CHAPTER 1

INTRODUCTION

Gas chromatography (GC) is one of the most widely employed techniques today. It has been extensively used for separating and analyzing mixtures of volatile compounds since its inception by James and Martin in 1952 [1]. This technique naturally has the greatest role in organic analyses where many compounds have suitable volatility and thermal stability. Metallic compounds, however, in general frequently cannot be volatilized at the temperature used in GC as a result of their ionic nature as the solid or in the solution; they also exhibit considerable chemical reactivity. Fortunately, it has now been reported that analysis of metals by gas chromatrography enjoys remarkable success via derivatization of metals as volatile metal chelates, especially as β-diketonates or derivatives of β-diketonate complex. Chelation is generally achieved by extraction of metals from an aqueous medium with the chelating agent. Analysis of metals by this technique has several advantages such as large linear range, speed, simplicity, high sensitivity, and ability to detect simultaneously [2]. The development in this field was first pointed out by Lederer [3] who suggested in 1955 that metal acetylacetonates might be separated by GC since they had been known to be somewhat volatile. Five years later, in 1960,Gesser and Biermann [4] described the first successful gas chromatographic elution of a mixture of beryllium, aluminium and chromium acetylacetonates. Brandt and Heveran [5] in 1962 reported the quantitative determination of chromium (III); they formed the acetylacetonate, extracted the chelate with carbon disulphide and injected this solution directly into a gas chromatographic column. After that, the use of GC for metal analyses became more explored by many workers, the successful works being those of suitable metal chelates. In 1965, an excellent monograph on GC of metal chelates by Moshier and Sievers [6] appeared. In 1974, Rodriquez-vazquez [2] reviewed a quantitative analysis of metals as metal chelates. Belcher, Khalique and Stephen reviewed the use of chelate compounds in metal analysis by gas-liquid chromatography in "Essays on Analytical Chemistry in Memory of Professor Ander Ringbom", a monograph edited by Wanninen in 1977 [7]. Also in 1977, Uden and Henderson [8] reviewed this field in detail and discussed β-diketone as ligand and other novel ligand systems including β-thioketone, β-ketoamine, salicylaldemine, and synergic mixed ligand system. Sievers and Sadlowski [9] in 1978 reviewed the properties and applications of volatile metal chelates together with numerous GC applications of trace metal analysis.

Although nowadays it has been established that many metals could be determined by GC, many analysts remain unaware of this powerful approach to metal determination in practice. The method of analysis for metals by GC is a relatively new technique for most laboratories. To the best of the author's knowledge, a literature survey of the research work in this field reveals that there has been no work on the analysis of metals by GC in Thailand up to now. Although the gas chromatographic technique is usually employed in analysis of organic compounds, it has been pointed out [3,9,10] that this technique combined with an eletron capture detector (ECD) can be used in metal analyses with several advantages comparable to other acceptable highly sensitive but relatively more expensive techniques such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), non—flame atomic absorption spectroscopy (non-flame AAS) and atomic fluorescence spectroscopy (AFS). The exceptional sensitivity of this technique can be seen from the fact that the detection limit for the determination of beryllium by GC using the ECD was 4×10^{-14} g [10]. Thus, it is quite interesting to study how to apply the technique of GC to the analysis of some metals in this research work.

1.1 Compound Requirements for Metal Analysis by GC

If GC is to be successfully applied to metal analysis, the derivative or the compound to which the metal is converted must also meet with the following requirements [3,6-8,11,12]

1.1.1 Volatility

The most important and restricting requirement is that compounds be sufficiently volatile to be chromatographed in the gas phase. For most practical purposes, the metal compounds must exhibit a vapour pressure on the order of 0.1 to 1 mm Hg at a column temperature used in order to move through the column at a reasonable rate. Again, the existence of large dipoles, adduct formation, polymerization and hydrogen bonding are among the factors which reduce volatility. It has been found that the types of metal compounds that are volatile at reasonable temperature include metal compounds of halides, alkoxides, carbonyls, hydride, π-bonded complexes and various metal chelates e.g. β-diketonates and porphyrins.

1.1.2 Thermal Stability

For a quantitative work, the metal complex met with the requirement of sufficient volatility must also be eluted without decomposition. However, in certain circumstances, it may be possible to obtain quantitave result even when thermal decomposition occurs if the extent of decomosition is slight and reproducible under a given set of conditions. Sievers et al. [13] have suggested that the thermal decomposition of the sample is indicated by the following observations:

(a) the presence of a residue in the injection port, probably this may also be due to incomplete vaporization of the sample resulting from the injection port temperature that is not so high enough; (b) an appearance of spurious chromatographic peaks or irregular baseline; (c) a discoloration of the column packing material; and (d) by collecting and identifying the eluted material which may be achieved by melting point determination, visible and ultraviolet spectroscopy and infrared spectroscopy.

1.1.3 **Ease of Formation**

For quantitative work, the type of metal compounds which can be applied to metal analysis by GC are limited to those that can be readily formed in quantitative or nearly quantitative and reproducible yield. These requirements make several compounds such as metal carbonyls, metal alkoxides and metal alkyls no further satisfy because they are usaully formed only with difficulty and rarely in quantitative yield. Their syntheses cannot be carried out in water owing to the solvolytic instability of the derivatives. On the other hand, certain chelating agents form complexes of high sovolytic stability with many metals by simple reaction that readily occur. Moreover, the reaction for forming metal chelates can be carried out in aqueous or non aqueous media with pH dependence and it permits the use of a masking agent, a feature making a complex problem of separation or measurement be readily solved.

1.1.4 Solvolytic Stability

In addition to being thermally stable, the metal derivative must be solvolytically stable with respect to the liquid stationary phase in the column. If the liquid phase itself can function effectively as ligands, solvolysis may occur through ligand substitution in the metal complex. Furthermore, the compound should also be nonreactive with the solid support and with the material of construction of the chromatographic system. From a practical standpoint, it is also desirable that the compounds be stable in the ambient atmosphere, so as to avoid special handling procedures. Several metal halides are sufficiently volatile, thermally stable and could be formed in quantitative yield, however, very few of these compounds have been employed for actual determinations of metals by GC mainly because of the experimental difficulties arising from their chemical reactivity. Most metal halides react with the usual liquid phase and with the metallic part of the flow system at the operating column temperature. It is therefore necessary to use inert materials for the stationary phase and the flow system. Owing to the fact that metal halides are easily hydrolysed by atmospheric moisture, it is essential to take special precautions to eliminate all traces of water from the carrier gas, stationary phase and to handle and inject the sample in an inert atmosphere such as enclosing the injection port in a dry box. These features make the method complicated or unattractive in practice.

According to the compound requirements as discussed above, metal chelates have proved to be the most appropriate compounds. Thus it is quite important to discuss the chelating agents which have been used in metal analysis by GC at this point.

1.2 Chelating Agents for Metal Analysis by GC

Up to now there are many chelating agents reported to have formed suitable metal chelates with appropriate metals. The types of chelating agents used in this area may be divided into 8 categories as discussed below.

1.2.1 β -Diketones

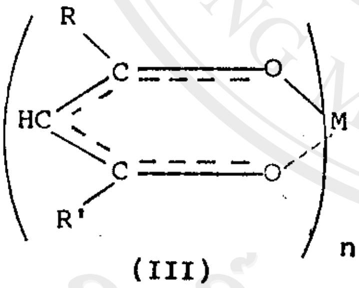
This is the first type of the chelating agent which has been applied for metal analysis by GC. The enolization and subsequent ionization of β-diketone is as follows [8]:

$$R-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-R' \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-CH=\overset{OH}{\overset{|}{C}}-R'$$

(I) (II)

where R, R' = CH_3, CF_3, CH_3C,...

In its enolic form (II), the β-diketone has hydrogen replacable by a metal and an oxygen donor atom; thus a six-membered chelate ring (III) can be formed, though its stability is remarkably affected by the conjugated double bonds in the enolic structure.

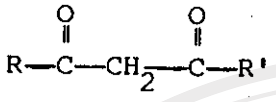


(n = oxidation state of the metal)

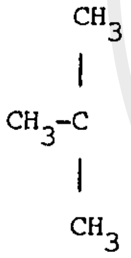
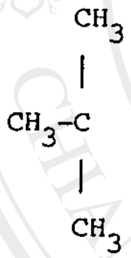
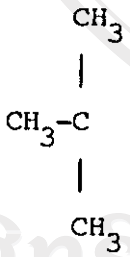
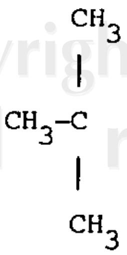
(III)

The β-diketone chelating agents that have been used successfully in the GC of metal chelates are summerized in Table 1.1

Table 1.1 β-diketones used in GC of metal chelates [8]



$$R-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-R'$$

R	R'	Names	Abbreviations
CH_3	CH_3	Acetylacetone	H(AA)
CH_3	CF_3	Trifluoroacetylacetone	H(TFA)
CF_3	CF_3	Hexafluoroacetylacetone	H(HFA)
CF_3	CF_2CF_3	1,1,1,5,5,6,6,6-Octafluoro-hexane-3,5-dione	H(OFHD)
CF_3	$CF_2CF_2CF_3$	1,1,1,2,2,6,6,7,7,7-decafluoro-heptane-3,5-dione	H(DFHD)
 $\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{CH_3-C}}$	 $\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{CH_3-C}}$	Trifloroacetylpivalylmethane	H(TPM)
CF_2CH_3	 $\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{CH_3-C}}$	Pentafluoroethanoylpivalylmethane	H(PPM)
$CF_2CF_2CF_3$	 $\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{CH_3-C}}$	Heptafluoropropanoylpivalylmethane or 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione	H(FOD)

The first pioneering work in the GC of metal chelates has been conducted largely on elution of acetylacetonate complexes of Al (III), Be(II) [12-17], and rarely on acetylacetonate complexes of Cu(II), Fe(III), V(IV) and Co(III) [13,15]. However, most acetylacetonate complexes lack sufficient thermal stability; they could not be eluted without decomposition at the temperature necessary [6-9]. The search for more volatile metal compounds led to exhaustive study of the fluorinated ligands derived from acetylacetone [H(AA)], namely trifluoroacetylacetone [H(TFA)] and hexafluoroacetylacetone [H(HFA)]. Other higher fluorinated β-diketone ligands such as H(OFHD) and H(DFHD) as well as some of their metal complexes have been synthesized and investigated [6,16-18]. However, hexafluoroacetylacetone and the more highly fluorinated β-diketone derivatives react with water to form hydroxy compounds, which make it difficult to prepare the metal chelates in the presence of water [8]. H(DPM), H(TPM), H(PPM) and H(HPM) (or HFOD) are among the ligands which have been proved to be useful for rare earth metals [19-22].

Generally, the gas chromatographic study of divalent metal β-diketonates is found to have limited application (except Be(II) and probably Cu(II)), owing to oxidation, polymerization and solvation of these chelates [9]. Thus attention has been paid to alternative ligand systems which will be discussed further.

1.2.2 β-Thioketones

β-Thioketones or mono-β-diketones are a thio derivative of β-diketone which contains a mercapto group instead of the enol function of the β-ketoenolate. The simplified reaction scheme shown in Fig. 1.1 indicates the relationships and mode of β-thioketone and β-ketoamines and their relationship to the parent β-diketones. The β-thioketones that

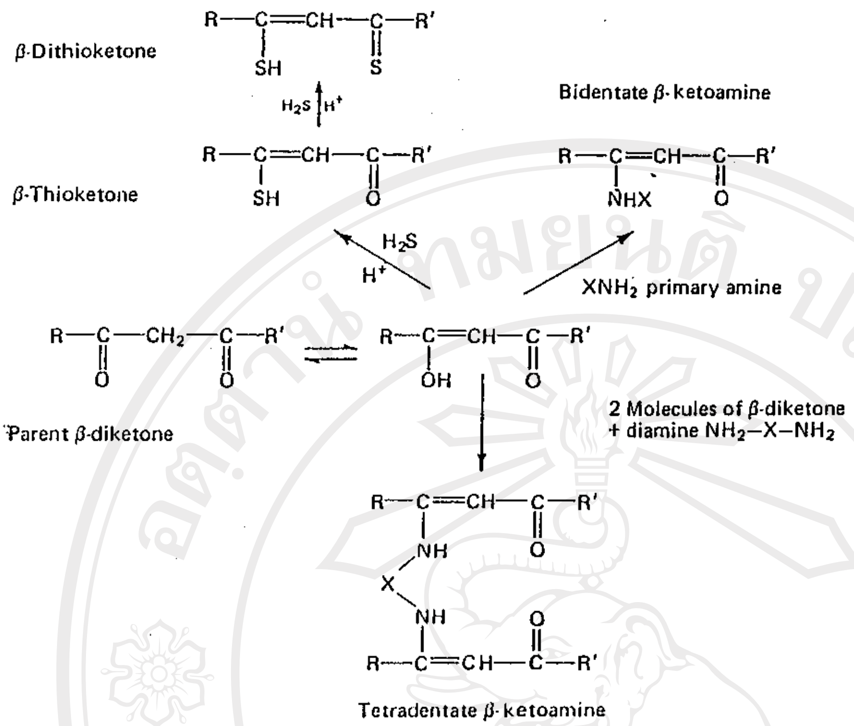
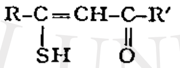


Fig. 1.1 Reactions of β-diketones and formation of β-thioketones and β-ketoamines.

Table 1.2 β-THIOKETONES (MONOTHIO-β-DIKETONES) USED IN THE GC OF METAL CHELATES



$$\mathrm{R{-}\underset{\displaystyle SH}{\underset{|}{C}}{=}CH{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R'}$$

R	R′	Name derived from parent β-diketone	Abbreviation
CH_3	CH_3	Monothioacetylacetone	H(TA) [or H(Tacac)]
CH_3	$C(CH_3)_3$	Monothioacetylpivalylmethane	H(TAPM)
CH_3	CF_3	Monothiotrifluoroacetylacetone*	H(TTFA)
CF_3	CF_3	Monothiohexafluoroacetylacetone	H(THFA)
$C(CH_3)_3$	CF_3	Monothiotrifluoroacetylpivalylmethane	H(TTPM)
$C(CH_3)_3$	C_2F_5	Monothiopentafluoroethanoylpivalylmethane	H(TPPM)
$C(CH_3)_3$	C_3F_7	Monothioheptafluoropropanoylpivalylmethane	H(THPM)

have been employed successfully in the GC of metal chelates are shown in Table 1.2.

Monothio-β-diketones have been proved to be useful for many divalent transition metals such as nickel, palladium, zinc, and cobalt[8,24]. The use of monothiotrifluoracetylacetone [H(TTFA)] enabled the first successful GC separation of three divalent transition metals. The major drawback of GC application of these ligands is that many are relatively difficult to prepare and handle [2,25].

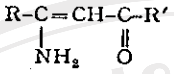
1.2.3 β-Ketoamines

β-ketoamines, sometimes called β-ketoenamines, have been developed as GC reagents in a fashion parallel to that of the monothio-β-diketone. Bidentate and tetradentate can be formed accordingly to the reaction schemes shown in Fig. 1.1 . These ligands are useful for application of gas chromatographic analysis to the determination of divalent transition metals. Successful GC work of the bidentate β-ketoaminates has been largely due to those of the ligands formed by condensation of β-diketone with ammonia. The complexes of copper, nickel and palladium with the ligands shown in Table 1.3. have been studied in detail [26], and it could be observed that the thermal and chromatographic behavior, and also volatility are lower than the bidentate [26,27]. Table 1.4 lists the tetradentate β-ketoamines that have been eluted gas chromatographically, mainly for copper, nickel, palladium, platinum and cadmium [26-31].

1.2.4 Synergic Mixed-Ligand System

As discussed before, many metal β-diketonates, especially those of divalent cations contain coordinated water, for which reason their recoveries from aqueous solution are very poor; other problems are

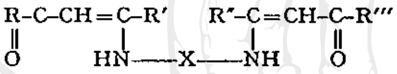
Table 1.3 β-KETOAMINES (β-IMINOKETONES) USED IN THE GC OF METAL CHELATES



$R{-}C{=}CH{-}C{-}R'$ with NH_2 on the first C and $=O$ on the second C

R	R′	Name derived from parent β-diketone	Abbreviation
CH_3	CH_3	Aminoacetylacetone (4-aminopent-3-en-2-one)	H(AP)
CH_3	CF_3	Aminotrifluoroacetylacetone (4-amino-1,1,1-trifluoropent-3-en-2-one)	H(ATFP)
CH_3	CH_2CH_3	Aminoacetylpropanoylmethane	H(AAPrM)
CH_2CH_3	CF_3	Aminotrifluoroacetylpropanoylmethane	H(ATPrM)
$CH(CH_3)_2$	CF_3	Aminotrifluoroacetylisobutanoylmethane	H(ATiBM)
CH_3	$C(CH_3)_3$	Aminoacetylpivalylmethane	H(AAPM)
$C(CH_3)_3$	CF_3	Aminotrifluoroacetylpivalylmethane	H(ATPM)
CH_3	$CH_2CH(CH_3)_2$	Aminoacetylisopentanoylmethane	H(AAiPnM)
$CH_2CH(CH_3)_2$	CF_3	Aminotrifluoroacetylisopentanoylmethane	H(ATiPnM)

Table 1.4 TETRADENTATE β-KETOAMINES USED IN THE GC OF METAL CHELATES



$R{-}C({=}O){-}CH{=}C(R'){-}NH{-}X{-}NH{-}C(R''){=}CH{-}C({=}O){-}R'''$

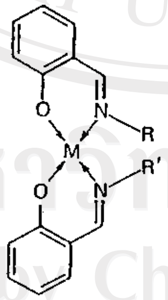
R	R′	R″	R‴	X*	Abbreviation
CH_3	CH_3	CH_3	CH_3	en	$H_2(enAA_2)$
CH_3	CH_3	CH_3	CH_3	pn	$H_2(pnAA_2)$
CH_3	CH_3	CH_3	CH_3	bn	$H_2(bnAA_2)$
CF_3	CH_3	CH_3	CF_3	en	$H_2(enTFA_2)$
CF_3	CH_3	CH_3	CF_3	pn	$H_2(pnTFA_2)$
CF_3	CH_3	CH_3	CF_3	bn	$H_2(bnTFA_2)$
$C(CH_3)_3$	CH_3	CH_3	$C(CH_3)_3$	en	$H_2(enAPM_2)$
$C(CH_3)_3$	CH_3	CH_3	$C(CH_3)_3$	pn	$H_2(pnAPM_2)$
CF_3	$C(CH_3)_3$	$C(CH_3)_3$	CF_3	en	$H_2(enTPM_2)$
CF_3	CH_3	CH_3	CH_3	en	$H_2(enAATFA)$
CF_3	CH_3	CH_3	CH_3	pn	$H_2(pnAATFA)$
CF_3	CH_3	CH_3	CH_3	bn	$H_2(bnAATFA)$

* en = $CH_2{-}CH_2$; pn = $CH(CH_3){-}CH_2$; bn = $CH(CH_3){-}CH(CH_3)$.

created by their inadequate thermal stability with strong retention or dehydration of the column, so that the possibilities of their GC application are then somewhat limited. However, it has been reported that these difficulties can sometimes be surmounted by using neutral donor organic in addition to a chelating β-diketone; such system is called "synergic mixed-ligand system". When a neutral donor or organic base such as tributyl phosphate (TBP), dibenzyl sulphoxide (DBSO), diethylamine, etc., is employed, there is a synergic enhancement of the extraction efficiency; and significant improvements in thermal stability as well as decreased column interaction can be found[2]. Butts and Banks [32] first applied mixed ligand systems such as H(HFA)-TBP to extraction and GC determination of the lanthanides. The utility of this approach has been shown in determination of cobalt (II), nickel and iron (II) [33,34] while uranium and thorium were successfully analysed as mixed HFA-DBSO chelate [35].

1.2.5 Salicylaldimines

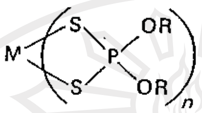
The general formula of salicylaldimines in the form of bidentate chelate is given as [8]:



It has been reported [36,37] that copper, nickel and zinc chelates of a range of bidentate salicylaldimines where R, R'is H, CH_3, C_2H_5, n-C_3H_7, etc., have been chromatographed. However, sample loss due to thermal instability is evidently below the microgram level [8].

1.2.6 Dialkyldithiophosphates

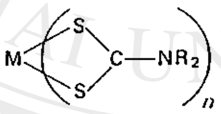
Dialkyldithiophosphates in the form [8]:



where R = CH_3, C_2H_5, iso-C_3H_7, etc., have been successfully eluted for the metal chelates of zinc, nickel, palladium, platinum, rhodium, cadmium, lead and chromium [36-40].

1.2.7 Dialkyldithiocarbamates

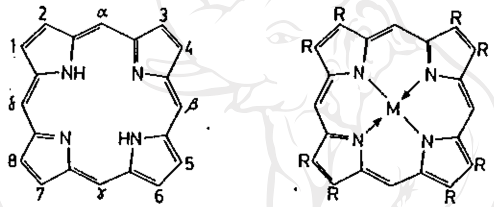
Dialkyldithiocarbamates are the metal complexes which have recieved most of the interest recently parallel with dialkyldithiophosphates and porphyrins. The general structure of dialkyldithiocarmates is given as [8]:



where R = CH_3, C_2H_5, iso-C_3H_7, etc., and M = Zn, Ni, Pt, Cd, Pb, Hg(II) and Co(III). There has been a report recently [39] that they could be eluted at column temperature between 210 and 270 degrees Celcius using FID as detector. The resolution of cadmium, zinc and lead chelate [25] and that of zinc, copper and nickel chelates are effective[40].Recently, determination of Zn, Cd, Cu, Ni, Pb, Hg and Co as their diethyldithiocarbamates have been made using both FID and mass spectrometry [41].

1.2.8 Porphyrins

GC of metalloporphyrins by using packed column in the past [42,43] failed to elute according to adsorption upon solid support within the packed column. Recently [44,45], porphyrins have proved to be a useful ligand which could be applied for metal analysis by GC when a flexible fused-silica capillary column is employed. They can form suitable complexes for GC with a variety of metal ions such as Cu(II), Zn(II), Ni(II), V(IV), Co(II), Pd(II), Pt(II), Al(III), Ga(III) and Rh (III). Important porphyrin ligands are 2,4,6,8-tetraethyl porphyrin (Aetio, 1) and 1,2,3,4,5,6,7,8-octaethyl porphyrin (OEP, 2). The general formulas of porphyrin and metalloporphyrin are given as [44]:



1, 2 3

1 Aetio^{I}; 1 = 3 = 5 = 7 = CH_3; 2 = 4 = 6 = 8 = C_2H_5; α-δ = H
2 OEP; 1-8 = C_2H_5; α-δ = H
3 *Metalloporphyrin*

1.3 Gas Chromatography of Metal Chelates

Gas chromatography is a physical method generally used for separating mixtures of volatile compounds. In this method, the components of a mixture are subjected to repeated partition between a gaseous, mobile phase and a liquid or solid stationary phase. The separation is based on difference in vapor pressure and solubility [6]; in other words, the separation is due to the difference in partition coefficient or distribution coefficient (K) which is defined as [46]:

$$K = \frac{\text{concentration of solute in stationary phase}}{\text{concentration of solute in mobile phase}} \qquad \text{---------(1.1)}$$

The components which is less soluble in the stationary phase and more volatile at the operating temperature will have low value of K and thus it can move through the column more rapidly than the component which is more soluble in the stationary phase and less volatile.

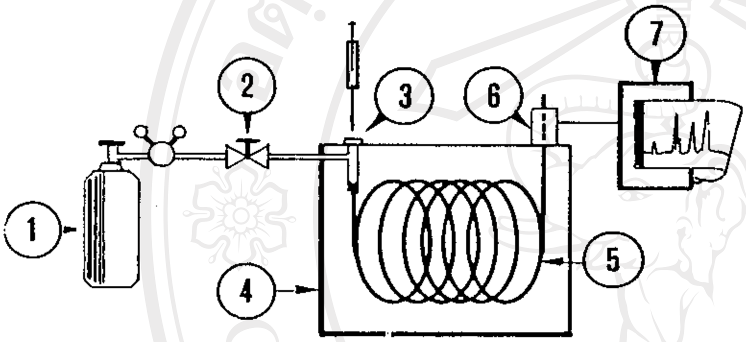


Fig. 1.2 chematic GC system. 1=Carrier gas supply; 2=flow control valve; 3=sample inlet system; 4=column thermostat; 5=column; 6=detector; 7=recorder or data handling system.

Fig. 1.2 shows schematically a GC system [47]. The operation of the instrument may be summed up briefly as follows. An inert gas stream, the so-called carrier gas, flows through the column at a constant rate. The sample under investigation is introduced (usually with a microsyringe) into the heated injection port, where it is vaporized and reaches the column together with the carrier gas. In the column, the components of the sample move in the direction of the gas flow with different velocities depending on their partition between the carrier gas and the stationary phase and they are thereby separated into individual components. The carrier gas and sample emerging from the column go through the detector which gives off the signals proportional to the quantity of the component; the signal passes to a recorder and generates a chromatogram, which is characteristic of the actual separation. In many cases, a data handling device automatically integrates the peak area, measures the retentiom times, performs calculation, and prints out a final report. Details of components of GC system or related features are among the current topics to be discussed in Sections 1.3.1-1.3.7.

1.3.1 Carrier Gas

The purpose of the carrier gas is to transport the sample components through the column to the detector. The carrier gas should be inert, convenient, available pure, inexpensive, and allow the detector to detect sensitively [48]. Gases commonly employed are nitrogen, hydrogen, helium, argon and carbon dioxide [46]. The selection of the carrier gas employed is usually limited by the detector used [49], e.g. helium is the preferred carrier gas for use with the thermal conductivity detector (TCD) while nitrogen is normally used with the flame ionization detector (FID) [50].

1.3.2 Flow Controller

The flow rate of the carrier gas should be carefully controlled in order to obtain reproducible retention times and to minimize detector drift and noise [46]. Flow controls can be done [48,49] by either control of the carrier gas flow rate by using flow controller or by control of the carrier gas inlet pressure. In the case of control of carrier gas inlet pressure, this can be achieved [47] by using : (1) the second stage regulator on the carrier gas cylinder (2) a pressure regulator mounted in the chromatograph (3) a needle valve (variable restrictor) mounted in the chromatograph and (4) a fixed restrictor mounted in the chromatograph. Since the column generally acts as a constant choke, a constant input pressure will itself ensure a constant flow [51]. Pressure controls are simpler than the flow rate controls [51] and are used more commonly. However, control of flow rate may be required in temperature-programmed runs since the flow rate is a sensitive function of temperature.

1.3.3 Sample Inlet System [46,48,49]

There are three methods of inserting measured samples: by valve, by ampoule, and by syringe. However, the sample may be gasous, liquid or solid, and the method of sample introduction may differ accordingly. Liquids are most conveniently introduced by means of microliter syringe through a self-sealing silicone septum. Gas may also be introduced by means of syringe, better, with a gas tight syringe. However, the sample valve method is especially accurate for gas samples. For solid samples, they can be weighed into a special heated chamber at the head of the column, where it is crushed mechanically while surrounded by flowing carrier gas. An alternative method for solid sample is to dissolve the solid sample in a volatile solvent and inject like a liquid sample.

1.3.4 Column

The column is the heart of the chromatograph since separation process occurs in this part of instrument. The column system consists of (a) material of construction or tubing, (b) a packing material which is either an adsorbent or a solid support coated with a liquid phase, and (c) packing retainer such as glass wool inserted into the tube ends. Analytical columns are ordinary 1/16" to 1/4 " o.d. tube from 3 to 30 feet in length.Gas chromatography is divided into two catagories according to a packing material [48] with the separation process as follows: gas-liquid chromatography (GLC) where separation occurs by partitioning a sample between a mobile phase and a thin layer of non-volatile liquid phase coated on a inert support, and gas-solid chromatography (GSC), which employs a solid of large surface area or adsorbent as the stationary phase. The wide range of the liquid phases with usable temperature up to 400 °C make GLC the most versatile and selective form of GC. Again, most of papers on GC of metal chelates have been conducted on GLC mode [2,6,8].

Two types of columns used for GLC are packed columns and open tubular or capillary columns [52]. In packed columns, the non volatile liquid phase is supported on a powder solid support which is contained by the tube while in capillary columns, the liquid phase is supported by the inner wall of a capillary. Determinations of metals previously have been carried out almost exclusively with packed columns [8]. however, recently, a successful separation of metal porphyrin on flexible fused capillary column has been reported [53]. Detail of column components, and column performance in terms of "column efficiency" and "resolution" will be discussed in the foregoing pages.

1.3.4.1 Material of Construction or Tubing

The column should be contructed of a material that is inert to the component being chromatographed. Thus, copper and aluminium columns have generally been avoided for the GC of metal chelete since their more reactive surfaces are subjected to corrosion and vapour-phase chelate formation [54], Glass and Teflon [PTFE] appear to be the best column materials for most applications. Glass columns have the disadvantage of being rather easily broken but they can be used at higher temperature than Teflon columns [55,56]. However,stainless steel columns are the simplest to work with and have been indicated [8] to use with success in determination of copper, nickel, palladium, chromium, beryllium and aluminium. In many instances in the literature where glass columns are specfied in a method for metal determinations

[57,58], the same analysis can be reproduced by using a stainless steel column [59,60].

1.3.4.2 Solid Support

The function of the solid support in GLC packed column is to provide an inert surface for supporting the liquid stationary phase in such a manner that the gaseous component can pass through it. The solid support should be inert, possesing a large surface area, robust and of high capacity for liquid phase [50]. The choice of the solid support for the metal complexes has been one of the most important parameters to be considered for successful analysis [8]. Adsorption of complexes on the support has been shown to be a major factor in poor chromatographic behavior even at high liquid loading[61]. Inertness of the solid support material can be increased in various ways such as silanizing it with reagent such as hexamethyldisilazane(HMDS) or dimethyldichlorosilane (DMCS), and treatment with alkali or acid [51]. The most successful analytical applications have employed either highly deactivated diatomaceous earth or silanized glass microbeads. However, the glass microbeads have a disadvantage of the limits range of liquid-phase loading which limits the selection of the retention parameter for analysis [2].

1.3.4.3 Liquid Phase

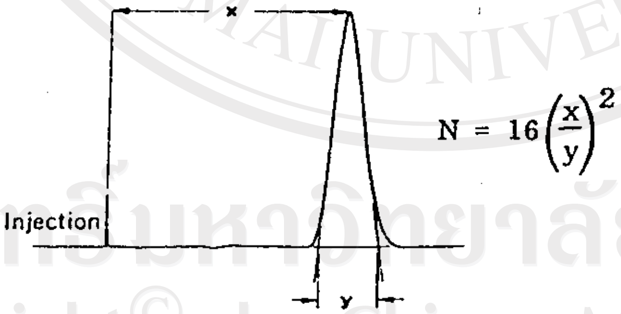
The stationary phase provides separation of the sample. In addition to having suitable selectivity for effective separation, the liquid phase must be thermally stable and chemically inert to the components being chromatographed at the operating column temperature. The general rule for selection of the liquid phase is "like dissolves like"[62]. Polar substances are usually better separated on a polar column, and non polar ones on a non-polar stationary phase.

Another approach is to use the Rohrschneider [63]/ McReynolds [64] constants to select the most appropiate stationary phase for a given separation.

The liquid phases that have been used successfully for the separation of metal complexes[2,6,8,65] include non-polar silicones, hydrocarbons and many silicones of moderate polarity. OV-1 or SE-30 (methyl silicone gum), OV-101 (methyl silicone liquid) and Apiezon L understandably have been the most widely used liquid phases. A moderately polar silicone that has received considerable attention is QF-1 (and its **variations** OV-210 and SP-2401). Carborane-silicone phases such as Dexil 300 GC, 400 GC and 410 GC, which can be operated up to 400 °C, also have been used for metal complexes which are eluted at relatively high temperature [28].

1.3.4.4 Column Efficiency [46,48,50,66,67]

The efficiency of the column is related to the relative broadness of the peak which appears on the chromatogram as illustrated in Fig. 1.3.



$$N = 16\left(\frac{x}{y}\right)^2$$

Fig.1.3 Calculation of theoretical plates.

The efficiency of the column can also be expressed by the height equivalent to a theoretical plate (HETP) which is given by [46,67]:

$$\text{HETP, } H = L/N \qquad \text{------------------(1.2)}$$

where L is the length of the column. HETP value allows comparisons between columns of different lengths and is the preferred measure of the column efficiency [46]. It can be seen that the smaller the HETP, the better is the column

The quantity of HETP can also be expressed in the manner to explain the process which can lead to peak broadening by using the rate theory of van Deemter, which can be useful for selection of optimum carrier gas flow rate further. The van Deemter equation [66] for packed column is

$$\text{HETP} = 2\lambda d_p + 2\frac{\gamma}{U}D_g + \frac{8K'}{\pi^2(1+K')^2}\,\frac{d_f^2}{D_l}\,U \qquad \text{--------------(1.3)}$$

where

λ = a constant which is a measure of the uniformity of the column packing ranging from 0.5 to 0.2
d_p = average particle diameter of the solid support (cm)
γ = a correction factor accounting for the tortuosity of the gas channels in the column
D_g = diffusivity of the solute in the gas phase ($cm^2\ sec^{-1}$)
U = linear gas velocity ($cm\ sec^{-1}$)
K' = capacity factor or partition coefficient of the solute
d_f = effective thickness of the liquid film which is coated on the particles of the support (cm)
D_l = diffusivity of the solute in the liquid phase ($cm^2\ sec^{-1}$)

Since for a given column all the parameters in the derived equation given above are all fixed except U, the simplified van Deemter equation can be written as

$$\text{HETP} = A + B/U + CU \tag{1.4}$$

where A = eddy diffusion (multipath) term, independent of mobile phase velocity, dependent on the particle shape, and size of the solid support,

B/U = molecular diffusion term, proportional to solute diffusivity in the carrier gas,

CU = resistance to mass transfer term, dependent on amount and viscosity of liquid on the solid support, partition coefficient and diffusivity of the solute in the liquid phase.

The plot of HETP against U in the van Deemter equation yields a hyperbola with a minimum HETP or $A + 2(B/C)^{1/2}$ as illustrated in Fig. 1.4. This minimum HETP corresponds to the optimum flow rate of the carrier gas which would give the maximum efficiency for a given column.

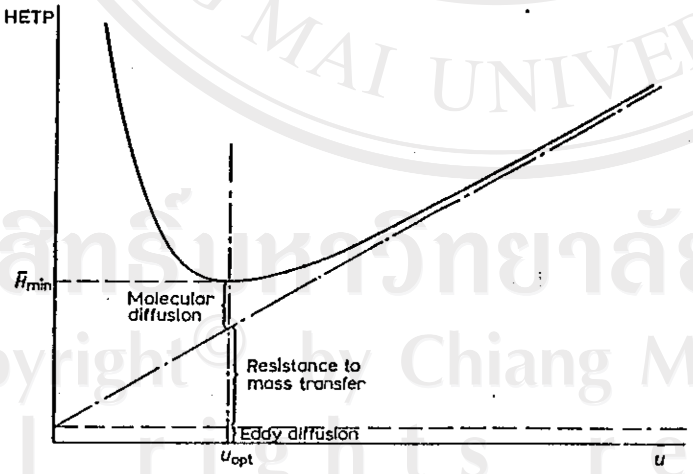


Fig. 1.4 Typical plot of plate height against linear gas velocity.

1.3.4.5 Resolution

Resolution (R) is a term used to express the degree of separation between two peaks and can be defined as[46,69].

$$R = 2(t_{R2} - t_{R1})/(W_1 + W_2) = 2(\Delta t_R)/(W_1 + W_2) \text{ ----------(1.5)}$$

where t_{R1} and t_{R2} are retention times of component 1 and 2 and where W_1 and W_2 are peak-base widths of the same components as illustrated in Fig. 1.5.

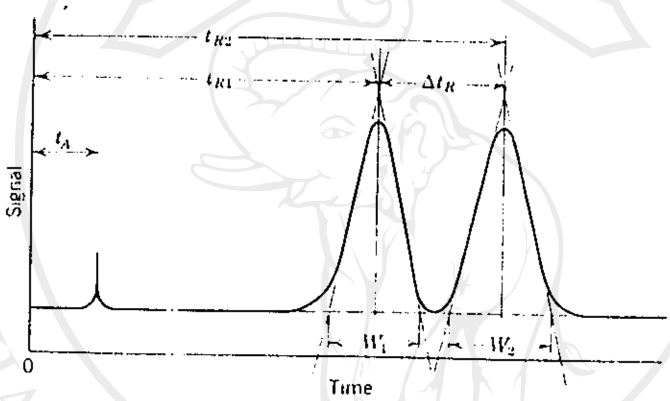


Fig. 1.5 Calculation of peak resolution between two consecutive peaks [69].

Two consecutive peaks are considered to be completely resolved when R = 1.5, but, for practical purposes, separation is usually adequate at R = 1 [52]. The resolution for a given stationary phase can be improved by lengthening the column, thus increasing the number of plates [70].

1.3.5 Temperature Control

When operating any gas chromatograph, it is necessary to control the temperature of the injector, column and detector. Details of each will be considered here.

1.3.5.1 Injector Temperature

The injector temperature or the injection port temperature should be operated high enough to cause rapid volatilization in order to avoid condensation of the sample in the injector which may produce broadened peaks in the resulting chromatogram. On the other hand, the injector temperature must be low enough so that thermal decomposition is avoided; this restriction is quite crucial for metal complexes. Injector temperature about 25-50 °C higher than the column temperature has proven to be generally satisfactory.

1.3.5.2 Column Temperature

The column temperature should be high enough for the analysis to be completed in a reasonable length of time, and yet low enough so that the desired separation is obtained. Increase column temperature will decrease retention time, and will usually decrease the relative retention between sample components and also decrease the amount of band broadening [52]. A general approximation by Giddings [71] reveals that the retention time is doubled for a 30 °C decrease in column temperature. For most samples, the lower the column temperature the better is the separation. In some cases, it is not possible to use a low temperature; and particularly in the case of a wide range of boiling point samples, it may be desirable to use temperature programming.

1.3.5.3 Detector Temperature

As a general rule, the detector temperature should be operated such that condensation of the sample and "column bleed" do not occur [47]. The temperature of the detector depends upon the detector employed [49]. TCD or ECD requires very accurate temperature control, however, temperature control of FID is not critical. The FID temperature should always be set above 100 °C to keep water, formed in the combustion process, from condensing inside the detector. Since the sensitivity of the TCD increases with an increase in temperature difference between the block and filament, it is advantageous to keep the temperature of the TCD cell as low as possible but never less than 10-15 °C aboved the column temperature. For the ECD, the radioactive source determines the maximum temperature limit for the detector. Finally, it should be noted here that injector temperature control and detector temperature control for some gas chromatograph may be the same bottom, e.g. the Perkin-Elmer Model F 17, which has been used in this research work.

1.3.6 Detector

The purpose of the detector is to monitor the carrier gas as it emerges from the column, and to response to change in its composition as solutes are eluted [72] Ideally, a detector should have the following characteristics [50]: rapid response, high sensitivity, large linear range, good stability and robustness, equivalent response for all chemical species and insensitivity to change in temperature and flow rate. In practice, however, no detector can have all these characteristics.

One of the major reasons for attempting the determination of metals by GC is to exploit the power of different detectors [8]. The classification of detectors frequenctly encountered [73] divides detectors into integral and differential detectors, concentration and mass detectors, destructive and non-destructive detectors, and universal and selective detectors. One of the most frequenctly used criteria classifies detectors into integral and diffential detectors the latter giving zero signal when pure carrier gas is passing through them, but when a component of a mixture is detected the signal is proportional to the concentration or mass of that component. Integral detectors, on the other hand, give a continuous signal which is proportional to the total amount of substance which has been eluted, as illustrated in Fig. 6.

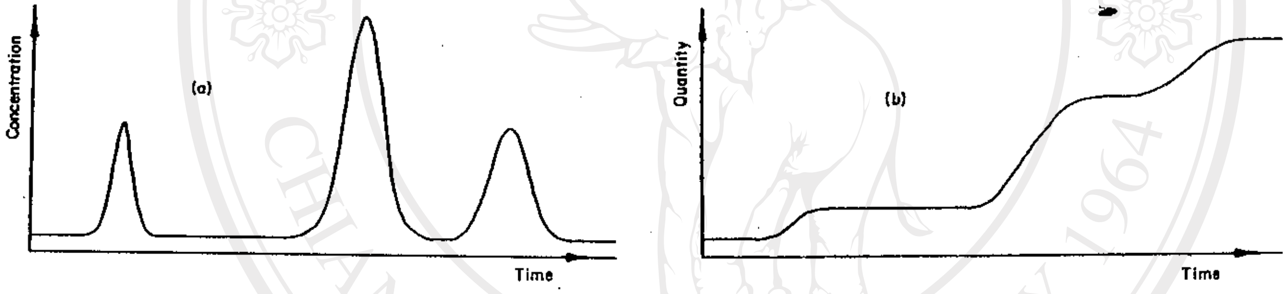


Fig. 1.6 (a) Peaks given by a differential detector. (b) steps given by an integral detector.

The choice of detector depends on the given analytical problem, the field of application and the concentration level which the user wishes to measure [6,74]. The detectors most widely used in detection of metal complexes are the thermal conductivity detector, the flame ionization detector , the electron capture detector and probably the flame photometric detector. Other detectors, e.g. microwave plasma, mass spectrometric and atomic absorption detector, have been used in a few cases [2,8]. Details of each detector will be discussed in terms of instrumentation and application. However, only application will be considered here for the last three mentioned detectors.

1.3.6.1 Thermal Conductivity Detector (TCD)

The TCD or katharometer, is based on the principle that a hot body (a metal filament or a metal oxide thermistor) loses heat at a rate which depends upon the thermal conductivity of the gas stream passing through it. Two pairs of matched filaments are aranged in a Wheatstone bridge circuit housed in a cell through which there are two gas channels, sample channel and reference channel. The bridge is balanced as long as the thermal conductivity of the gas through the sample side of the bridge is the same as that flowing across the reference side; when a component appears in the carrier gas, this will alter the thermal conductivity of the gas stream and thus the bridge becomes unbalanced. This imbalance of which the magnitude depends on the concentration of the solute in the carrier gas, is then fed to a recorder, as shown in Fig. 1.7.

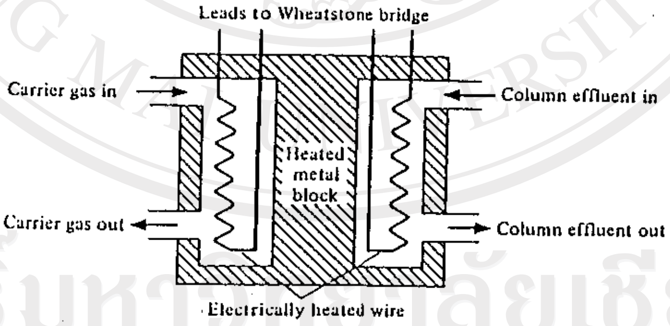
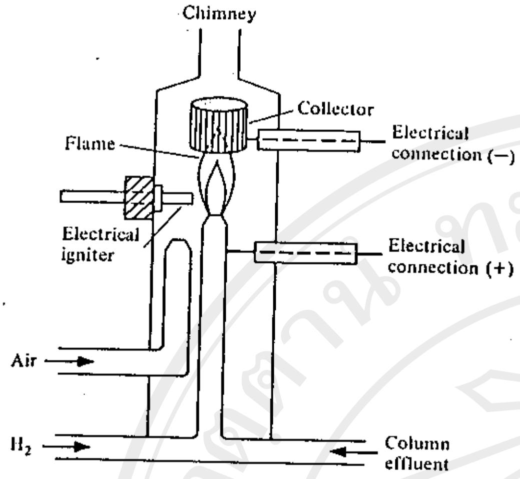


Fig. 1.7 Diagram of a two - filament thermal conductivity detector [52].

The TCD is robust, easily to operate, and non-destructive, but has only a moderate sensitivity, about 10^{-4}-10^{-5} g of metal [2]. It is appropriate for survey studies, where it is necessary to collect samples from the eluates and examine them to determine whether or not decomposition has occurred [6], or when high sensitivity is not required for quantitative work. Much of the earliest work in the GC of metal chelates was accomplished using the TCD primarily owing to its availability in most of the instrument systems of the late 1950's [8]. The difficulties encountered in the use of the TCD include decomposition of metal complexes on the high temperature filament, causing contamination and loss of sensitivity, and corrosion of the filament by free ligand vapour [82]. In general, the TCD is not a detector of choice for the determination of metal complexes, and even when a non-destructive detector is necessary, using an effluent splitters and more sensitive detectors gives a greater certainty of eluting the metal complexes [8].

1.3.6.2 Flame Ionization Detector (FID)

FID has become one of the most popular measuring devices used in GC. The FID principle is based on the measurement of variation in the ionization current in a hydrogen-oxygen flame (air, commonly used as a source of oxygen) due to the presence of eluted substance. The hydrocarbons are proportional to the number of carbon numbers, while substance that contains oxygen, sulphur, or a halogen yielding smaller resonse depends on the hetero-atom-carbon character and the electron affinity of the combustion products [73]. The FID responses only to organic compounds; some of the gases such as air, noble gases, water, CO, CO_2, CS_2, NO, SO_2 and H_2S do not give the signal [47].



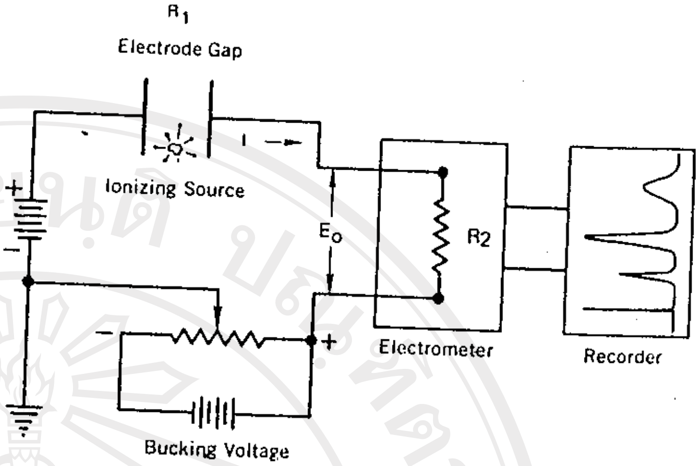


Fig. 1.8 Diagram of a flame ionization detector [52].

Fig. 1.9 Shematic ionization detector circuit [48].

Fig. 1.8 shows a typical FID in which the the effluent gas from the column is mixed with hydrogen and burned in air or oxygen at a jet above which is placed a cylindrical metal electrode. the potential difference applied across flame tip and collector (acts as negative and positive electrode, respectively) is about 200 V [46]. Ions and **electrons** formed enter the electrode gap, thus cause a current, I, to flow across the gap, and through a measuring resistor R_2 (see Fig. 1.9). The resulting voltage drop E_o across R_2 is applied by an electrometer and fed into a recorder [48]. The sensitivity of the FID could be maximized by using optimum hydrogen and air flow rate for each column flow rate [47].

The FID has been used successfully for the detection of metal complexes since the early 1960's [75]. The sensitivity of the FID is about 1000 times better than that of the TCD, i.e. about 10^{-7}-10^{-10} g of metal [2]. The wide linear range makes this detector one of the most useful detectors [27,28].

1.3.6.3 Electron Capture Detector

Unlike the FID, the ECD depends on the recombination of ions with free electrons and therefore measures a reduction in signal [47]. When the carrier gas (usually nitrogen) flows through the detector, a tritium (^{3}H) or ^{63}Ni source which is commonly used as a β-ray source ionizes the gas, so free electrons and positive ions are produced. The charge particle formed will migrate to the appropiate electrode, which is applied potential difference of 20 to 50 V [72]. The velocity of the electron is about 10^{4} times greater than the velocity of the positive ions so recombination is negligable and constant ion current appears [76]. If a solute with a high electron affinity is eluted from the column, some of the electrons are "captured", and consequently negative ions are produced. These negative ions combine with the positive ions which have been formed in the carrier gas and the current ions will decrease. Schematic diagram of the ECD is illustrated in Fig. 1.10.

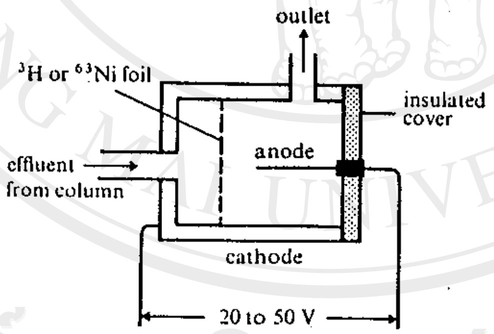


Fig. 1.10 Electron Capture Detector.

This detector is selective and very sensitive to compounds containing halogen and sulphur, anhydrides, peroxides, conjugated carbonyls, nitriles, ozone and organomettalics, but it is virtually insensitive to hydrocarbons, amines, alcohols and ketones [62].

Additionally selectivity in ECD can be obtained by increasing the applied potential when the response of weakly electron-capturing compounds is eliminated.

It has been found that introduction of fluorine atoms into the chelate increases the response from the ECD, which is opposite to the FID [14]. The response of ECD is also strongly dependent on the metal, e.g. a signal from chromium (III) trifluoroacetylacetonate is about ten times greater than that of the corresponding aluminium complexes at the same concentration [12]. The performance of the ECD is strongly affected by the type of the solvent in which the complexes are dissolved [12,55]. Solvents with high electron affinity, e.g. carbon tetrachoride and other halogenated compounds, must be avoided if the detector is to response faithfully [12,77]. A removal of the large excess of highly electron-capturing free ligand from oganic extract, has been suggested to be an important step when the ECD is used [24,55].

1.3.6.4 **Flame Photometric Detector (FPD)**

The FPD uses a hydrogen-air flame, as does the FID. A sketch of an FPD is depicted in Fig. 1.11. Rather than measuring the amount of ionization of the sample component in the flame, the FPD uses a photomultiplier tube to measure the radiation emitted in the flame by the sample components [52]. The selectiviy of the FPD is based on the fact that every eluted compound can be detected at an appropiate wavelength of the particular emission spectrum, which is pariculary useful if there are overlapping peaks of two metallic compounds [6]. The sensitivity of the FPD for the metal compound with strong emission line is similar to that of the FID, but the linear range is narrower [2].

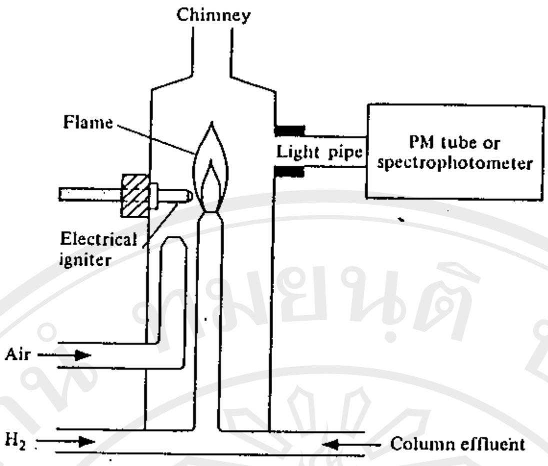


Fig. 1.11 Diagram of a flame photometric detector [52].

Since sensitivity of the FPD for many metals shows much poorer sensitivities than those obtained with the FID, it is limited to a few metal complexes such as dialkyldithiophosphate complexes [38].

1.3.6.5 Other Detectors

Other detectors have also been used for analysis of metals in a few cases, and their application will be discussed briefly as follows.

A microwave plasma detector (MPD) has been used as a selective system for the detection of various metals eluted as β-diketones [78,79]. The detector has been reported to be highly selective with a sensitivity close to that of the ECD [79,80], and the detector response being independent of metal, e.g. the detector response for acetylacetonate and trifluoroacetylacetonate of the same metal has been reported to be of the same degree [79].

Several workers have used an interface wih a mass spectrometer for GC detection (GC-MS) in the analysis of metal complexes. In this case, both total currents and electron multiplier output at selected mass have been mornitored [11], the latter offering a high degree of selectivity through the choice of m/e ion fragments specific for determination of chromium as trifluoroacetylacetonate. The GC-MS system also has an advantage for the confirmation of the successful elution of the complexes unchanged from the GC [27,81,82].

A GC interfaced to an atomic - absorption spectrophotometer allows the determination of a wide range of chromium complex. These systems provide selectivity for the metal, however, the sensitivity obtained is less than those for MPD and ECD [82].

1.3.7 Recorder and Data Handling System [49,51]

By far, the most frequently used vehicle for display of GC data is the strip-chart recorder, and analytical measurement of retention, peak areas, peak heights or concentration of samples can be made manually from the chromatogram it produced. However, most of the manual procedures usually are tedious, time consuming, and of limited accuracy and precision. Nowadays, there are various types of integrators such as ball and disc integrators, electronic analog integrators, computing integrators, reporting integrators, reporting chromatographs and computer based integrators, which automatically produce a continuous summation of the detector output with respect to time. Ball and disc integrators usually are available with a number of strip-chart recorder; they automatically integrate peak areas by following the tracking of the recorder pen but only peaks which are on scale on that recorder can be properly integrated and retention time and concentration have to be calculated manually.The next level of automation is the electronic or digital integrator which uses analog logic and circuitry for peak detection, baseline correction, and retention time measurement but reports time and areas digitally. The computing integrator is a microprocessor-based device that combines the function of peak integration and final calculation of concentrations;it converts the analog signal from the detector or electrometer-amplifier to a digital signal. Reporting integrator (also called "data module") is a modified form of computing integrator which incorporates a built-in printer/plotter. Such printer/plotter provides a record of each setting change, draws and labels chromatograms, prints the analytical reports, and a written list of all integrator settings. A further level of automation is a digital reporting gas chromatograph, a modern chromatograph which consolidates all the functions of the gas chromatograph, computer integration, computing integrator and a printer/plotter into one unit providing a powerful performance in both routine and research application. For a laboratory which has a number of chromatographs, a computer based integrator may be required. The integration and complete data analysis job is done in the computer. This also allows the user to write and execute special program without deteriorating the real time system operation.

1.4 The Aims and Scope of the Research Work

The aims of the research work may be summarized as follows:

(1) To investigate the possibility for analysis of some metals as metal chelates by GC employing a common ligand such as acetylacetone, and trifluoroacetylacetone.

(2) To study and develop an analytical method for qualitative and quantitative analysis of some metals as metal chelates investigated in step (1) by GC using a flame ionization detector.