague and needs improvement to precisely classify this important set of molecules. Gas chromatography (GC) is the single instrument used to study volatiles and it can analyse molecules whose boiling points are as high as 250 ˚C or more. But it is important to not to introduce non-volatile materials in to the GC column. So, there is a requirement of a safe sampling device for GC. The currently available Head Space sampler and TDS are expensive and is again biased to a single property called thermal desorption.

IV. CONCLUSION

Although it is now over 40 years old, headspace-gas chromatography continues to be a very powerful analytical tool. There are many methods in use today based on this technique and more continue to be developed. This document was designed to assist with the understanding of some of the fundamental relationships involved in HS sampling so that a user can develop better methods to get better and faster data.

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