# Chromatographic Detectors and Column Hold-up for Organics–PDMS Systems

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*Abstract*—Gas chromatographic detector types and application, as well carrier gas flow rate and column hold-up measurements are discussed in this paper. The flame ionization and hot wire detectors are discussed in detail. The measurement of carrier gas flow rate using a soap film bubble flow meter is explained. Column hold-ups for 4 poly(dimethylsiloxane) packed columns were measured using the homologous series method.

*Keywords*—Column hold-up, detector, homologous, poly(dimethylsiloxane), retention, thermodynamic function

## I. DETECTORS

DETECTORS may be divided into main classes (i) Those which respond to the total mass of material emerging from the column for example the automatic titration system and these are called integral detectors (ii) Those, which respond to the concentration of the vapour in the carrier gas at any instant for example the Katharometer and these are called differential detectors. Detectors of the type have obvious advantage in quantitative analysis since this only requires the measurement of step heights.

However the two types of detectors are limited in their application. Several types of detectors are used in gas chromatography such as the hot wire detectors (HWDs), flame ionisation detectors (FIDs), flame photometric detectors (FPDs) and the electron capture detectors (ECDs). The main purpose of the detector is to identify the components by means of their retention times and to measure their concentrations. Selection of detectors depends on many factors, for example, sensitivity (minimum detection), stability (linearity), selectivity (signal to noise ratio), response time and the components involved. In this work, the flame ionisation and the hot wire detectors are discussed in detail while other detectors are discussed briefly.

Thermal conductivity detectors have been widely used in the chromatographic determination of thermodynamic data. They are simple in construction and permit direct determination of the gas hold-up of the chromatographic column by the timing

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of an air peak. However, since their response depends on the difference between the thermal conductivity of the organic solute and that of the carrier gas, this response is reduced considerably when there is a constant bleed of pure volatile organic solvents into the detector. For volatile solvents, thermal conductivity detectors are expected to be limited in applicability to systems where thermal conductivities of solvent and solute vapours are different. A more suitable detector would be the flame ionisation detector. One drawback in the use of flame ionisation detectors in the accurate determination of retention data has been the elaborate and indirect method of measuring the column gas hold-up. This is because the detector is insensitive to air under the conditions prevailing in a conventional column. The other drawback associated with flame ionisation detectors when volatile solvents are used is the decrease in sensitivity of the detector due to the increase in ion concentration between the electrodes. This eventually leads to complete insensitivity when the condition of ion saturation is reached. However, since a non-volatile solvent (PDMS) was used in this work, this drawback was eliminated. FIDs are very useful in the detection of volatile organic compounds in very low concentrations, say down to the 1ppm range. Therefore, the flame ionisation detector was used in this work as the focus is in very dilute regions.

### A. The Flame Ionization Detector (FID)

- Principle of operation

This detector was developed by McWilliam and Dewar (1958) [1] and it is based on the principle that the electrical conductivity of a flame burning hydrogen and oxygen mixture increases when the organic molecules enter the flame. This is mainly as a result of the difference in the ionisation potentials of the gas (15.8 – 24.5ev) and organic molecules (9-12ev). However, the ionisation of the organic molecules that takes place in the flame is not well understood. The increase in conductivity of the flame is much more than would be expected from the normal ionisation potential of the organic compounds. The potentials of organic molecules are in the range 9-12ev while the effective ionisation potential is about 5ev. One explanation as postulated by Stern (1951) [2] in [3] could be the formation of carbon aggregates within the flame and their subsequent ionisation. This explanation is strengthened by the fact that the ionisation potential of solid carbon is 4.6ev and the detector response is essentially proportional to the number of carbon atoms in the organic

molecules. Under the conditions prevailing in the conventional chromatographic column, the flame ionisation detector is insensitive to air, carbon dioxide, water vapour and hydrogen sulphide.

- **Lighting the detector flame**

No attempt was made to light the detector flame until the detector temperature was at least $100^{o}C$, below this temperature, water condensation can take place inside the detector producing a noise signal. When lighting the detector flame, the following procedure was followed. The first step was to ensure that the combustion gases (air and hydrogen) were turned on at the cylinders. The cylinder pressure regulators for air and hydrogen were set to 280kPa and 84kPa respectively. Sufficient time was allowed for the hydrogen to purge the plumbing and the supply at pneumatics panel was turned off. This was followed by setting the air pressure to 138kPa and the optimum air pressure was found by experiment. The next step was to remove the lower oven door cover. Then, the igniter was held against the FID chimney, the hydrogen supply was turned on and the flame was light. A distinct "pop" sound was heard as the flame ignites. A precaution was taken to make sure that the ignite filament was glowing before turning the hydrogen; this ensured that the combustion takes place at the jet and not above the collector. The filament lighting was checked by holding a cool shiny object against the detector end and water from the flame should condense onto the cold surface.

- **FID optimisation**

The hydrogen and air flow rates were set to values within the ranges in Table I.

TABLE I
FID OPTIMIZATION FLOW RATES

| Gas | Flow (ml/min) | Approximate inlet pressure | |
| --- | --- | --- | --- |
| | | kPa | PSIG |
| Air | 430 | 152 | 22 |
| Hydrogen | 33 | 83 | 12 |

Investigation of the optimum pressure was done by measuring the flow rate at the manifold at the bottom of the oven door with a soap film bubble flow meter.

*B. The Hot Wire Detector (Katharometer)*

- Principle of operation

The word katharometer meaning pure in Greek, was originally suggested by Shakespeare (1921) [3] to an instrument he devised for measuring the purity of hydrogen gas by thermal conductivity. The katharometer as used in the GLC is a type of detector, which works on the principle that the resistance of a heated wire placed in a flowing gas changes according to the thermal conductivity of the gas components. When heated filaments are placed in a flowing carrier gas they maintain a definite constant temperature and resistance. If the resistance of the carrier gas changes due to eluted solute sample, its thermal conductivity also changes. This will alter the rate of heat loss from the heated filaments. Thus the temperature and resistance will also change. Usually a pair of matched filaments are used, one being exposed to the carrier gas, "reference filament" and the other to the column, called the "sample filament". The reference and sample filaments are incorporated in Wheatstone bridge with the out of balance potential passing to the recorder. The schematic view of the hot wire detector is shown in Fig. 1.
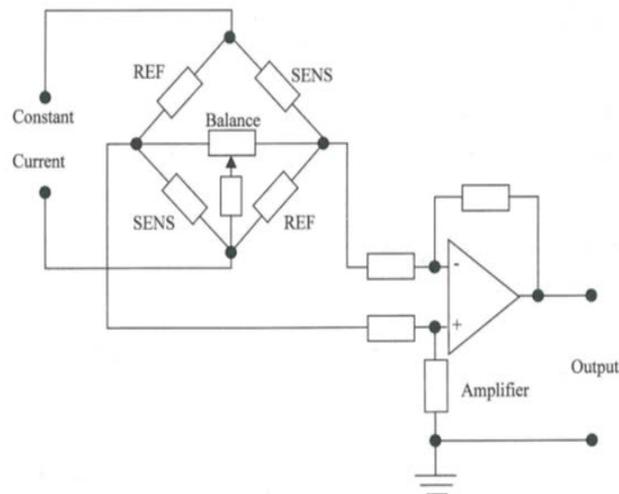


Fig. 1 Schematic view of the hot wire detector

As shown in Fig. 1, four tungsten rhenium filaments are connected as a bridge circuit, two filaments being located in each channel. The presence of a sample component in the carrier gas flowing channel changes the resistance of the filament in that channel, unbalancing the bridge and producing a signal related to the sample concentration from which the chromatogram is plotted. The detector is mounted on a standard cylindrical detector module and is mounted in the lower part of the oven door with the amplifier board positioned below it. The detector has two heated zones, the detector block and the interface which are separately controlled but are always set at the same temperature.

- **Choice of carrier gas**

Helium is the recommended carrier gas for use with a hot wire detector because of its high thermal conductivity. The use of helium is avoided when helium or hydrogen content of the sample is being analysed. The use of hydrogen is a possibility, but great care must be taken because of its high flammability. Therefore, it is very necessary to make sure that all the connections inside the oven are leak free. In the event of the helium or hydrogen content of the sample being analysed, nitrogen or argon may be used as the carrier gases. When nitrogen or argon is used, positive or negative peaks are obtained depending on whether the thermal conductivity of the particular sample content is smaller or larger than the thermal conductivity of argon. Sometimes samples containing hydrogen may show anomalous behaviour resulting in M-shaped peaks when helium is used as the carrier gas. This can be eliminated if a helium / hydrogen mixture containing

between 8 and 9 % by volume of hydrogen is used as the carrier gas.

### C. The Flame Photometric Detector (FPD)

This is similar to the flame ionisation detector. It is a combination of the FID and an optical system, which has a very high selectivity with adequate sensitivity towards phosphorus and sulphur. It can detect sulphur compounds down to ppb levels.

### D. Electron Capture Detector (ECD)

This is the most sensitive detector available for the non-destructive detection of electrophilic substances, such as chlorinated hydrocarbons. It is very useful for pesticide residue determinations. It depends on the ability of the compounds to capture electrons. Many compounds have high electron affinities thus allowing their detection with this system.

### E. Nitrogen Phosphorus detector (NPD)

This is a thermionic detector that is sensitive to organically bound nitrogen and phosphorus. It can be operated in either two modes, NP mode in which both nitrogen and phosphorus are detected and quantified as well as the P mode in which the phosphorus is the only detected and quantified component. The NPD destroys the sample being analysed.

### F. Choice of Detector

In summary the ideal detector should possess the following properties (i) A high sensitivity which allows small amounts of impurities to be detected, small samples to be analysed, and low column temperature to be used (ii) A small internal volume, which ensures that the resolution of the components, which are only just separated by the column is not lost, and the shape of the peaks is not distorted by the detector (iii) An operating temperature such that no appreciable amount of the eluted vapours condenses in it (iv) Insensitivity the variation of carrier gas flow rate and column temperature (v) A rapid and reproducible response, produced by simple ancillary electrical equipment, accompanied by stability of the baseline (vi) For qualitative analysis – a response which can be adjusted so that identification is assisted (vii) For quantitative analysis – a linear response with concentration or amount of component so that the compositions may be calculated (viii) A response to all substances independent of their chemical nature which depends on a simple law reducing calibration to a minimum (ix) Low cost and reliability

It is important to note that no detector fulfils all the desirable characteristics, therefore selection is based on the task to be performed. For some problems however there will be reasons for choosing one detector rather than another. For instance, ionisation detectors will almost always be preferred for work with open tubular and packed columns containing only a small loading of stationary phase because of the need for high sensitivity. However, except for measurement with open tubular columns, it is probably not a big drawback as the effluent from a large column can be split allowing only a small

part to the detector. An important limitation of the FID is its lack of response to permanent gases. The Hot wire detector which can be made to respond to any substance is oftenly used for gas analysis. The drawback of the hot wire detector is that its sensitivity falls when the temperature is raised above $100^{\circ}C$.

## II. FLOW RATE MEASUREMENT

The carrier gas flow rate is one important quantity which has to be measured with great accuracy for reliable retention data. Several methods of measuring flow rates are conventionally available. The method must meet two essential requirements, namely, the method must be non-destructive and accurate for small flow rates without causing any disturbance to the flow. In this study, the soap film bubble flow meter was selected as it met the two requirements.

In this work, the soap film bubble flow meter was made of a 100ml calibrated burette with a small glass jet attached to its base. The burette was thoroughly cleaned with chromic acid and rinsed with distilled water before assembling. When the carrier gas from the GC entered the jet, it created a thin soap film travelling vertically up the burette. The rate of travel of the soap film was timed with a stopwatch. The walls of the soap film flow meter were well wetted by sending many bubbles completely through the burette before measuring. Any dryness of the walls will lead to irreproducible flow rate measurements. The flow rate was measured at room temperature and then corrected to that of column temperature. Accurate flow rate measurements were easily achieved with the flame ionisation detector as it diluted the gas streams. A schematic diagram of the soap film bubble flow meter used in this work is shown in Fig. 2.
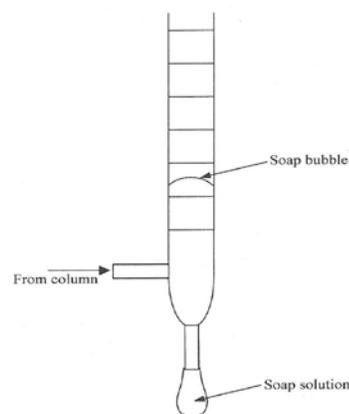


Fig. 2 Soap film bubble flow meter

## III. MEASUREMENT OF GAS HOLD-UP

The gas hold-up time, $t_M$ is a basic parameter in gas – liquid chromatography (GLC). It is important for the determination of solution thermodynamic functions derived from solute

retention [4]. Measurement of the absolute and the relative retention data requires the knowledge of the column gas hold-up volume. Errors in the measurement of the gas hold-up volume can introduce serious errors in the retention data especially when the later are comparatively small. In gas – liquid columns, the gas hold-up contributes 1 to 10 percent of the total retention volume. The accuracy of the measurement required is about up to 10 percent which often leads to the net retention volume accuracy of 0.1 to 1 percent which is adequate for many applications. The air peak, homologous series and geometrical calculation methods can be used to measure the gas hold-up. Although, the air peak method is the simplest and most common, the homologous series procedure was used in this work because of the desirable high sensitivity of the flame ionization detector at dilute concentrations of organic compounds. When using detectors such as Katharometers, which respond to permanent gases, the gas hold-up can be directly measured from the air peak corresponding to the elution of a non-absorbed air sample. The ionisation detectors used in this work are insensitive to permanent gases and hence the direct "air peak" method was not applicable. Therefore an indirect method was proposed based on the linear relationship of the logarithm of the corrected retention time and the carbon number of a homologous series. Using this linear relationship the gas hold-up was evaluated as a "mathematical air peak" and as "calculated dead time" from the retention times of three members of a homologous series. No attempt was made to use the indirect "methane peak" procedure as it is an unreliable due to the small solubility of methane in organic solvents.

### A. Air Peak Method

The "air peak" or "inert gas peak" method is the most often used because its simplicity. It involves injecting the sample of air or other non-sorbed gas whose retention volume is considered as the gas hold-up. The selection of a non-sorbed gas depends on the detection system. In the case of Hot Wire Detectors, any gas such as air, hydrogen, helium or methane maybe used. When hydrogen or helium is used as a carrier gas, a small volume of air should be added with the sorbed solute while hydrogen can be used to provide the inert gas peak when nitrogen is the carrier gas. Air may also be used to provide the inert air peak but it has to be injected in a separate run in large volumes (100µl to 1ml) because of the small thermal conductivities of nitrogen and oxygen.

### B. Geometrical Calculation Method

The gas hold-up is obtained from the empty column volume and the true (absolute) solid density determined under a liquid such as water or kerosene. This method depends on the assumption that the liquid occupies all the intraparticle pore space. There is a considerable variation in hold-ups obtained in this manner compared to other procedures.

### C. Homologous Series Method

In literature, the determination of $t_m$ has been derived from a relationship for the retention of n-alkanes and other homologous series [5]. This relies on the accepted generalisation that the logarithm of the adjusted retention time $(t_R - t_M)$ is a linear function of the carbon number in any homologous series. Thus

$$\log(t_R - t_M) = an + b \qquad (p \text{ and } T = \text{constants}) \qquad (1)$$

In (1) $a$ and $b$ are constants for the solute class and stationary phase. A known gas hold-up time $t_M$ can be determined as the value that will linearise a plot of this equation. This simplicity neglects extra-column effects and interfacial phenomena [4]. The retention times $t_R(n)$, of different n-alkanes are measured under the same conditions ($p$ and $T$) and preferably on the same chromatogram, making the carbon number ($n$) the only unique variable. The gas hold-up is calculated from (2) derived from (1).

$$t_M = \frac{t_{R_1} t_{R_3} - t_{R_2}^2}{t_{R_1} + t_{R_3} - 2t_{R_2}} \qquad (2)$$

The relationship expressed in (2) is also valid for homologous members of carbon numbers $n$, $(n + k)$ and $(n + 2k)$ where $n$ and $k$ integers. Also any three members not necessarily successive members of a homologous series may be used and the gas hold-up is calculated from the iterative solution of (3).

$$\frac{\log \dfrac{t_{R_2} - t_M}{t_{R_1} - t_M}}{n_2 - n_1} = \frac{\log \dfrac{t_{R_3} - t_M}{t_{R_1} - t_M}}{n_3 - n_1} \qquad (3)$$

The success of the homologous series method depends on the relationship (1) being obeyed and in some cases the plots are not linear as the lowest homologues depart from linear behaviour.

## IV. RESULTS AND DISCUSSION

The gas hold-up is a measure of the total volume of space available to the mobile phase in the system, that is column dead void volume, injector and detector volumes as well as the volumes of any connecting tubing for example from column to detector [6]. The gas hold-up volume ($V_m$) is defined in (4), where F and $t_m$ are carrier gas flow rate and retention time respectively.

$$V_M = F t_m \qquad (4)$$

A sample containing pentane, hexane and heptane was injected into the GC at selected flow rate and temperature at constant pressure. The retention times of the three solutes were then used to calculate the gas hold-up volumes using (2). The gas hold-up volumes for the 4 poly(dimethylsiloxane) packed columns described in Table II are presented in Tables 3 to 6.

TABLE II
DESCRIPTION OF COLUMNS

| Code | 1 | 11 | 111 | 1V |
|---|---|---|---|---|
| Length, m | 1 | 1 | 1 | 1 |
| Chromosorb W or P, g | 6.158 | 7.291 | 7.186 | 4.86 |
| PDMS | 0.688 | 0.825 | 0.804 | 0.54 |
| Wt % PDMS | 10.05 | 10.16 | 10.06 | 10 |
| Viscosity of PDMS, cs | 5 | 10 | 50 | 500 |
| Mw of PDMS | 760 | 1000 | 3200 | 13000 |

TABLE III
GAS HOLD-UP VOLUME COLUMN I

| Temp (K) | Mean retention time $t_R$ | | | Mathematical air retention time $t_M$ (min) | Gas hold-up $V_M$ (ml) |
|---|---|---|---|---|---|
| | Pentane | Hexane | Heptane | | |
| 303 | 4.95 | 12.39 | 32.43 | 0.56 | 10.561 |
| 313 | 3.93 | 9.13 | 22.36 | 0.56 | 10.561 |
| 323 | 3.03 | 6.53 | 14.99 | 0.56 | 10.561 |
| 333 | 2.43 | 4.99 | 10.44 | 0.56 | 10.561 |

TABLE IV
GAS HOLD-UP VOLUME COLUMN II

| Temp (K) | Mean retention time $t_R$ | | | Mathematical air retention time $t_M$ (min) | Gas hold-up $V_M$ (ml) |
|---|---|---|---|---|---|
| | Pentane | Hexane | Heptane | | |
| 303 | 2.61 | 6.76 | 17.98 | 0.17 | 5.909 |
| 313 | 1.97 | 4.64 | 11.28 | 0.17 | 5.909 |
| 323 | 1.51 | 3.3 | 7.48 | 0.17 | 5.909 |
| 333 | 1.16 | 2.39 | 5.15 | 0.17 | 5.909 |

TABLE V
GAS HOLD-UP VOLUME COLUMN III

| Temp (K) | Mean retention time $t_R$ | | | Mathematical air retention time $t_M$ (min) | Gas hold-up $V_M$ (ml) |
|---|---|---|---|---|---|
| | Pentane | Hexane | Heptane | | |
| 303 | 1.75 | 4.38 | 11.44 | 0.19 | 6.834 |
| 313 | 1.39 | 3.22 | 7.83 | 0.19 | 6.834 |
| 323 | 1.12 | 2.36 | 5.25 | 0.19 | 6.834 |
| 333 | 0.85 | 1.69 | 3.6 | 0.19 | 6.834 |

TABLE VI
GAS HOLD-UP VOLUME COLUMN IV

| Temp (K) | Mean retention time $t_R$ | | | Mathematical air retention time $t_M$ (min) | Gas hold-up $V_M$ (ml) |
|---|---|---|---|---|---|
| | Pentane | Hexane | Heptane | | |
| 303 | 1.62 | 3.77 | 9.49 | 0.33 | 13.203 |
| 313 | 1.27 | 2.68 | 6.21 | 0.33 | 13.203 |
| 323 | 1.03 | 1.98 | 4.22 | 0.33 | 13.203 |
| 333 | 0.84 | 1.5 | 3 | 0.32 | 12.803 |

The results show that gas hold-up volumes were constant with temperature suggesting a true measure of column void volume. This work has shown that the homologous series method can be reliably used to measure gas hold-up time, $t_M$, an important parameter in the derivation of thermodynamic functions of mixing such infinite dilution activity coefficients, enthalpies, entropies and partial molar free energy from solute retention.

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