Metal Diethyldithiocarbamates - Preparation and GLC Analysis

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ABSTRACT

METAL DIETHYLDITHIOCARBAMATES - PREPARATION AND GLC ANALYSIS

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This study involved the synthesis, characterization and investigation of the gas chromatographic behaviour of metal diethyldithiocarbamates of Ni, Cu, Zn, Cd, Pb, Hg, Co, Fe and Mn.

A successful method of preparation was developed. Characterization testing included the use of thermal analysis, atomic absorption and UV spectroscopy. UV data not previously reported in the literature were obtained.

Metal chelate mixtures of up to five components were successfully separated and quantitated. Difficulties were encountered with $Fe(DDC)_3$ and $Mn(DDC)_3$.

The best results were obtained using silanized glass tubing (60 cm x $^1/_8$") packed with a mixed liquid phase of OV-101 and QF-1 on Chromosorb W-HP. Plots of FID response versus amount of sample injected were linear in most cases.

Analysis of aqueous synthetic mixtures of up to five divalent metals present in ppm amounts was accomplished with % errors ±4.5% and relative standard deviations of ±5.0%

HPLC studies were attempted, briefly, but separation of only four compounds was accomplished using 2% ethylacetate in cyclohexane as the mobile phase and LiChrosorb-C as the adsorbent. There were no immediate advantages evident compared to GC.

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1.0 Purpose of this Thesis

The purpose of this thesis was to study the gas chromatographic behaviour of metaldiethyldithiocarbamates of Ni, Cu, Zn, Co, Cd, Hg, Pb, Mn and Fe with emphasis on their detection, separation from synthetic mixtures and quantitation.

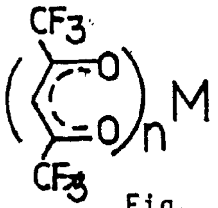
These metals are commonly important in studies of ocean waters. It was expected that the results obtained would be useful in the development of a gas chromatographic method of analysis for traces of these metals in marine samples.

1.1 Introduction

The use of gas chromatography (GC) as a quantitative method for determination of metals has been studied for the last 28 years, ever since Lederer (1) suggested that neutral metal complexes such as acetylacetonates might be amenable to GC analysis. Metal derivatization to form volatile metal complexes may be considered as a counterpart in approach to the familiar proton derivatization through esterification, and silanization of polar compounds such as fatty acids. The ligand(s) used in order to form a neutral volatile complex must bring to the metal ion a total opposite charge of equal magnitude. Typical ligands are mono and dianions of organic acids that effectively derivatize the metal ion by substituting it for their ionisable protons. The criteria involved are similar to those for organic solvent extractions of neutral complexes (2).

Most of the early work in this field was done with β-diketonates and their fluorinated derivatives. These complexes proved to be valuable for the determination of trivalent metal ions such as Cr(III), Al(III), Sc(III), Rh(III) and the lanthanides, but rarely for divalent ions except for Be(II) (3). Divalent metal ions such as Ni(II), Co(II) and Fe(II) present some problems because either hydrated chelates are formed which are of lower volatility and increased polarity which leads to undesirable GC behaviour like tailing, or nonsolvated chelates result which may polymerize or react with active sites present on the support (and the liquid phase in some cases) of the column to give excessive peak broadening or even irreversible adsorption at low levels (4).

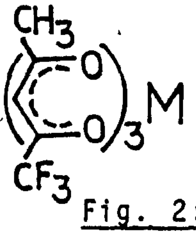
The most widely studied and analytically developed of the fluorinated β-diketones are the hexafluoroacetylacetones (Fig. 1). This particular system has made possible the analysis by GC of many chelates including those of metals such as In(III), Sc(III), V(IV), Rh(III) and Cu(II) with no apparent evidence of decomposition (5,6). One problem that has been encountered with these complexes is that they have not yet been analyzed quantitatively below the microgram level (7,8).



; M= In(III), Sc(III), V(IV), Ru(III), Cu(II)

Fig. 1: Hexafluoroacetylacetone

Trifluoroacetylacetones (Fig. 2) have shown more favorable behaviour with Co(III) and Rh(III) at submicrogram levels (9), with electron capture being employed for subnanogram level detection (10,11).



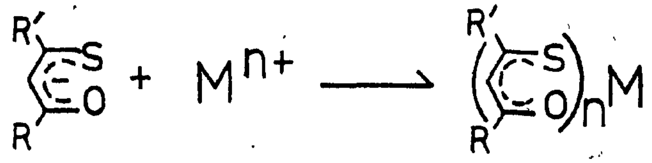
; M= Rh(III), Co(III)

Fig. 2: Trifluoroacetylacetone

Rodriguez-Vasquez (3) has pointed out that hexafluoroacetylacetonates and the more highly fluorinated β- diketone derivatives react with water to form hydroxy compounds which makes it difficult to prepare the metal chelate in the presence of water. Moreover, many of these metal chelates contain co-ordinated water. This can lead to poor recoveries from aqueous solutions. Other problems are created by their inadequate thermal stability, long retention times and dehydration in the column. This limits the possibility of their application in gas chromatography.

More recently, major efforts have been directed towards the investigation of other metal chelate systems, basically for the determination of divalent metals.

Beta-thioketones (Fig. 3) proved to be useful for divalent metal ions such as Ni, Pd, Pt, Zn and Co (12), the most notable success being with nickel which was detected at levels as low as 10 pg as its monothiotrifluoroacetylacetonate (13).

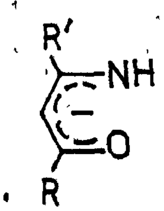


M = Pt(II), Pd(II), Co(II), Zn(II) and Ni(II).

R and R' = CF_3—, CH_3—, etc.

Fig. 3: β-Thioketones

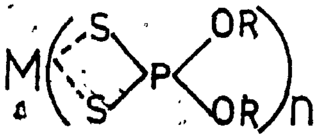
The β-ketoamine (Fig. 4) group of ligands has been used in both bidentate and tetradentate forms to chelate metals such as Cu, Ni, Pd and Pt (7). The tetradentates show good stability and chromatographic behaviour and have been investigated for the determination of Ni and Cu as fluorinated derivatives of β-ketoamines at the picogram level using electron capture detection (14).



R and R' = CH_3, CF_3

Fig. 4: β-Ketoamines

The range of ligands amenable to GC of chelates has lately been extended to include dialkyldithiophosphates, (Fig. 5) and dialkyldithiocarbamates (Fig. 6).



M= Ni(III), Cu(II), Zn(II)

Fig. 5: Dialkyldithiophosphates

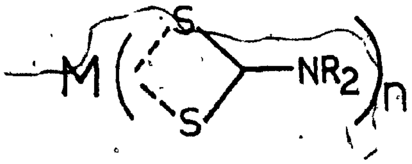


Fig. 6: Dialkyldithiocarbamates

Cardwell et al. (15) examined a wide range of metal dialkyldithiophosphates and showed that the diethyl and diisopropyl derivatives of Ni(II), Pd(II), Cr(III) and Rh(III) could be successfully eluted by GC on inert diatomaceous earth supports coated with silicone stationary phases. The corresponding Zn-chelates, although volatile, showed considerable tailing. Separation of Ni(II), Pt(II) and Pd(II) diisopropyldithio-phosphates was accomplished using a column packed with 2.5% OV-101 on Chromosorb W-HP (C-W-HP). Detection limits were found to be of the order of 5 to 8 ng using flame ionization detection (FID). Thermal analysis of other dialkyldithiophosphates showed them to be nonvolatile and unsuitable for GC.

The ligand used in this project was diethyl-dithiocarbamate $(C_2H_5)_2NCS_2^-$ (i.e. DDC^-). It was used in the form of its trihydrated sodium salt ($NaDDC \cdot 3H_2O$).

The wealth of information available on liquid-liquid extraction and other analytical procedures using diethyldithiocarbamate makes this system particularly attractive for further development of methodology for quantitative determination of metals.

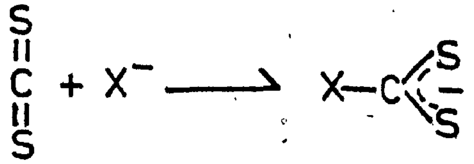
The DDC-ligand forms complexes with monovalent, divalent and trivalent metal ions. The complexes formed have the general molecular formula:

$$M(DDC)_n \quad \text{or} \quad M[S_2NC(C_2H_5)_2]_n$$

where M is a metal ion with charge n and DDC is the ligand. D'Ascenzo and Wendlandt (19) studied the thermal properties of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Hg(II) complexes of DDC by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Their research showed that these compounds are volatile and thereby amenable to GC analysis. However, D'Ascenzo and Wendlandt (20) showed in later work that $Fe(DDC)_3$ decomposes after melting at 230°C.

2.0 Structure of Some Diethyldithiocarbamates

Dithiocarbamates are part of a family of a major class of sulphur-containing ligands which are obtained by reaction of carbon disulfide with various nucleophiles. This major class of ligands is more generally referred to as 1,1-dithioacids. They are obtained as follows:



where X^- is usually a nucleophile such as:

$-NR_2$	for dithiocarbamates
$-OR$	for xanthates
$-SR$	for thioxanthates

When X is $N(C_2H_5)_2$ the ligand is known as a diethyldithiocarbamate (DDC). It forms water soluble salts with alkali metals such as Na, K, etc. and forms water insoluble chelates with most divalent and trivalent metals.

$Na(C_2H_5)_2NCS_2 \cdot 3H_2O$ ($NaDDC \cdot 3H_2O$) is usually used to extract metal ions from aqueous solutions into organic solvents as their complexes formed according to the reaction:

$$M^{n\pm} + nDDC^{-} \longrightarrow M(DDC)_n$$

where M^{n+} is Pb(II), Hg(II), Cd(II), Cu(II), Zn(II), Ni(II), Co(III), Fe(III), Mn(II), etc.

The structures of some of these complexes have been studied by X-ray crystallography. $Pb(DDC)_2$ has been shown to be a distorted square pyramid in the solid state with two sets of sulphur atoms at 2.74Å and 2.80Å respectively (21). No evidence of dimerization of the Pb complex has been found.

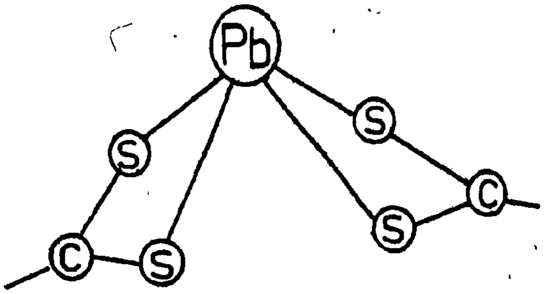
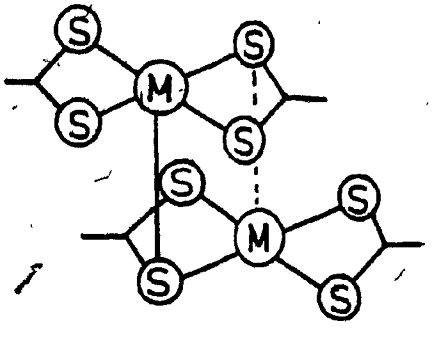


Fig. 7: $Pb(DDC)_2$ Structure

$Cu(DDC)_2$, $Zn(DDC)_2$, $Hg(DDC)_2$ and $Cd(DDC)_2$ have been found to be dimers in the solid state (22,23).



M = Cu, Cd, Zn and Hg.

Fig. 8: $M(DDC)_n$ Dimers

$Cu(DDC)_2$ is monomeric and square planar in solution (24,25A) in solvents such as benzene and chloroform.

The geometry of the co-ordination of Cu is closely related to a tetragonal pyramid, Cu having a co-ordination number of five with normal bonding to four sulphurs, and a fifth long bond to a sulphur atom of the centrosymmetrically related molecule (25).

$Zn(DDC)_2$ and $Cd(DDC)_2$, also dimeric in the solid state, are isomorphous and isostructural. In these complexes the metal ion is a five co-ordinate with geometry intermediate between tetragonal pyramidal and trigonal bipyramidal. $Zn(DDC)_2$ seems to have a normal (monomeric) molecular weight in benzene. $Cd(DDC)_2$, however, appears to be dimeric in chloroform in concentrations of 7.3×10^{-3} M to 3.3×10^{-2} M (25B,25C).

$Hg(DDC)_2$ has been found to crystallize in three different forms. One consists of isolated dimeric units which have similar structure to that of $Cd(DDC)_2$ and $Zn(DDC)_2$. The second form consists of monomeric $Hg(DDC)_2$ with square planar co-ordination. A third form is known to occur when the complex is prepared with an excess of $HgCl_2$ according to the equation:

$$nHgCl_2 + 2DDC^- \xrightarrow{H_2O} Hg(DDC)_2 \cdot (HgCl_2)_{n-1}$$

where n is believed to be as high as five (26). The formation of these complexes has been attributed to the affinity of Hg towards sulphur donors and the availability of the lone pair of electrons on co-ordinated S-atoms in the $Hg(DDC)_2$ complex.

$Ni(DDC)_2$ forms a 4-co-ordinate planar complex (25). It has been shown to be a monomeric compound in organic solvent solutions.

$Fe(DDC)_3$ is formed when either Fe(II) or Fe(III) are reacted with DDC^- in aqueous solution under normal atmospheric conditions (27). $Fe(DDC)_3$ decomposes under acidic conditions to CS_2 and the respective diethylamine salt. $Fe(DDC)_3$ has been found to be monomeric and with a distorted octahedral geometry. As is the case for Fe, Co also forms $Co(DDC)_3$ even when the starting material is Co(II) (28). Co(II) oxidizes very readily to give $Co(DDC)_3$ in aqueous solution. $Co(DDC)_3$ has also been found to be octahedral and monomeric.

$Mn(DDC)_2$ is very air-sensitive with a structure similar to that of $Ni(DDC)_2$. $Mn(DDC)_2$ oxidizes very rapidly to $Mn(DDC)_3$ and then to $Mn(DDC)_4$ (29).

3.0 Chromatography of Diethyldithiocarbamate Chelates

3.1 Gas Chromatography

Reports on the volatility and stability of diethyldithiocarbamate complexes have been available since 1940 when Malatesta (30) observed these properties for $Ni(DDC)_2$ and $Co(DDC)_3$.

G. D'Ascenzo and N.W. Wendlandt (19,20) studied and reported the thermal properties of $Ni(DDC)_2$, $Cu(DDC)_2$, $Cd(DDC)_2$, $Zn(DDC)_2$, $Hg(DDC)_2$ and $Na[Co(DDC)_3]$. $Na[Co(DDC)_3]$

was later shown to be $Co(DDC)_3$ by Holah and Murphy (28). The volatility of these compounds suggested that they could be analyzed by gas chromatography.

Daughtrey et al. (16) reported a procedure for GC analysis of inorganic and of methylated arsenic as a diethyldithiocarbamate complex in water and urine samples. Arsenic determinations were made at the 1 ppm level by electron capture detection (ECD) using a column packed with 5% OV-17 on 80/90 mesh Anakrom As (Analabs Inc.).

J. Masaryk et al. (17) studied divalent and trivalent diethyldithiocarbamate chelates of Cu, Ni, Pb, Zn, Cd, Fe, and Co. They found these complexes to be unstable under thermal analysis. It was shown that with increasing temperature they first melt and then decompose. It was also reported that $Zn(DDC)_2$ forms dimers in the solid and gas phase, while $Cu(DDC)_2$ forms dimers only in the solid state. $Ni(DDC)_2$ was found to be a monomer. Nevertheless, J. Masaryk et al. reported a separation of $Ni(DDC)_2$ and $Zn(DDC)_2$ on 3% SE-30 on Chromosorb W-HP at 250°C.

Villa et al. (31) showed, by mass spectroscopy, that $Zn(DDC)_2$ forms a dimer in the gas phase while $Ni(DDC)_2$ and $Cu(DDC)_2$ are monomeric.

J. Krupcik et al. (18) showed separation of some Ni(II) dialkyldithiocarbamates. The diethyl, dibutyl and diisopropyl dithiocarbamates of Ni(II) were separated on 3% SE-30 on Chromosorb W-HP (C-W-HP), 60/80 mesh, at 270°C.

The expected structure of $Ni(DDC)_2$ in the gas phase was confirmed by mass spectroscopy. The thermal properties of these compounds were studied by thermal analysis and it was concluded that GC could be used to analyse them.

Cardwell and Desarro (32) studied the diethyldithiocarbamates of Ni, Cu, Pd, Zn, Cd, Hg, Pb, Pt, Ag, Fe and Co. They found that Ni, Zn, Fe and Co were completely volatile under the conditions used for GC. The other complexes were less volatile and decomposed slightly. In all the cases, the TGA curves showed one-step weight losses. In general, all the compounds they studied proved to be thermally stable, with initial inflection points on the TGA curves appearing in the range of 240°C (Cu and Ag) to about 300°C (Ni, Co, Pb and Pt).

These results indicated that GC could be used for analysis of these complexes if the experimental conditions are properly selected to minimize decomposition and to ensure rapid volatilization.

It was reported by Cardwell et al. (32) that 5% OV-101 on Chromosorb W AW-DMCS (CW-AW-DMCS) can be used for GC of metal diethyldithiocarbamate complexes. All these complexes, except for $Fe(DDC)_3$ and AgDDC were eluted successfully at column temperatures in the range of 220°C to 245°C and with the injector-detector at 250°C. The eluted samples were analyzed by mass spectroscopy which showed that no decomposition had occurred. A separation of a synthetic mixture containing $Zn(DDC)_2$, $Cd(DDC)_2$ and $Pb(DDC)_2$ was obtained at 220°C using the above mentioned packing. Column tubing did not appear to make any difference when glass or stainless steel were used.

Tavlaridis and Neeb (33) have done gas chromatography on diethyldithiocarbamates and their fluorinated analogs. They found that separation of synthetic mixtures of Pb, Ni, Cu, Cd and Zn as their diethyldithiocarbamate chelates is possible on 3% OV-25 on CW-HP at a column temperature of 240°C with the injection port at 265°C. Also, separation of Zn, Ni, Cd, Pb, Sb and Bi as fluorinated diethyldithiocarbamate chelates was accomplished on 5% GESE-30 on Chromosorb Q at a column temperature of 185°C with the injection port at 220°C. The fluorinated compounds proved to be more volatile than the non-fluorinated counterparts.

In another publication, Tavlaridis and Neeb (33A) claimed that multi-elemental analysis of up to at least nine elements was possible by GC if metal chelates of fluorinated diethyldithiocarbamate were used. A separation of a synthetic mixture of Bi, Pb, Fe, Co, Hg, Cd, Ni, Cu and Zn chelates was reported on 3% OV-25 on CW-HP with the column temperature programmed from 120°C to 210°C at 2°C/min and the injection temperature at 210°C.

Studies of other alkyldiethyldithiocarbamates have been reported. For example, separation of Pb, Ni, Cu, Cd and Zn as the diisobutyldithiocarbamate chelates on 3% OV-25 on

CW-HP using column temperature programming, 220°C-265°C at 2°C/min, was reprted by Tavlaridis and Neeb (33B). They claimed that $Ni(DDC)_2$ can be detected by ECD in amounts as low as 20 pg and that other metal chelates can be detected at the 100 pg level.

Tavlaridis et al. (33C) reported separation of synthetic mixtures of Ni, Cu and Zn dipropyldithiocarbamates using 5% GESE-30 on Gas Chrom Q and CW-HP as the packings.

J. Krupcik et al. (34) did studies on several dialkyldithiocarbamates of Ni, Cu, Cd, Co and Zn. They found that Zn chelates of diethyl, dimethyl, dibutyl and diisopropyldithiocarbamate can be separated at 230°C using 2% SE-30 on CG-AW-DMCS as the packing. When capillary columns coated with OV-101 and SE-30 were used the complexes were adsorbed on the walls of the glass capillary. In a capillary column coated with OV-101 a separation of Ni-chelates of diethyl, diisopropyl, dipropyl and dibutyldithiocarbamate was obtained at 270°C.

Krupcik et al. (34) also reported that $Cd(DDC)_2$ and $Cu(DDC)_2$ decomposed above 230°C on 3% SE-30 on Gas Chrom-P.

Ahmad and Aziz (35) determined ECD detection limits for Pb, Zn, Ni, Hg and Cd diethyldithiocarbamate chelates following their separation on 3% SE-30 on Varaport-30. It was found that at a column temperature of 250°C it was possible to detect from 2.0 to 6.0 ng of each complex.

Radecki et al. (36,37) have done some marine bottom sediment analyses by GC. It was shown that Ni, Cu and Zn could be extracted from marine bottom sediments and successfully separated by GC as diethyldithiocarbamate chelates without any interference. This is interesting because other methods for determination of metals in marine sediments involve either inductively coupled plasma emission spectroscopy (ICP) or atomic absorption spectroscopy where prior separation is needed to avoid interferences due to other components in the sediments and the reagents used. By using GC these interferences are eliminated and simultaneous analysis of several elements is clearly possible.

3.2 Liquid Chromatography

Liquid Chromatography of dialkyldithiocarbamate chelates has been reported in recent years. Heizmann and Ballschmitter (38) reported the separation of synthetic mixtures containing $Ni(DDC)_2$ and $Cu(DDC)_2$, and $Cu(DDC)_2$ and $Co(DDC)_3$, using a silica gel packing (LiChrosorb SI 60) in 15 cm x 2 mm (Lxid) glass column. Benzene was used as the mobile phase and UV detection at 330 nm. Separation of more than two complexes was found to be difficult mainly because of pronounced tailing of samples on the silica gel.

Uden and Bigley (39) reported the separation of $Ni(DDC)_2$, $Co(DDC)_3$ and $Cu(DDC)_2$ using a mixture of Skelly B (a petroleum hydrocarbon), diethylether and acetonitrile (15:5:80) as the solvent system (mobile phase) on a 4 mm x

25 cm (idxL) stainless steel column packed with 8 um diameter Sperisorb-SGP. UV detection limits at 254 nm were reported to be in the 5 to 10 ng range for each metal. Identification of chelates was achieved by using an interfaced d.c. argon plasma emission spectroscopy detection system in series with the UV detector. It measured the metal content of each peak.

O'Laughlin and O'Brien (40) studied the behaviour of Ni, Co, Cu, Zn, Cd, Hg and Pb chelates of diethyldithiocarbamic acid on silica gel columns with toluene as the mobile phase. Separation of Pb and Hg, and Co and Ni, was possible but separation of a mixture containing all these complexes was difficult because of tailing of peaks. Calibration plots of peak area vs. amount of metal chelate injected indicated linear response over the low nanogram to microgram range. The detection limits using a UV detector at 254 nm were found to be in the range of 5 to 210 ng with the best results for $Ni(DDC)_2$ and the poorest for $Pb(DDC)_2$.

Moriyasu and Hashimoto (41) described adsorption chromatography of diethyldithiocarbamate chelates of Hg, Cd, Pb, Cr, Bi, Cu and Ni on deactivated silica gel. Separation of synthetic mixtures of Hg, Cu, Cd, Pb, Ni and Bi were reported on LiChrosorb-S1-100 using the solvent system Hexane/Ethylacetate (98:2) as the mobile phase. Separative microdetermination of these chelates was accomplished within 12 minutes. Detection limits at 254 nm were in the range of 10 to 20 ng. Selective determinations were also achieved by changing the detector wavelength. Separation of synthetic mixtures of Hg, Cu, Pb, Cr, Ni, Bi and Co were also reported using the same conditions. In all cases, however, the resolution was very poor.

Reversed phase HPLC has also been done on some diethyldithiocarbamate chelates. Simultaneous determination of Cr(III) and Cr(VI) in water using NaDDC as the chelating agent has been reported by Tande et al. (43). Separation of the chelate formed was obtained using a column packed with LiChrosorb PP-8 (particle size 10 um) and methanol-water (65:35) as the mobile phase. UV detection at 254 nm of amounts as low as 2 to 10 ppm of Cr(III) and Cr(IV) was possible.

G. Schweds (42) and (42A) has reported separation of diethyldithiocarbamates of Pb, Ni, Co, Cu and Hg using LiChrosorb 18 (10 μm particles) as the packing, 65:35 acetonitrile-water as the mobile phase and UV detection at 254 nm. Separation of mixtures containing Cd, Pb, Ni, Co, Zn, Cu and Hg were also reported using LiChrosorb RP-8 as the packing and 70:30 methanol-water as the mobile phase. Separations were obtained within 25 minutes. The published chromatograms show very poor resolution of the mixtures in question.

A.M. Bond and G.G. Wallace (44) reported methods specifically for the determination of Cu based on reversed phase liquid chromatography with electrochemical detection.

It was found possible to detect amounts as low as 2 ng of Cu without interferences from many other elements.

4.0 Introduction to Gas Liquid Chromatography

Gas chromatography (GC) is an instrumental method of analysis for separation, identification and quantitation of volatile mixtures. Permanent gases (such as oxygen and carbon dioxide), volatile liquids, volatile solids and pyrolyzed solids can all be separated by Gas Chromatographic techniques (45).

In gas chromatography the separation takes place in a column where the components of the sample distribute themselves between an active stationary phase and an inactive mobile phase (carrier gas). The moving phase is an inert gas and the sample components are introduced into the gas phase. The column is usually a metal or glass tube packed with the porous particles of a relatively inert material (diatomaceous earth is very commonly used) on which the stationary liquid phase is distributed in the form of a thin film. The sample is injected into a heated block where it is evaporated and its vapour carried by the carrier gas through the column. During this period the molecules of the sample components spend part of their time in the stationary phase, the other part in the carrier gas. The relative retardation of different components is different and, thus, they emerge at the end of the column separated in time. The eluted components are detected by a suitable detector and the detector signals are electronically recorded to give a chromatogram. The chromatogram consists of a series of peaks, each of which indicates the elution of a component and the amount eluted. The time of elution may be used to identify the components of the mixture and is defined as the elution time or retention time for a particular component (45,46).

A basic gas chromatograph is shown in Fig. 9 (45).

5.0 Column

The column consists of a glass or metal tube packed with a solid support coated with a stationary liquid phase.

5.1 Solid Support

The purpose of the solid support is to hold a thin uniform film of liquid phase. An optimum support should have certain characteristics (46):

(i) A large specific surface area (from 1 to 20 m^2/g).

(ii) A pore structure with uniform pore diameter in the range of 1 μm or less.

(iii) Inertness (a minimum of chemical and adsorptive interaction with the sample).

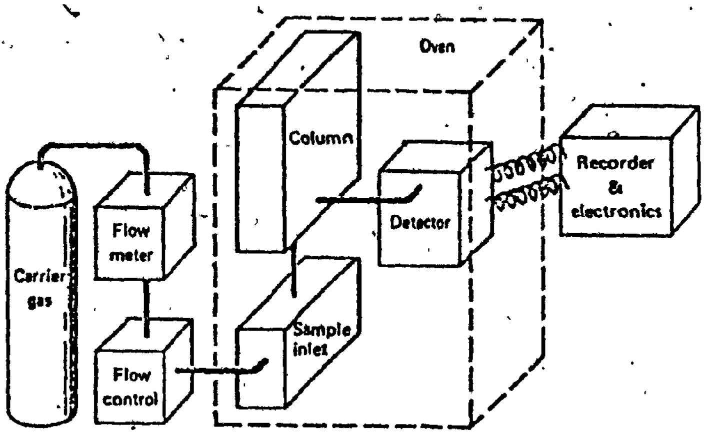
(iv) Regularly-shaped particles, uniform in size for efficient packing and efficiency of chromatographic operation.

(v) Mechanical strength - it should not crush on handling.

No material has yet been found which fills all these requirements. However, several suitable supports are commercially available, but it is necessary to

FIGURE 9

SCHEMATIC OF A GAS CHROMATOGRAPH



compromise in choosing between efficiency and strength.

The most popular gas chromatographic supports are those prepared from diatomaceous earth, which is also known as diatomaceous silica or kieselguhr (47,48). Two different treatments are used to prepare diatomaceous earth supports for use in gas chromatography, resulting in white-coloured and pink-coloured supports.

The white-coloured supports are prepared by calcination of diatomaceous earths above 900^{0}C with sodium carbonate added as flux. In the heating process, the diatomaceous earth is fused and held together by sodium silicate glass and the silica present is partially converted to crystalline cristobalite. The resultant product is white in colour due to the conversion of iron oxide into a colourless complex of sodium iron silicate. These white products are used to prepare the most inert supports such as Anakrom A, Anakrom Q and Chromosorb W supports. These white ~~flux~~ calcined supports are, however, fairly fragile.

The pink-coloured supports, e.g. Anakrom C-22 or Chromosorb P, are prepared from crushed firebrick in which the diatomaceous earth has been calcined with a clay binder at temperatures above 1000^{0}C. The metal impurities remaining form complex oxides which contribute to the pink colour of these supports. These pink supports are denser than white supports because of the greater destruction of the diatom structure during the calcining treatment. These supports are harder and less friable than the white supports and are capable of holding larger amounts of liquid phase (up to 30%) without becoming too sticky to flow freely. The surface of pink supports is more adsortive, however, than that of white supports and they are not suitable for analysis of polar compounds.

Neither the pink nor the white supports give generally acceptable performance without pretreatment of their surfaces to remove active sites, and thereby reduce the possibility of tailing of peaks (47,49). These adsorptive sites are attributed to metal oxides (Fe, Al) on the surface, which catalyze degradation (48), and to surface silanol groups, -SiOH, which are capable of forming hydrogen bonds with polar compounds. Mineral impurities are removed by acid washing with hydrochloric acid, which leaches out iron and aluminum from the surface of the support. Surface silanol groups are eliminated by one of several possible silanization processes described in the literature (46,47,48).

Silanization of supports is effective but these supports must be used with caution. The silanized supports have hydrophobic rather than hydrophilic surfaces, as are found on non-silanized diatomite support surfaces. Polar stationary phases such as polyesters and silicones with a high content of cyano groups (such as OV-275) do not wet such surfaces. They spread better on the surface of non-silanized supprts to provide a more evenly coated surface. At high temperatures, water and free acids when injected onto silanized supports, will remove surface silyl ether groups and regenerate an active surface.

Among the supports evaluated in this study were Chromosorb W-AW-DMCS (CW-AW-DMCS), Chromosorb G-HP (CG-HP) Chromosorb W-HP (CW-HP), and Gaschrom Q (GC-Q), all acid washed and silanized materials. CW-HP and GC-Q are equivalent supports. These are specially treated supports and recommended by their manufacturers as the most efficient and inert of the diatomaceous earths,

5.2 Stationary Liquid Phase

It is the liquid phase which distinguishes between the solutes in the sample through differences in their solubilities and interactions under the operating conditions. Where these differences are small, the chromatograph must be operated at maximum efficiency to obtain a satisfactory separation.

The most important requirement of a liquid phase is that it should be differentially selective for the components in the mixture for which it is to be used. Although a liquid phase that cannot separate the components is useless, the fact that it can separate them is not sufficient. A liquid phase must also satisfy other requirements (50):

(i) The liquid phase must be a liquid under the conditions of column operation. This seems obvious, but it should be realized that many compounds used as stationary phases are solids at room temperature (e.g. SE-30, OV-1). If a column is used below the melting point of the liquid phase, the solubility of the sample components is greatly reduced, causing overloading of columns, poor resolution, short retention times and distorted peak shapes.

(ii) The liquid phase should have low volatility to prevent its bleeding which would rapidly reduce the life of the column. Also, some detectors will lose sensitivity as the level of bleeding increases.

(iii) The liquid phase should be stable under the conditions of operation. This is important for two reasons. First, a decomposing liquid phase behaves the same way as a bleeding liquid phase, resulting in high noise level, detector saturation and shortening of column life. The second factor is that decomposition can change the properties of the liquid phase and render it unsuitable for analysis (51).

(iv) The liquid phase must not react with the samples to be separated.

(v) For maximum stability the upper temperature limit of the liquid phase must be relatively high when compared to the intended operating temperature.

Liquid phases are usually classified according to their polarity (polar, semipolar and nonpolar). How this is done is well documented in the literature (49,50,52,53, 54,55). In this research the following liquid phases were used: OV-101, SE-30, QF-1 and OV-17, individually, and as mixtures (56). These liquid phases are silicone polymers with the general formula:

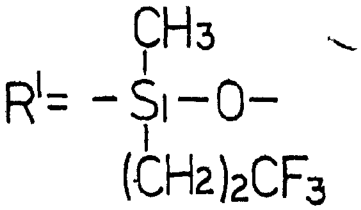
$$(CH_3)_3-Si-O-R^1_n-R^2_m-Si(CH_3)_3$$

For OV-101 and SE-30 (nonpolar) the ratio of n/m is one ad R^1 and R^2 are:

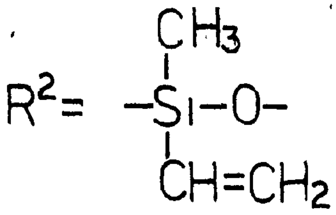
$$R^1 = R^2 = -Si(CH_3)_3-O-$$

OV-101 is a fluid which has a temperature limit of 350°C and can be dissolved in solvents such as chloroform, toluene and dichloromethane to prepare support coating solutions. SE-30 is a gum that has a temperature limit of 300°C and can be solubilized in chloroform, toluene or dichloromethane.

QF-1, a semipolar liquid phase, is a fluid where R^1 and R^2 are:



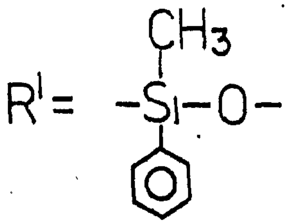
$$R^1 = -\overset{\displaystyle CH_3}{\underset{\displaystyle (CH_2)_2CF_3}{Si}}-O-$$



$$R^2 = -\overset{\displaystyle CH_3}{\underset{\displaystyle CH=CH_2}{Si}}-O-$$

The n/m ratio is very large. The temperature limit of QF-1 is 275°C and it is soluble in chloroform, acetone, and ethylacetate.

OV-17, also a semipolar liquid phase, is a fluid with R^1 and R^2 being:



$R^2 = -Si(CH_3)_2O-$

The n/m ratio is very large and the temperature limit is 375°C. OV-17 can be coated on the support from toluene or chloroform solutions. More detailed information on these liquid phases is available in the literature (49, 57). It is possible to use a combination of two or more liquid phases in the column. In this case, the polarity or separating power of the column will be a function of the composition of the binary liquid phase system (58). If the components of the mixed liquid phase differ markedly in polarity, the polarity of the mixed column can be varied over the full range by changing the composition. These mixed liquid phases can be utilized as mixed bed columns in which each support particle is coated with a single pure stationary phase, or they can be used as blended columns with each support particle coated with the binary liquid phase (56).

5.3 Preparation of Column Packing

The packing consists of a definite percent of loading of stationary phase (usually 2 to 10%) on a deactivated solid support surface. The amount of liquid phase and support required to give a specific loading is given by the following equation:

$$\%\ \text{loading} = \frac{\text{Wt. Stationary Phase}}{\text{Wt. Stationary Phase + Wt. Support}} \times 100$$

There are three common methods for making GC packings (batch coating, in-place coating and filtration coating), each of which has its advantages (49,57,59 & 60). The batch coating method was used in this project and is described in the Experimental (10.3.1).

5.4 Column Conditioning

Every freshly prepared column requires conditioning before its application in analytical work (49,50). Conditioning is necessary: (i) to remove any remaining solvent, water or other volatile contaminants; and (ii) to achieve a more uniform distribution of liquid phase on the support or tube wall. Conditioning is done by heating the column for several hours (2 to 12 hours) at a temperature 25°C above that at which the column is to be used, but below the maximum temperature limit of the liquid phase, with a small carrier gas flow passing through (usually 5 to 15 ml/min.) (46).

6.0 Detectors in Gas Chromatography

As sample components emerge from the column, they must be detected by a suitable device which relays an electrical signal, via an amplifier, to a strip chart recorder establishing a permanent record of the analysis referred to as a gas chromatogram. More than twenty different types of detectors have been developed for use in GC. However, relatively few of these are in common use today, the most common being the thermal conductivity detector (TCD), the flame ionization detector (FID) and the electron capture detector (45,46,61,62 & 63). The flame ionization detector which was used in this project is described below.

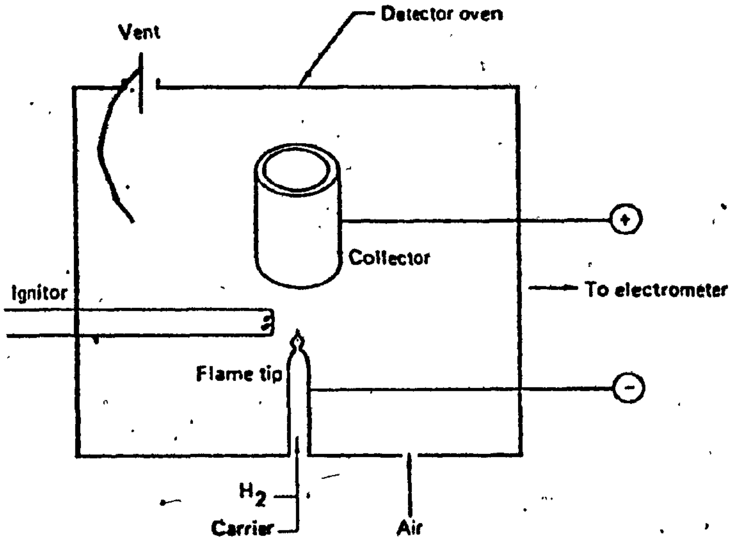
6.1 Flame Ionization Detector (FID)

The FID is the most frequently used GC detector. It is a nearly universal detector responding to all but a few gases, such as the permanent gases like nitrogen and oxides of nitrogen, and H_2S, SO_2, COS, CS_2, CO, NH_3, CO_2, H_2O and HCOOH. Actually, this insensitivity can be used to good advantage by using H_2O and CS_2 as solvents, since potentially large solvent peaks are eliminated. The presence of these compounds can have some effect on detector performance, however. While some other detectors are more completely universal, the FID has the advantage of being able to detect concentrations as low as 10^{-12} g/ml of many hydrocarbons.

A schematic representation of the FID is given in Fig. 10 (45,63). An electrical field is established between the burner jet, where hydrogen gas burns, and the positively charged collector electrode. Column effluent is burned in the flame and any negative ions produced are collected at the positive electrode. This process can be understood also by considering that the ions and electrons formed in the flame decrease the resistance between the two electrodes (known as the gap resistance) thus permitting a current to flow in the external circuit. In practice, gap resistance is greatly diminished when organics burn in the flame. This change in resistance is what is measured in practice. To ensure total combustion of the effluent an excess of oxygen is introduced into the FID chamber by introducing air at the base of the flame jet.

FIGURE 10

FLAME IONIZATION DETECTOR



The limitations of the FID are:

(i) It is a destructive detector. Therefore, use of a sample splitter is required if the effluent is to be further analyzed.

(ii) Atoms like oxygen, nitrogen, phosphorus, sulphur and halogens in the sample compounds decrease the sensitivity of the FID to an extent dependent on the degree of substitution in the sample.

7.0 Interpretation of Chromatographic Data

In chromatography the aim is to separate the components of a sample. The components, as they pass through the column, spend part of the time in the stationary phase while another part of the time they are carried through the column by the carrier gas.

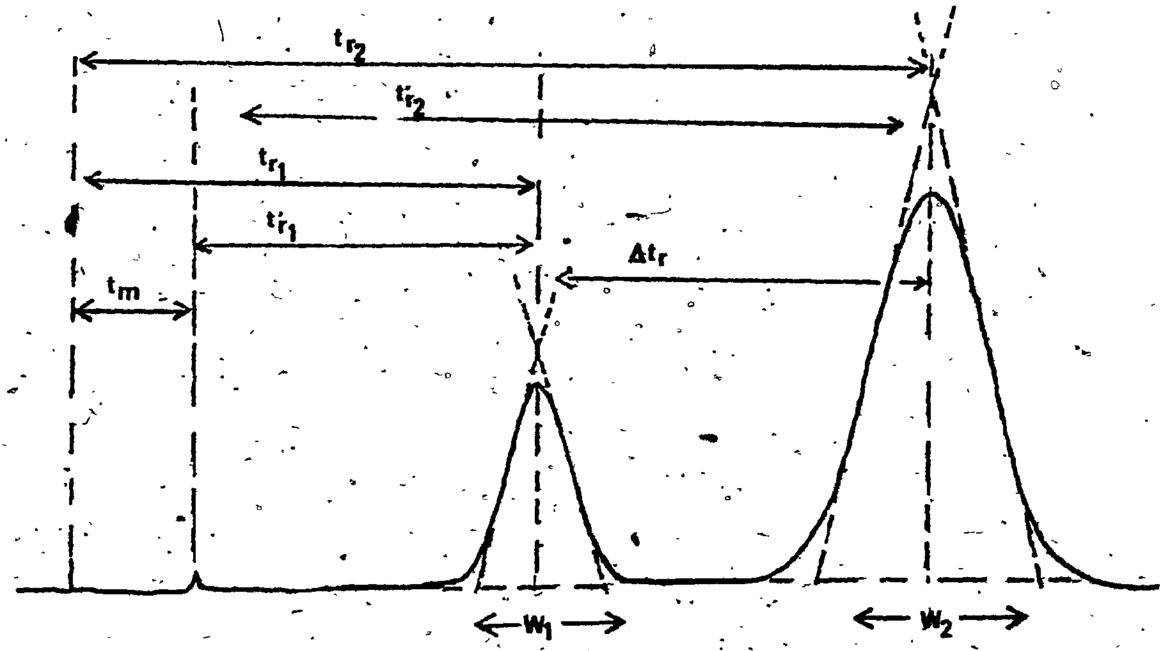
The volume of the gas phase in the column can be expressed in terms of the holdup time, t_m. The time spent by a sample component in the liquid phase is known as the adjusted retention time, t_r' , which is the retention time, t_r , corrected for the holdup time, t_m (Fig. 11), as follows:

$$t'_{r_1} = t_{r_1} - t_m \quad \text{(Eq-1)}$$

Both t_{r_1} and t'_{r_1} are of value in making qualitative identification. Notice that t_m is usually taken as the retention time of a non-retained component, such as air,

FIGURE 11

INTERPRETATION OF CHROMATOGRAMS



injected together with the sample.

Other parameters such as capacity factor, k, partition coefficient, k_r, and phase ratio, β, can be calculated using the following relationships (64).

$$k = \frac{t_r - t_m}{t_m} \qquad \text{(Eq-2)}$$

and

$$K_r = \frac{C_l}{C_m} = \beta \frac{W_l}{W_m} \qquad \text{(Eq-3)}$$

where:
C_l = concentration of solute in the liquid phase, g/ml
C_m = concentration of solute in the mobile phase, g/ml
W_l = weight of solute in the liquid phase, g
W_m = weight of solute in the mobile phase, g
β = phase ratio

The implications of these equations in practice are that the amount of sample that can be injected into a column without overloading it depends on the amount of liquid phase on the column which, in turn, influences the phase ratio (β). A higher amount of liquid phase leads to a lower phase ratio.

Efficiency of the column depends on the capacity ratio (k), the smaller the capacity ratio the more difficult it is to achieve a separation. Column efficiency, and parameters governing it, are well reviewed in the literature (46,50,59,65,66,67, 69) and will not be discussed here.

7.1 Resolution

The true separation of two consecutive peaks is described by the Resolution, R, defined as:

$$R = \frac{2\Delta t_r}{W_1 + W_2} \qquad \text{(Eq-4)}$$

where Δt_r is the distance between the two peak maxima, and W_1 and W_2 are the widths of the two peaks in question (Fig. 11). This expression is commonly used in GC.

Another useful expression that can be derived is:

$$R = \frac{\sqrt{N}}{4}\left(\frac{k}{k+1}\right)\left(\frac{\alpha-1}{\alpha}\right) \qquad \text{(Eq-5)}$$

where α is the selectivity factor defined by:

$$\alpha = \frac{t'_{r_2}}{t'_{r_1}} \qquad \text{(Eq-6)}$$

and N is the number of theoretical plates (68). These expressions are commonly used in HPLC work.

It has been claimed in many cases that a Resolution of R=1 gives a separation which is about 97% complete, while a Resolution of 1.5 represents a complete separation

(59). Any value of resolution larger than 1.0 is usually adequate for analytical purposes (70,71).

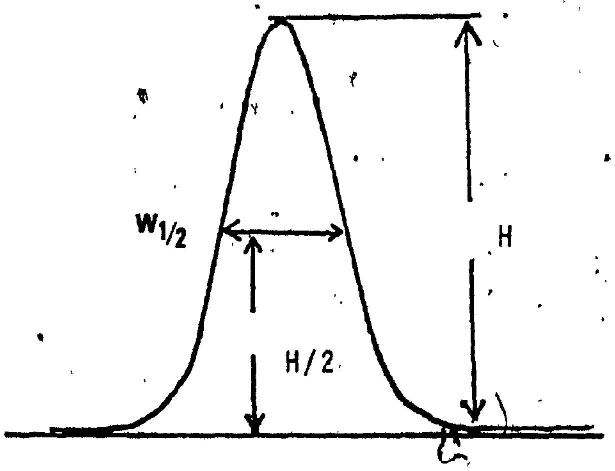
Consideration of theoretical factors led to the choice of experimental conditions used in the present study. The approach that was taken as much as possible was to decrease stationary liquid phase loading and column temperature to improve resolution, to avoid column bleeding under temperature programming conditions and to reduce the possiblity of degradation.

8.0 Quantitative Analysis by GC

The quantitative principle of GC depends on the fact that the size of a chromatographic peak is proportional to the amount of component eluted from a column. The size of a peak can be measured in a number of ways using one of two basic concepts. The first is measurement of peak height. The second is measurement of peak area with a wide variety of methods available (46,50,65). The more readily reproducible peak area method was chosen in this project. Of different techniques available for peak area measurement, that of (peak area measurement by height x width at half height) was chosen (Fig. 12). Normal gaussian peaks can be approximated well in this way. This technique is fast and simple, and the results are good with symmetrical peaks of reasonable width. Ball et al. (72,73,74,75) have reported

FIGURE 12

PEAK AREA CALCULATION



that this measurement technique can give peak area data with relative standard deviations of about 2.58% for peaks of areas of about 150 mm^2, and 0.5% for peaks of areas of 1500 mm^2.

9.0 High Performance Liquid Chromatography (HPLC)

In liquid chromatography as in all other types of chromatography the separation of a mixture is accomplished by distributing its components between two phases. One of them is a stationary phase while the other, the mobile liquid phase, percolates over the stationary phase. Separation is due to differences in the distribution coefficients of the individual sample components between the stationary and mobile phases. The column can be an adsorbent (such as silica or alumina) or a stationary phase bonded polymer on a silica type support. In practice, two modes of operation, depending on the relative polarity of the two phases, are used: normal HPLC and reversed phase HPLC. In normal HPLC the stationary phase is polar in nature (e.g. silica), and the mobile phase is nonpolar (such as hexane, cyclohexane, etc.). Polar samples are retained longer on such a column than nonpolar samples. In reversed phase HPLC the stationary phase is nonpolar in nature (a hydrocarbon), while the mobile phase is a polar liquid, such as water or an alcohol. Here the more nonpolar the sample components, the longer they will be retained on the column.

9.1.0 Instrumentation of HPLC

A block diagram of a typical HPLC apparatus is shown in Fig. 13. The basic components of such a system are: a pump to propel the mobile phase; a device for sample introduction; a column containing the stationary phase; a detector to determine when sample components are eluted and provide data permitting the qualitative and quantitative evaluation of the results and a recording system to display the response of the detector in the form of a chromatogram.

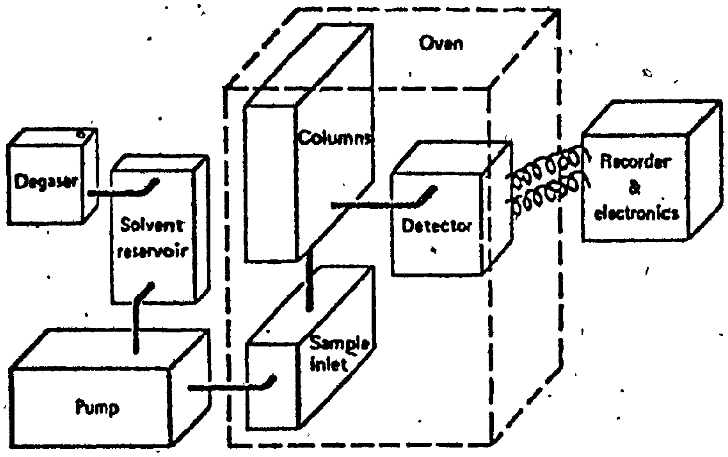
9.2.0 Separation Modes in HPLC

There are four principal separation modes that can be used in liquid chromatography: liquid-solid or adsorption chromatography; liquid-liquid or partion chromatography; size-exclusion chromatography and ion exchange chromatography.

In this particular research the only mode attempted was liquid-solid chromatography and, therefore, only it will be discussed here. Other modes of liquid chromatography are described in many references (76,77).

FIGURE 13

HPLC APPARATUS



9.2.1 Principles of Liquid-Solid Adsorption Chromatography

The methanism of separation in adsorption chromatography is a subject of much debate. L.R. Snyder (78), however, has proposed a simple mechanism which is easy to understand and provides for many liquid-liquid chromatography separations. The adsorption chromatography mechanism can be visualized by considering the establishment of an equilibrium inside the column. The mobile phase and solute molecules compete for the active sites on the adsorbent surface as is illustrated for the system shown in Fig. 14.

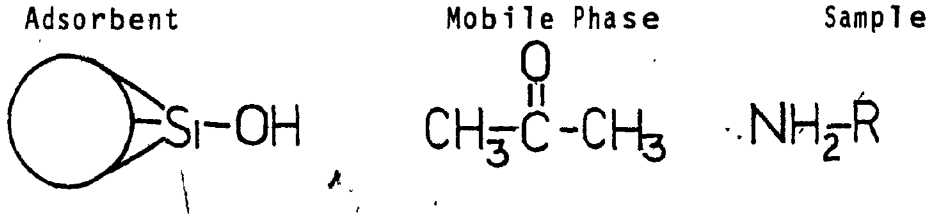


Fig. 14: Adsorption Chromatography Separation

The mobile phase (acetone) chosen is one with a polarity approximately equal to (or slightly weaker than) that of the sample. The sample molecule (amine) attached to a hydroxyl group on the packing surface, is continuously bombarded by the moving stream of mobile phase molecules.

This physical flushing weakens the sample-to-packing bond and the sample is displaced and moved downstream to the next available OH group where its slightly higher polarity compared to that of the mobile phase allows it to dislodge resident mobile phase molecules previously there. The greater the number of such successive steps or stages, the greater the probability that sample components having slightly different polarities may spend greater or lesser amounts of time attached to the adsorbent surface, and thereby separate one from another. This competition of the mobile phase and solute molecules for the active sites of the adsorbent can be represented by:

$$\text{Acetone} + (\text{Adsorbent} - \text{Amine}) \rightleftharpoons (\text{Acetone-Adsorbent}) + \text{Amine} \qquad [\text{Eq} - 7]$$

From equation [Eq-7] the following relationship can be obtained:

$$K_{eq} = \frac{[\text{Amine}]\,[\text{Acetone-Adsorbent}]}{[\text{Acetone}]\,[\text{Adsorbent-Amine}]} \qquad [\text{Eq} - 8]$$

This expression shows that adsorbent-solute or mobile phase interaction is the most important parameter governing the separation in liquid-solid chromatography. As the relative adsorption of the mobile phase increases, the adsorption of the solute must decrease which makes the sample elute from the column more quickly.

9.3.0 Column Packing for Adsorption Chromatography

The adsorbent in liquid chromatography usually consists of silica particles (or less commonly, alumina, charcoal, Florisil, calcium carbonate, etc.) packed into suitable tubing. The particles used originally in liquid chromatography were fairly large (40 um in diameter), and porous. Such particles have large surfaces and thereby high sample capacity. Their drawback, however, is that it may take different amounts of time for the same sample molecules to diffuse into and out of various pores of the particle, resulting in excessive band broadening (77). This problem is reduced by using pellicular particles which have a solid, nonporous core (e.g. glass beads) coated with a thin layer of a porous phase (e.g. an adsorbent). In this case, the sample molecules only migrate through a relatively thin layer of adsorbent reducing differences in adsorption times for the same kinds of samples, which leads to narrower peaks.

According to the theory of chromatography (45,50,79) smaller particles give high efficiency at relatively high velocities. This has led to the use of small particles with fairly uniform diameter and regular shape. The particles used in modern HPLC have a diameter of 10 um and, in some cases, even as low as 2 um. They can be made fully porous since due to their small diameter, sample migration through their pores is rapid.

9.4.0 Detector In HPLC

There is a number of detectors that are used in HPLC. They are well documented in the literature (76,77,80). Some of these detectors are very specific, such as variable UV-detectors, while others are fairly universal, such as the refractive index detector. The selection of a particular detector depends on the sample being analyzed and the required sensitivity.

A fixed wavelength UV detector was used in this study since it was the only one available.

10.0 Experimental

10.1 Preparation of Metal Diethyldithiocarbamate Chelates

The metal diethyldithiocarbamate chelates, $M(DDC)_n$, were made by a modified version of the procedures outlined by Wyttenback and Bajo (81,81A) and others (33, 33A,33B,33C).

10.1.1 General Procedure

To a solution containing 5.0 mmoles of the particular divalent metal salt ($Ni(NO_3)_3 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, etc.) in 50 ml of water, a solution containing 10.5 mmoles of $NaDDC,3H_2O$ (certified, A.C.S. Fisher Scientific Co.), was added dropwise with continuous stirring. The precipitate formed after all the reagent has been added was recovered by filtration and washed several times with distilled water and twice with 10 ml of absolute ethanol. The product was allowed to dry at 110°C for 1 to 2 hours and the yield recorded.

The $M(DDC)_n$ were recrystallized from benzene, or chloroform, or ligroin, or 1:1 ether/chloroform, or 1:1 chloroform/ethanol, with 1:1 $CHCl_3$/ethanol giving the best results.

To make complexes of trivalent ions the starting amounts were changed to 15.5 mmoles of $Na.DDC.3H_2O$ for 5.0 mmoles of metal.

10.1.2 Recrystallization from 1:1 $CHCl_3$/Ethanol

To recrystallize the $M(DDC)_n$ chelates 5 mmoles of the particular chelate were dissolved in the required amount of chloroform (30 ml was usually enough) and filtered from the solution. To the filtrate was added an equal amount of absolute ethanol. The solution was heated at 70°C until the volume was reduced to about half of the original amount. The solution was cooled down to room temperature and recrystallized product was filtered and dried at 110°C for one hour. The product was weighed and the yield recorded.

10.2.0 General Procedure used for Elemental Analysis

The sample of $M(DDC)_n$ was weighed accurately (sample size ranged from 0.0500g to 0.1200g) and transferred to a 100 ml beaker. It was treated with 20 ml of 1:1 HNO_3 which was added slowly, and the beaker was covered with a watch glass, to avoid sample loss. The mixture was heated on a hot plate for a few minutes until a clear solution was obtained. The solution was allowed to cool down to room temperature and transferred to a 100.0 ml volumetric flask where it was diluted to the mark with deionized water. Finally, the solution was transferred to, and stored in, a 125 ml polyethylene bottle. All the samples were analyzed in triplicate, with blanks prepared for each analysis.

10.2.1 Flame Atomic Absorption Spectroscopy

Sample concentrations were determined by using the calibration line method of flame atomic absorption spectroscopy. Standard solutions were prepared by dilution of concentrated stock solutions (1,000 ppm) of the particular metal being analysed.

The instrument used was a Perkin Elmer Model 505 Atomic Absorption Unit.

10.3.0 Preparation of Column Packing

The method used to prepare the packing for this study was the batch coating (evaporation) method, outlined by Supina (82) and Leibrand (60).

The supports and stationary liquid phases used were obtained from Chromatographic Specialities Ltd. and Applied Science Laboratories.

The supports used are listed in Table I below.

TABLE I

Supports Used to Prepare Column Packings

Support	Mesh Number	Source
Chromosorb W-HP (CW-HP)	80/100	Chromatog. Spec. Ltd.
Chromosorb G-HP (CG-HP)	80/100	Chromatog. Spec. Ltd.
Chromosorb W-AW-DMCS (CW-AW-DMCS)	60/80	Chromatog. Spec. Ltd.
Gas Chrom-Q (GC-Q)	60/80	Applied Science Lab.

10.3.1 Typical Procedure for Preparation of a Coated Support: e.g. 5% OV-101 on CW-HP

To make 5.00 g of packing, 4.75 g of CW-HP was weighed out. A solution of 0.25 g of OV-101 in the required amount of chloroform (50 to 100 ml) was prepared. Then the CW-HP support was slowly poured into the solution of stationary phase. The container was swirled to mix the particles with the liquid phase solution. The solvent was evaporated by heating gently at about 70°C or by applying a stream of nitrogen gas while swirling the mixture very carefully. When the packing became free-flowing it was weighed to confirm that the right amount was obtained (5.00 g). This method gave a final weight within 0.1% of what was expected.

For mixed liquid phases, OV-101 + QF-1, the same procedure was used since chloroform was an adequate solvent for both phases. Had the same solvent not been suitable for both liquid phases, then each would have had to be coated individually onto the support from different solvents.

It should also be pointed out that when low liquid loadings are used, degassing of the mixture of support and liquid phase solution may be required.

10.3.2 Silylation of Glass Tubing

When glass columns are used the surface of the tubing is made inert as much as possible, by treating it with a 5% dimethyldichlorasilane in toluene solution. For example, Sylon CT, obtained from Supelco, was used for silylation of glass tubing before packing. It is equivalent to a 5%

dimethyldichlorosilane in toluene solution and provides deactivation at temperatures up to 350°C to 400°C.

10.3.3 Procedure for Silylation of Glass Tubing

The glass tubing was washed with toluene, and then filled completely with Sylon-CT. This solution was allowed to stand in the tubing for at least one minute. The Sylon-CT was then drained and the tubing rinsed, first with toluene and then with methanol. Finally, the tubing was dried by passing N_2 gas through it. This procedure was repeated whenever the glass tubing was to be filled with a new packing.

10.3.4 Procedure for Packing a Column

All the stainless steel columns were packed by inserting a silanized glass wool plug in one end and attaching a funnel to the other end. The packing was then poured in very slowly. The column was tapped or vibrated gently while the packing was added. When the column was completely filled another plug of silanized glass wool was inserted in the other end. Finally, ferules and nuts were placed on the tubing.

For packing a glass column a plug of silanized glass wool was inserted in the outlet end of the tubing which was connected to a vacuum source. The inlet end was introduced into a 50 ml beaker containing the packing and packing sucked into the tubing. The vacuum source was controlled gently to allow packing the column without breaking the particles. When the column was completely filled another plug of silanized glass wool was inserted into the inlet end of the column. Finally, ferules and nuts were connected to the glass tubing.

10.3.5 Conditioning of Columns

All the columns were conditioned at 250°C with nitrogen at a flow rate of 15 ml/min. passing through for 12 hours. During conditioning the exit end of the column was left disconnected from the detector to avoid contaminating it.

10.3.6 GC Instrumental Parameters

All the GC studies were done with a Shimadzu Gas Chromatograph Model GC - 6AM, equipped with a differential flame ionization detector, Model FID - 6.

The chromatograms were displayed using a Watanabe Servorecorder Model SR6200 (Chart speed, 1 cm/min.).

Sample injections were carried with a 10 ul Hamilton Microsyringe, Model 701N. It has an accuracy and reproducibility of ± 1%.

Table II shows the typical experimental conditions for the GC study. It should be noted that the column temperature was varied depending on the analysis.

TABLE II

TYPICAL EXPERIMENTAL CONDITIONS FOR GC

Parameter	Concentration Range	
	High	Low
Nitrogen Flow Rate	60 ml/min	60 ml/min
Hydrogen Flow Rate	46.7 ml/min	46.7 ml/min
Air Flow Rate	0.9 l/min	0.9 l/min
Injector-Detector Temperature	300°C	260°C to 275°C
Sensitivity	10^2	10^3
Attenuation (range)	2 to 8	2 to 4
Recorder Chart Speed	1.0 cm/min	1.0 cm/min
Recorder Range	2.0 mv	1.0 mv

10.4.0 Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) - Conditions and Instrumentation

TGA and DTA studies were done using DuPont Model 950 and 900 units respectively.

The DTA studies were done using a set of Chromel-Alumel thermocouples and glass beads as reference material. Sample tubes were 2mm x 3 cm (O.D. x length) in size.

The TGA studies were done using a Pyrex tube furnace and aluminum pans to hold the samples.

The instrumental parameters used for both DTA and TGA analysis are given in Table III.

TABLE III

Experimental Conditions for DTA and TGA Analyses

Parameter	DTA	TGA
Starting temperature	45°C	45°C
Heating Rate	20°C/min.	15°C/min.
Atmosphere	Air at 760° mm	N_2 flow at 60 ml/min.
Reference	Glass beads	-
Sample size	3 mm depth of microtube	10 to 20 mg

Calibration of the DTA instrument was done with the high purity standards listed in Table IV. The readings obtained from the instrument were plotted vs. the actual transition temperatures of the standards. Fig. 15 shows the calibration line obtained.

TABLE IV

CALIBRATION OF DuPONT 900 DTA UNIT

Standard	Transition Temp. (83)	Transition	Instrument Reading
$KClO_4$	299.9°C	Solid-solid	322.0°C
Benzoic Acid	122.4°C	Solid-liquid	131.0°C
Adipic Acid	151.4°C	Solid-liquid	163.0°C
KNO_3	127.7°C	Solid-solid	137.0°C

This calibration line was later used to calculate the transition temperatures of each metal chelate studied.

10.4.1 Determination of Melting Points

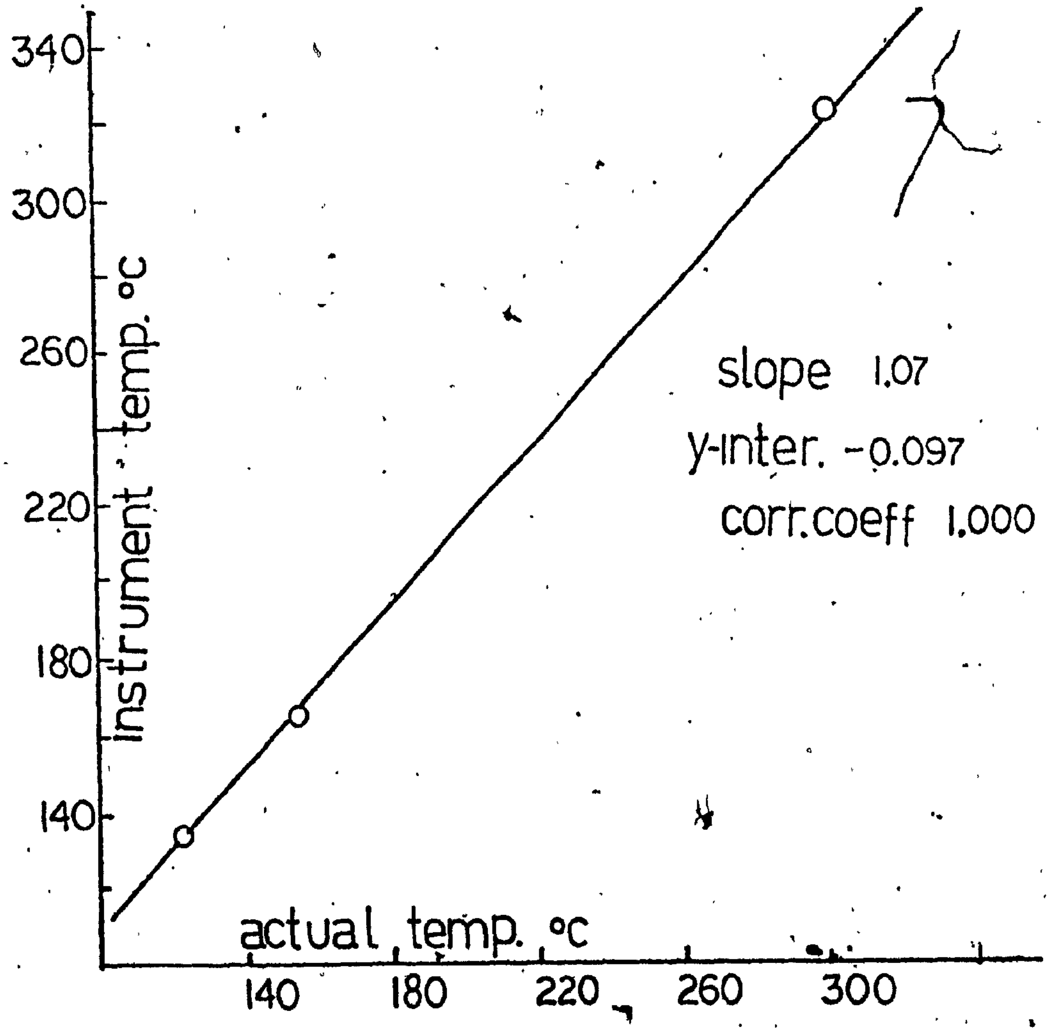
Melting points were determined by using a Gallenkamp melting point apparatus.

10.5.0 UV Spectra

The UV spectra of each $M(DDC)_n$ were obtained in spectrograde solvents (Anachemia Ltd) which included chloroform, methanol and ethanol. The instrument used was a Perkin-Elmer 552 UV/VIS Spectrophotometer. The spectra of most chelates was obtained only in the range 190-390 nm, except

FIGURE 15

CALIBRATION PLOT FOR DuPONT 900 UNIT



for $Ni(DDC)_2$, $Co(DDC)_3$ and $Fe(DDC)_3$, where the visible region of the spectra was also recorded.

The concentration of each sample in the above solvents was kept in the range 1.0×10^{-3} to 3.0×10^{-2} mg/ml. In chloroform these solutions were prepared from concentrated stock solutions (1.00 mg/ml) since the $M(DDC)_n$ are very soluble in chloroform. In the case of alcohols, solutions of about 8 mg of $M(DDC)_n$ in 250 ml of solvent had to be prepared and then diluted as necessary, since the $M(DDC)_n$ are not very soluble in alcohols.

TABLE V

INSTRUMENT PARAMETERS FOR PERKIN-ELMER 552 UV/VIS SPECTROPHOTOMETER

Slit	2.0
Scan Speed	60 nm/min.
Mode	Abs.
Ord max.	Varied appropriately
Ord min.	Varied appropriately
λ range studied	350-190 nm (also 600 to 190 nm)
Recorder speed	60 cm/min.

10.6.0 Preparation of Standard M(DDC)$_n$ and Metal Salt Test Solutions

Standard chloroform solutions of each metal chelate were prepared by dilution of stock solutions of the metal chelates. The solvent used was pesticide grade chloroform (Anachemia). Most of the stock solutions prepared were in the concentration range of 0.50 to 1.000 mg/ml (e.g. 0.1000 ± 0.0002 g/100.0 $\pm$ 0.08 ml) M(DDC)$_n$ in chloroform.

Test solutions were prepared by dilution of aqueous stock solutions of metal salts (usually of 100 ppm or thereabouts) to give the required concentration of metal ion, usually in the low ppm level (1.0 to 10.0 ppm).

Soluble metal salts such as $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, $Zn(NO_3)_2.6H_2O$, $CuSO_4.5H_2O$, $HgCl_2$, $Pb(NO_3)_2$ (all analytical grade reagents) were used for the preparation of metal ion solutions. These reagents were obtained from J.T. Baker Chemical Co. (Baker Analyzed Reagents) or from Fisher Scientific Company (Certified).

Also, some solutions were prepared by using the pure metal, particularly Zn and Cu (certified reagent Fisher Scientific Company) (90), but no significant differences were found when analyses were performed.

10.7.0 Procedure for M(DDC)$_n$ Formation in Sample Solutions (Test Solutions)

(i) Solutions of known low ppm concentration were prepared for each metal ion tested, starting with metal ion stock solutions previously prepared (section 10.6.0).

(ii) Measured volumes (usually 50.0 to 100.0 ml) of the ppm metal ion solution were transferred to a 125 ml separatory funnel and treated with 50 mg of citric acid to prevent formation of metal hydroxides (91,92). The pH was usually kept between 2.6 to 5.0 units.

(iii) The resulting solution was treated with 5.0 to 10.0 ml of 2% (w/v) NaDDC.$3H_2O$ (certified A.C.S. from Fisher Scientific Co.). The solution formed was shaken for about 1.0 min. and the reaction allowed to come to equilibrium.

(iv) The cloudy mixture obtained was generally extracted with four 5.0 ml-portions of chloroform and the extract was diluted to volume in a 25.0 ml volumetric flask. In some cases the solutions were extracted with three 3 ml-portions of chloroform and the extract diluted to volume in a 10.0 ml volumetric flask.

(v) A measured amount of the extract was injected into the gas chromatograph and the peak area of the respective metal chelate measured. At least two injections were made per sample.

10.8.0 HPLC Instrumentation

All the HPLC instrumentation used was from Waters Associates (Milford, MA). A Model 6000A solvent delivery system with a Model U6K universal injector and a Model 440 constant wavelength (254 nm) detector system.

The column used was a stainless steel column 25 cm x 0.46 cm (length x O.D.) packed with LiChrosorb-6, particle size 10 um.

Table VI below shows the experimental parameters used. It should be noted in Table VI that two mobile phases were used; 2% chloroform in cyclohexane and 2% ethylacetate in cyclohexane.

TABLE VI

HPLC CONDITIONS

Pressure limit	4,000 psi
Operating range	0 to 6,000 psi
Mobile phase flow rate	1.0 to 2.0 ml/min.
Detector	UV at λ = 254 nm
Recorder range	10 mv
Recorder speed	1 cm/min.
Sensitivity (attenuation)	0.2 to 0.01
Column dimensions	25 x 0.46 cm
Column packing	LiChrosorb-6, 10 um silica 106-310
Mobile phase	2% $CHCl_3$ in cyclohexane and 2% ethylacetate in cyclohexane

11.0.0 Discussion of Results

11.1.1 Preparation of $M(DDC)_n$ and Their Identification

The modified version of procedures outlined in the literature (33,33A,33B,33C,74,81 & 81A) used in this study gave very satisfactory results for Ni, Cu, Zn, Cd, Hg, Co and Fe. For manganese, however, it was found that $Mn(DDC)_2$ oxidised rapidly to $Mn(DDC)_3$, then to $Mn(DDC)_4$, and finally to MnO_2 which precipitated out of chloroform solution. This problem has been reported previously (29).

The results obtained in the synthesis of each $M(DDC)_n$ are shown in Table VII. The yields obtained were excellent even after recrystallization, being over 90%, an indication that the reaction was quantitative.

Identity of these chelates was confirmed by melting point determination, DTA, TGA, UV spectroscopy and atomic absorption spectroscopy elemental analysis.

The melting points obtained with a melting point apparatus, and as established from DTA results, and the corresponding values reported in the literature are given in Table VIII. There is some disagreement between the literature values of melting points and those obtained in this study using the melting point apparatus. In many cases, however, values reported in the literature differ from source to source, as for example for $Pb(DDC)_2$, $Zn(DDC)_2$ and $Co(DDC)_3$. The reason for these differences in melting points

TABLE VII

PREPARATION OF $M(DDC)_n$ AND YIELDS

$M(DDC)_n$	Reactant Salt mmoles	Grams of Chelate	% Yield (unrecryst)	% Yield (overall) recryst from $ETOH/CHCl_3$
$Ni(DDC)_2$	5.0 mmoles $Ni(NO_3)_2 \cdot 6H_2O$	1.70	95%	92%
$Zn(DDC)_2$	5.0 mmoles $Zn(DDC)_2 \cdot 6H_2O$	1.73	96%	90%
$Cu(DDC)_2$	5.0 mmoles $Cu(SO_4) \cdot 5H_2O$	1.76	98%	93%
$Hg(DDC)_2$	5,0 mmoles $HgCl_2$	2.37	96%	92%
$Pb(DDC)_2$	10.0 mmoles $Pb(NO_3)_2$	4.96	98%	91%
$Cd(DDC)_2$	10.0 mmoles $Cd(NO_3)_2 \cdot 4H_2O$	4.09	98%	95%
$Fe(DDC)_3$	5.0 mmoles $Fe(NO_3)_3 \cdot 9H_2O$	2.49	99.6%	90%
$Fe(DDC)_3$	10.0 mmoles $FeSO_4 \cdot 7H_2O$	3.20	91%	90%
$Co(DDC)_3$	10.0 mmoles $Co(NO_3)_2 \cdot 3H_2O$	4.63	99%	92%

TABLE VIII

$M(DDC)_n$ - MELTING POINTS AND TRANSITION TEMPERATURES, °C

$M(DDC)_n$	DTA Transition Temps.		Melting Point		References
	Major peak	Minor peak	Experimental	Theoretical	
$Ni(DDC)_2$	235	279	233-234	235-236	(17,33B)
$Cu(DDC)_2$	202	240	201-202	201-202, 196	(17,33B)
$Zn(DDC)_2$	180	269	178-179	178-179, 225	(17,33B)
$Cd(DDC)_2$	247	273	247-248	252-253, 254	(17,33B)
$Pb(DDC)_2$	210	-	208-209	209-210, 208	(33B,84)
$Hg(DDC)_2$	135	92	128-130	127-130, 139-141, 138-139	(21,33B,84)
$Co(DDC)_3$	263	273	260-262	263-264, 266	(17,21)
$Fe(DDC)_3$	252	-	248-249	252-255, 252	(17,21)

may be variable degrees of decomposition of the same sample at high temperature.

In order to more reliably characterize the samples prepared elemental analysis was performed to confirm that the chelates contained the metal in question in the expected amount. The analyses were done by atomic absorption spectroscopy. Atomic absorption spectroscopy was also expected to prove that the metal in question was present in each chelate.

The results obtained by using the calibration line method are shown in Table IX. The absorption line used (H.C.L.) and the calibration ppm range is also given in Table IX.

It should be noted that for Fe(DDC)$_3$ the same percent Fe was found regardless of whether Fe(DDC)$_3$ was prepared from Fe(II) or Fe(III) salts. This is consistent with observations made by others (21) that Fe(DDC)$_2$ oxidizes quickly to Fe(DDC)$_3$.

The percent deviations reported in Table IX are in the same range as those found by D'Ascenzo and Wendlandt (19) using mainly titration methods for determination of metal content.

Elemental analysis gave good evidence to indicate that the desired compounds had been prepared. Further confirmatory evidence was obtained from the study of the thermal properties of each M(DDC)$_n$ by DTA and TGA.

TABLE IX

ELEMENTAL ANALYSIS OF M(DDC)$_n$ BY ATOMIC ABSORPTION SPECTROSCOPY

Compound	λ (nm)	% Metal		% Deviation	ppm Range for Calibration Line
		Found Avg ± STD Deviation	Theoretical		
Ni(DDC)$_2$	232.0	16.68±.19	16.53	0.9	1.0 to 5.0
Cu(DDC)$_2$	324.8	17.95±.16	17.65	1.7	1.0 to 5.0
Zn(DDC)$_2$	213.9	17.79±.07	18.06	1.5	0.25 to 1.0
Pb(DDC)$_2$	283.3	41.38±.57	41.13	0.6	5.0 to 25.0
Hg(DDC)$_2$	253.7	40.50±.29	40.35	0.4	50 to 200
Co(DDC)$_3$	240.7	11.44±.24	11.70	2.2	1.0 to 5.0
Fe(DDC)$_3$	248.3	11.28±.40	11.16	1.1	1.0 to 5.0
Cd(DDC)$_2$	228.8	27.78±0.15	27.49	0.5	0.5 to 2.5

11.1.2 Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

DTA and TGA were carried out on each sample. The TGA curves for each metal chelate are shown in Figs. 16 to 19. The DTA transition peaks are reported in Table VIII. In most cases DTA showed a major peak due to fusion (melting). This major peak has been identified by D'Ascenzo and Wendlandt (19,20). The minor peaks obtained after the fusion point were attributed by these authors (19) to partial volatilization of the sample. In the case of $Fe(DDC)_3$ more than one minor peak was observed (Fig. 19B). This was reported by D'Ascenzo and Wendlandt (20), as being due to decomposition of the sample, and to sample loss by splattering. In most cases, the thermograms obtained were consistent with what was reported by D'Ascenzo and Wendlandt. However, in the case of $Hg(DDC)_2$ it was found that there was a minor peak before the fusion point. This additional peak is believed to be due to a crystal transition of the Hg complex. This would be consistent with the observation by Iwasaky (85) that $Hg(DDC)_2$ crystallizes in both an α-form and a β-form, based on x-ray studies. For all the chelates studied, the TGA curves (Figs. 16 to 19) showed one step weight losses with incomplete volatilization. In general, the complexes showed an initial inflection point of 220^0 to 300^0C. The fact that the TGA curves did not return to zero percent

FIGURE 16

THERMAL ANALYSIS OF Cu AND Ni

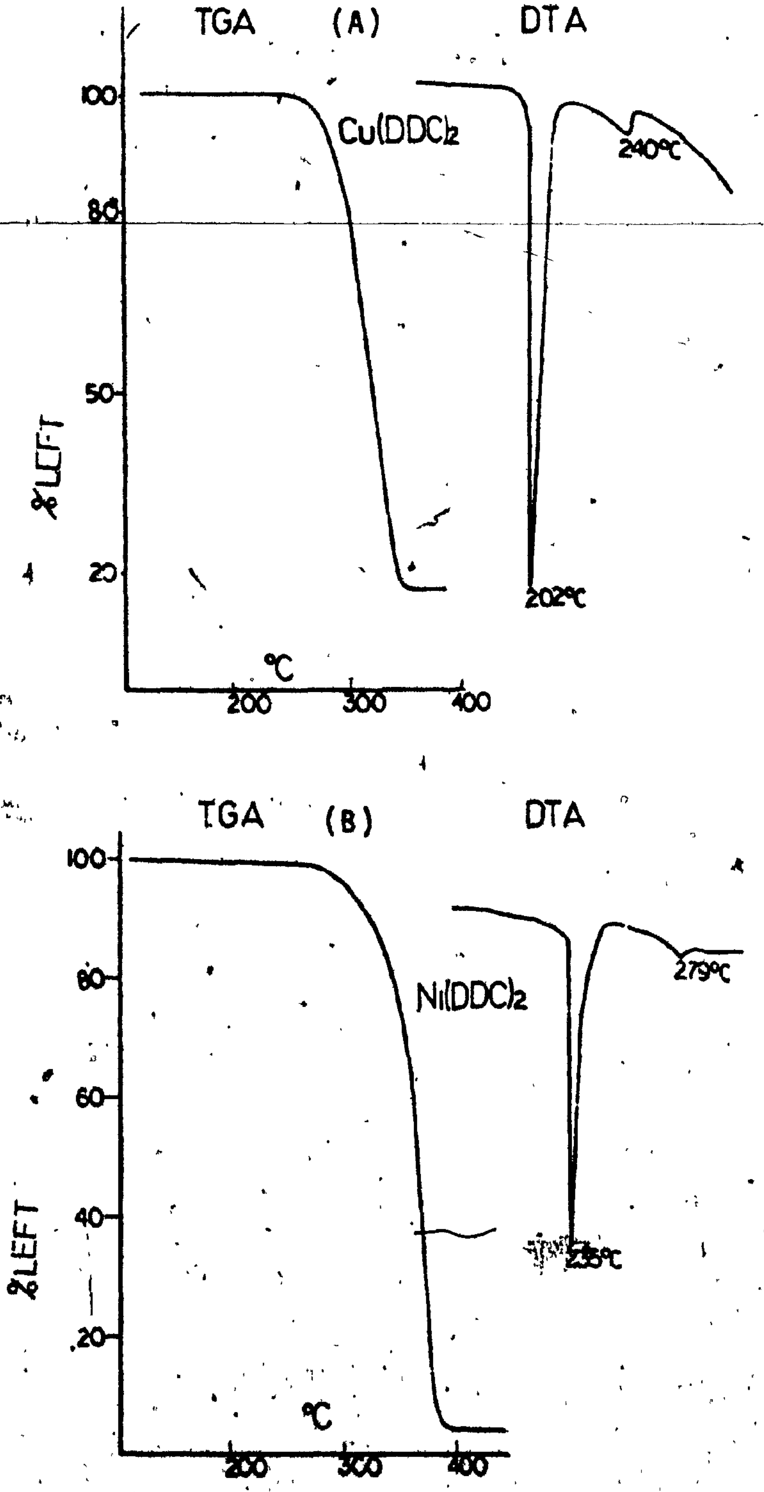


FIGURE 17

THERMAL ANALYSIS OF Pb AND Zn

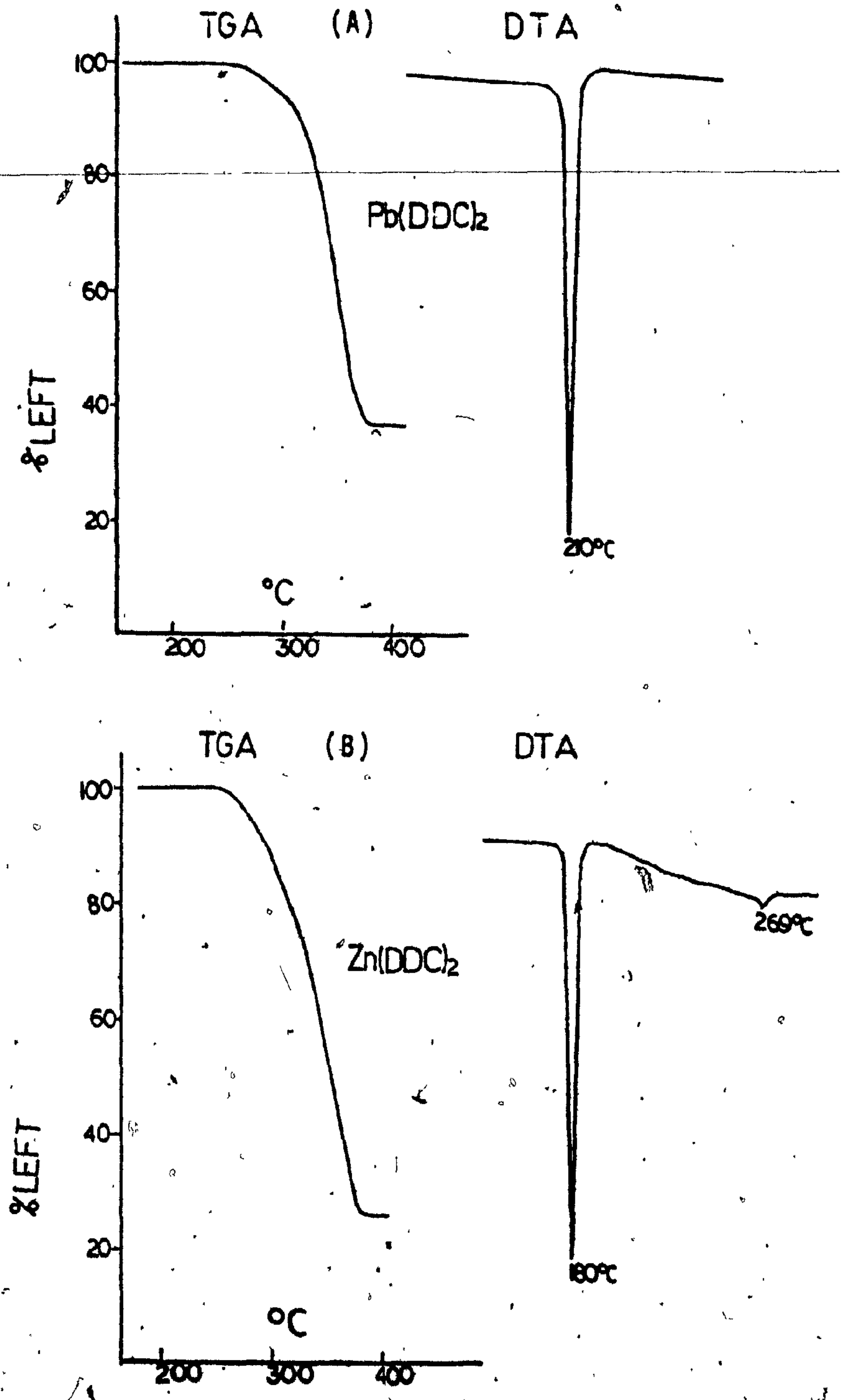


FIGURE 18

THERMAL ANALYSIS OF Cd AND Hg

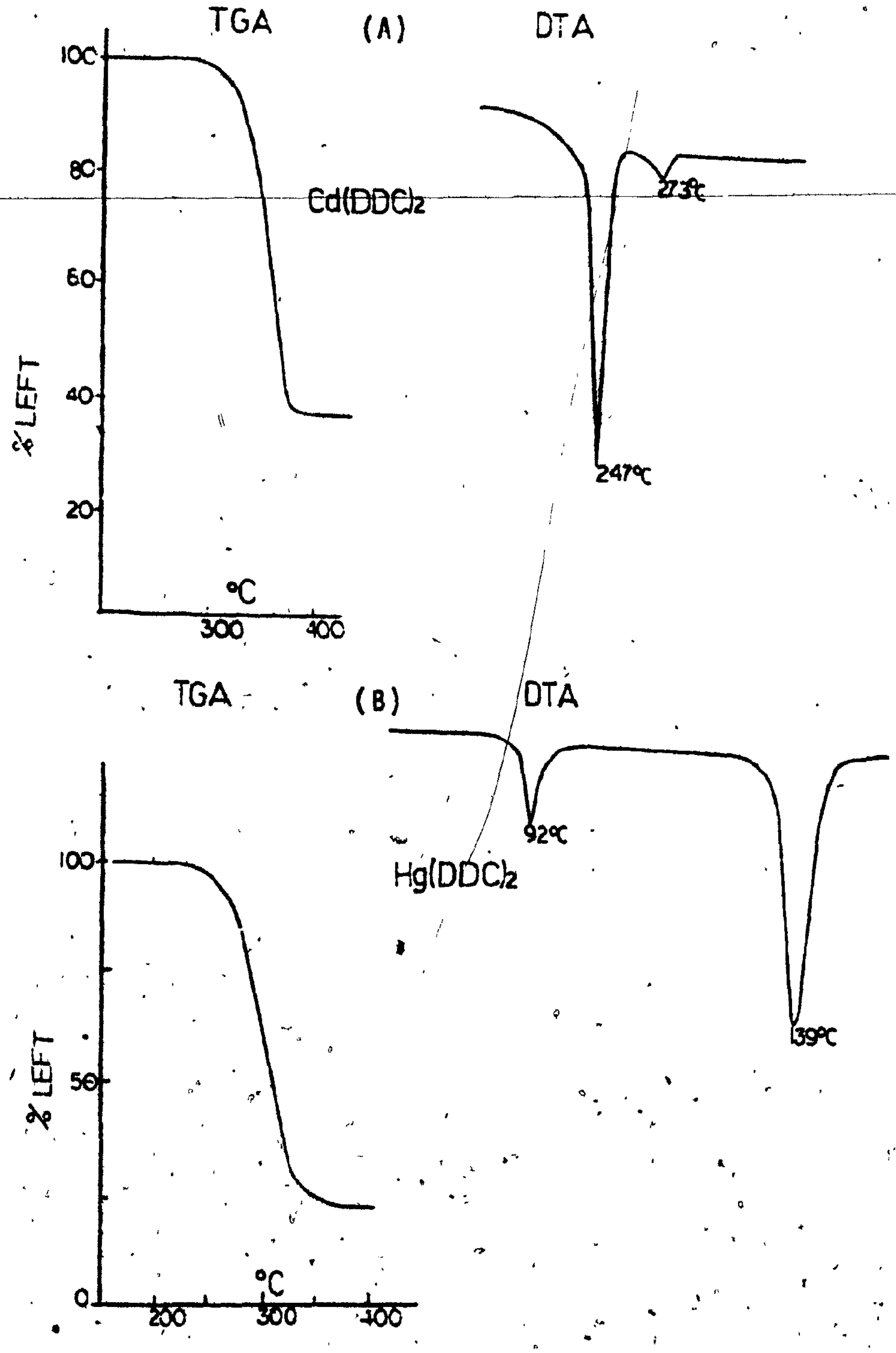
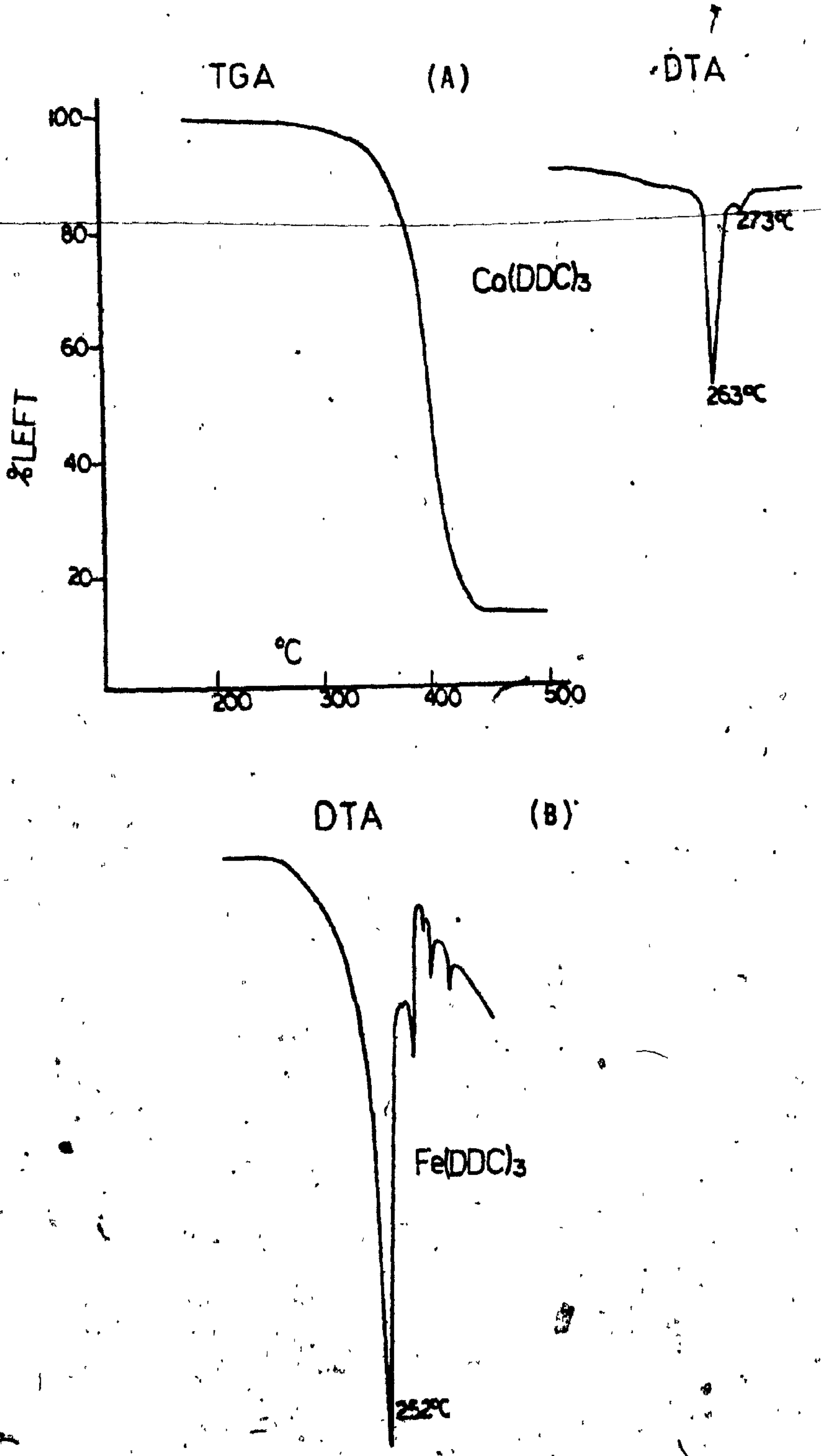


FIGURE 19

THERMAL ANALYSIS OF Co AND Fe



indicated that there was some thermal decomposition which occurred above 220^{o}C for most samples. Consideration of the literature showed that Sceney et al. (86) have studied the decomposition of Cu(DDC)$_2$ by DTA, TGA and GC/MS techniques. It was shown in their work that Cu(DDC)$_2$ decomposes to Cu_2S, CS_2, Et_2NH and $(Et_2N)_2CS$ in a nitrogen atmostphere when heated to 350^{o}C. This might be the case for other M(DDC)$_n$ as well and could be the explanation for our findings.

These results are important considerations to be taken into account when selecting chromatographic conditions for analysis of these compounds since decomposition of the sample will reduce its detectability, reductions in detector response for the chelates occurring because of sample losses.

It could be also concluded from the TGA curves that Ni(DDC)$_2$ and Co(DDC)$_3$ should take longer times to elute from a GC column than any other M(DDC)$_n$ since they appear to be the least volatile. All other samples of M(DDC)$_n$ studied appeared to have similar volatilities to one another.

11.1.3 UV Spectra

Atomic absorption spectroscopy (section 11.1.1) confirmed the presence of the expected metal atom in each chelate. In the same way, UV spectra were expected to confirm the presence of the DDC ligand. A few literature references are available. UV spectra have been used by some investigators (24,33B,37,88,89) to characterize $M(DDC)_n$ chelates. The UV spectra of $Ni(DDC)_2$, $Cu(DDC)_2$, $Co(DDC)_3$ and $Zn(DDC)_2$ have been published by Radecki et al. (37) and Uden et al. (89).

Figs. 20A to 20G show the spectra for the $M(DDC)_n$ chelates prepared in this study. The spectra obtained for Ni, Cu, Co and Zn chelates were in good agreement with those reported in the literature (37,89).

The UV spectra of $Fe(DDC)_3$, $Cd(DDC)_2$, $Hg(DDC)_2$ and $Pb(DDC)_2$ have not been previously reported as such. However, some of their absorption wavelengths along with a few values for molar extinction coefficients are available (24,33B,87,88).

A comparison of absorption bands recorded in different solvents for the $M(DDC)_n$, with those reported in the literature, is given in Table X. Consideration of the data clearly indicated that the expected metal chelates had been successfully prepared.

It is interesting to note that R. Dingle (88) pointed out that salts of the DDC ligand dissolved in polar solvents such as water, ethanol, etc., giving a UV spectrum that shows three strong bands (290 nm, 258 nm and 206 nm), as well as

FIGURE 20(A)

UV SPECTRA OF $Cd(DDC)_2$ IN DIFFERENT SOLVENTS

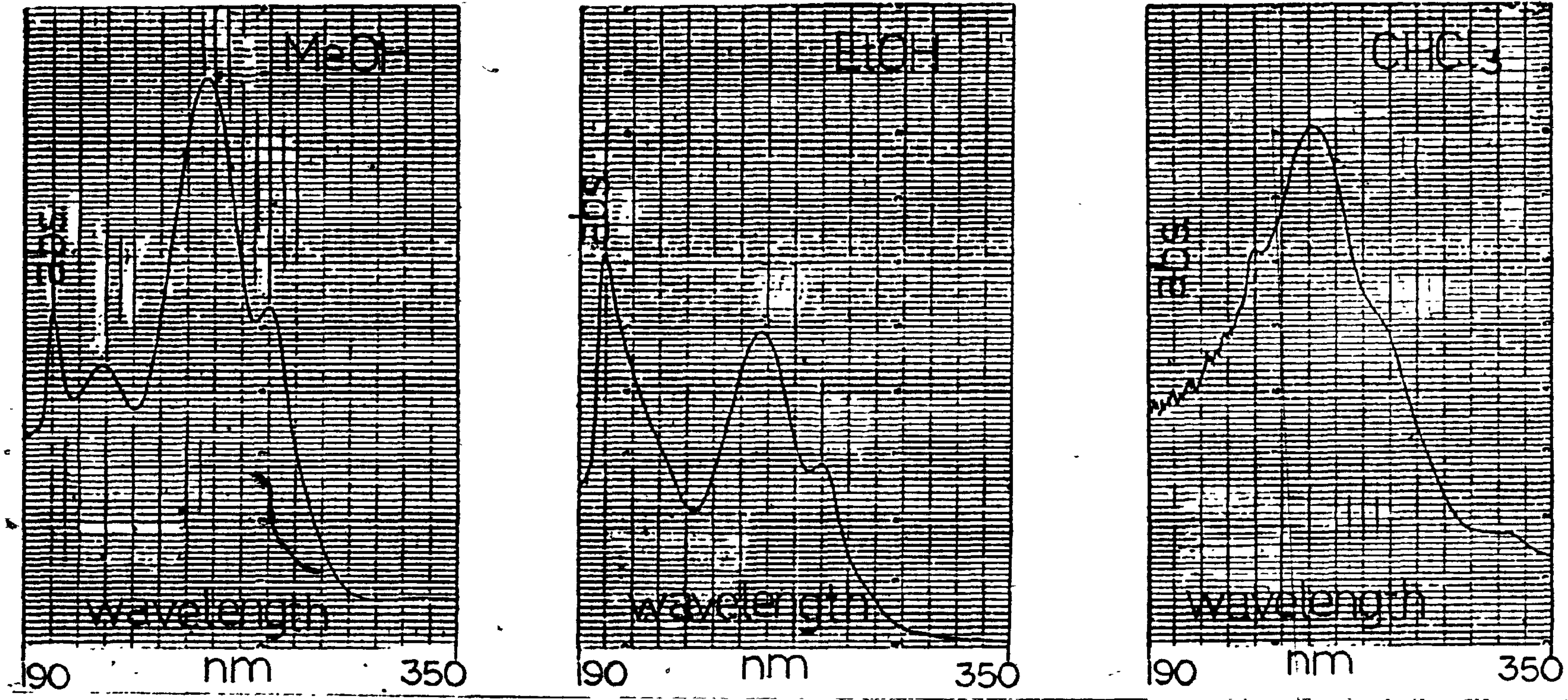


FIGURE 20(B)

UV SPECTRA OF $Zn(DDC)_2$ IN DIFFERENT SOLVENTS

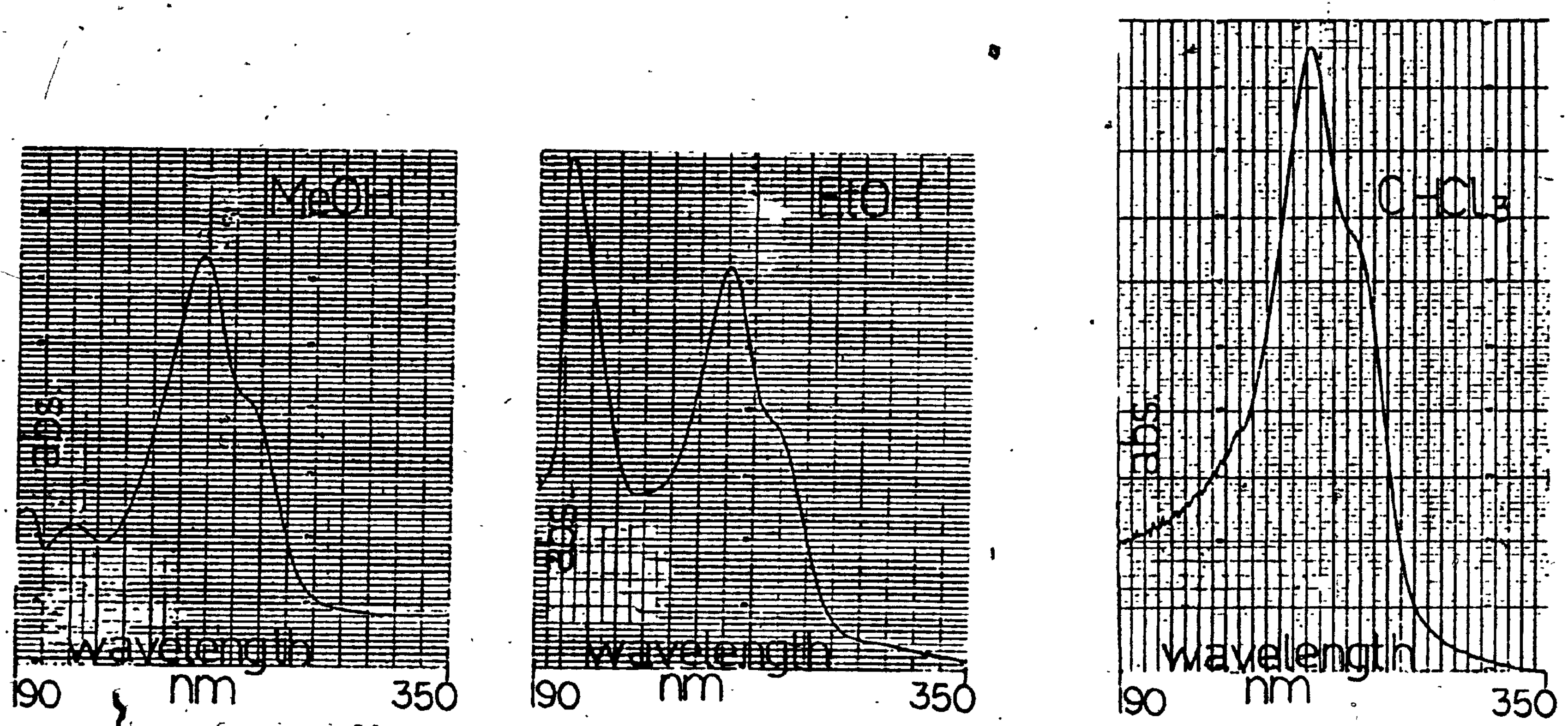


FIGURE 20(C)

UV SPECTRA OF $Cu(DDC)_2$ IN DIFFERENT SOLVENTS

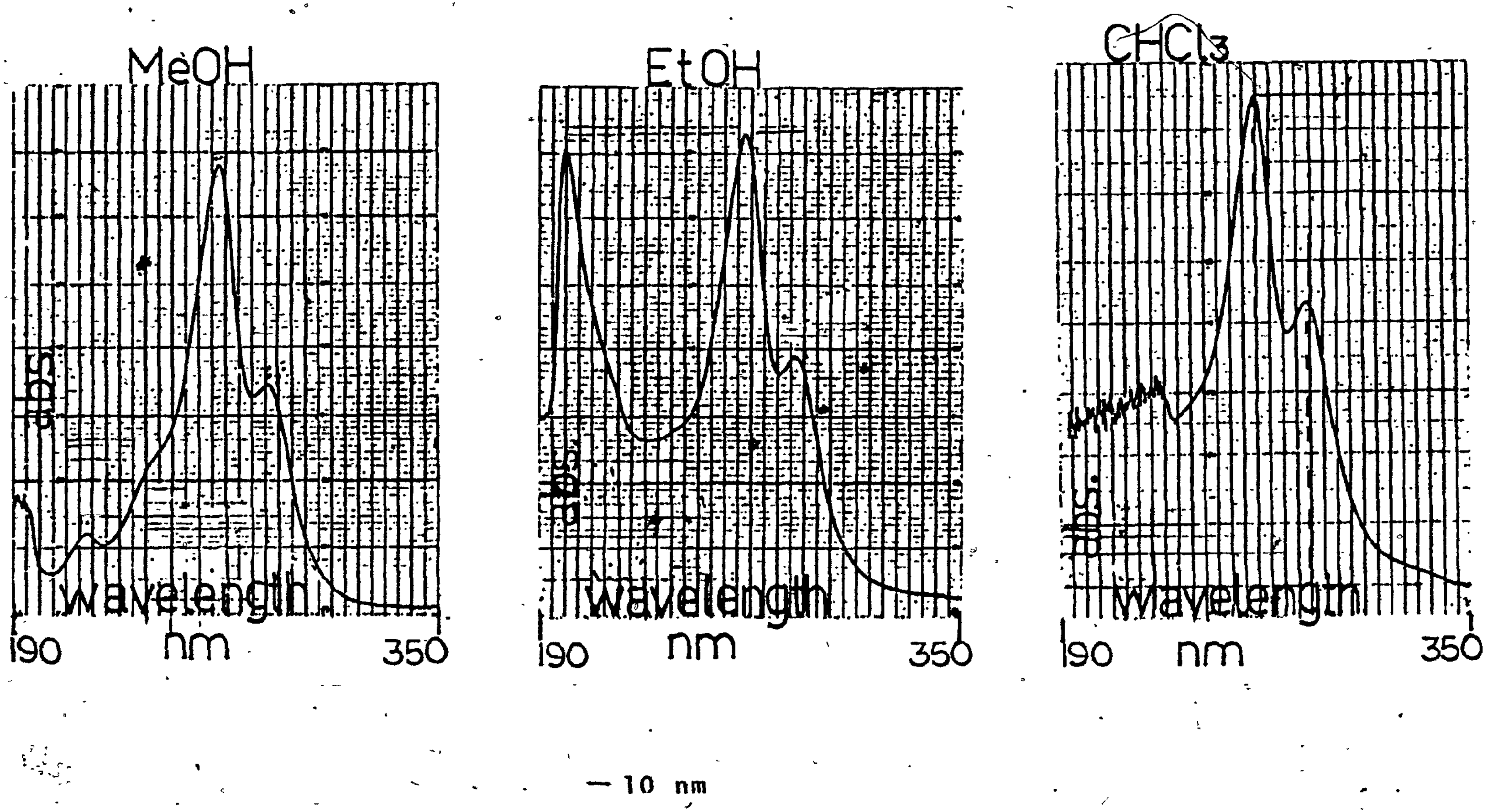


FIGURE 20(D)

UV SPECTRA OF $Hg(DDC)_2$ IN DIFFERENT SOLVENTS

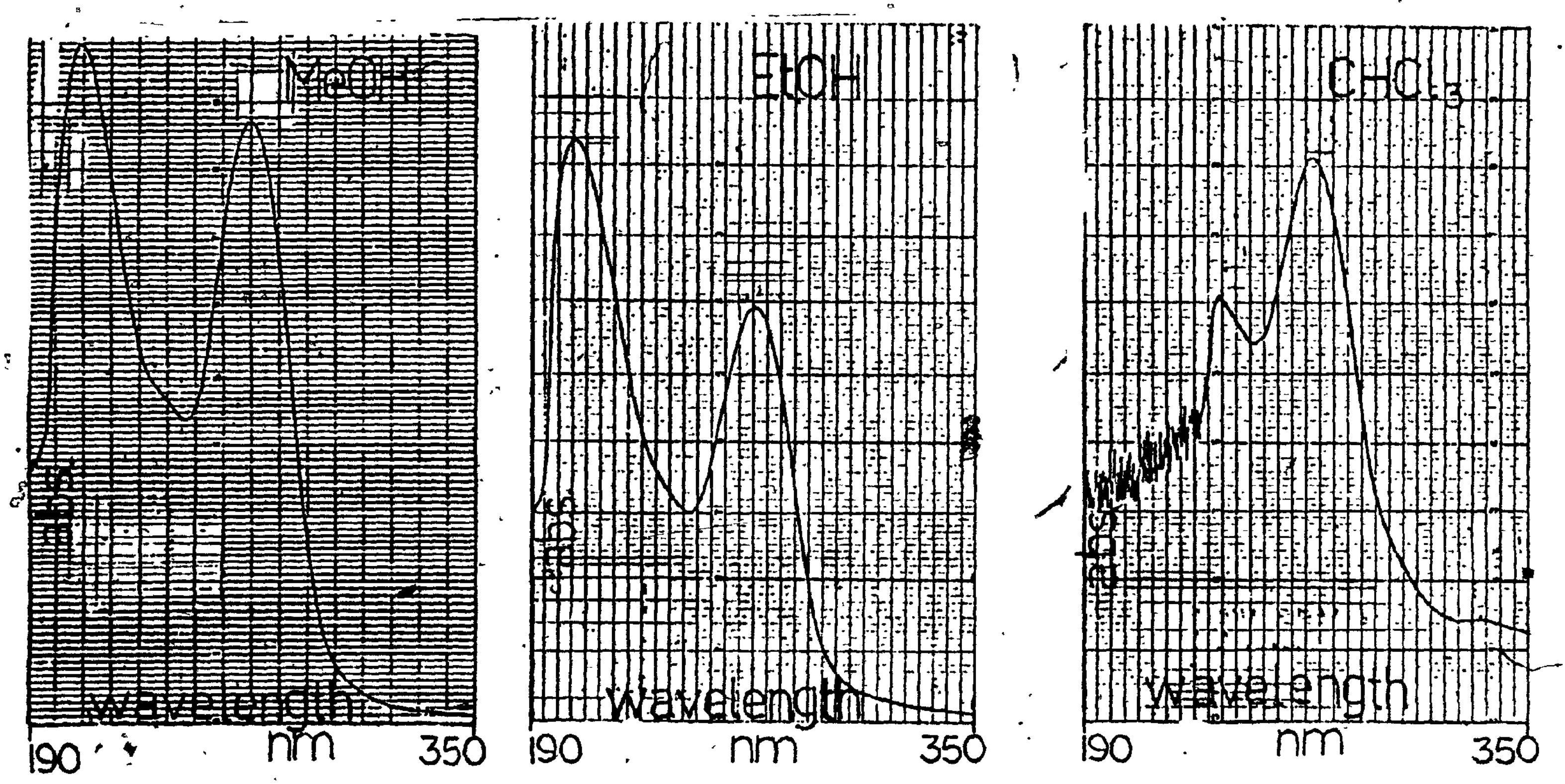


FIGURE 20(E)

UV SPECTRA OF Fe(DDC)$_3$ IN DIFFERENT SOLVENTS

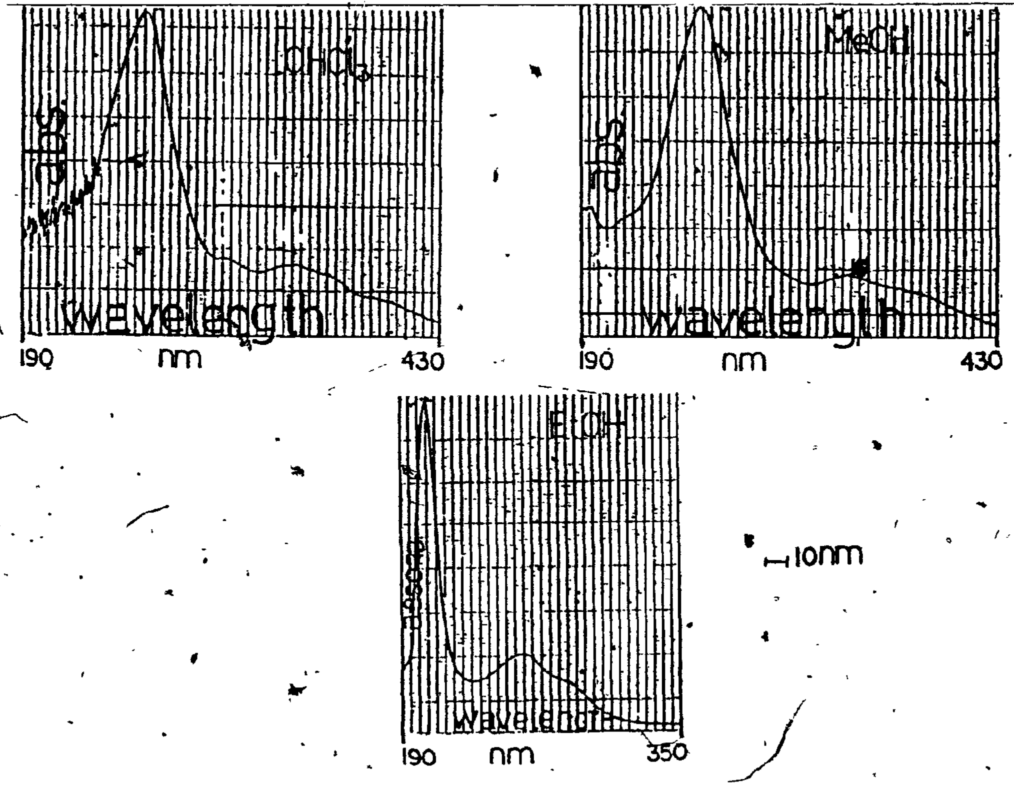


FIGURE 20(F)

UV SPECTRA OF $Co(DDC)_3$ IN DIFFERENT SOLVENTS

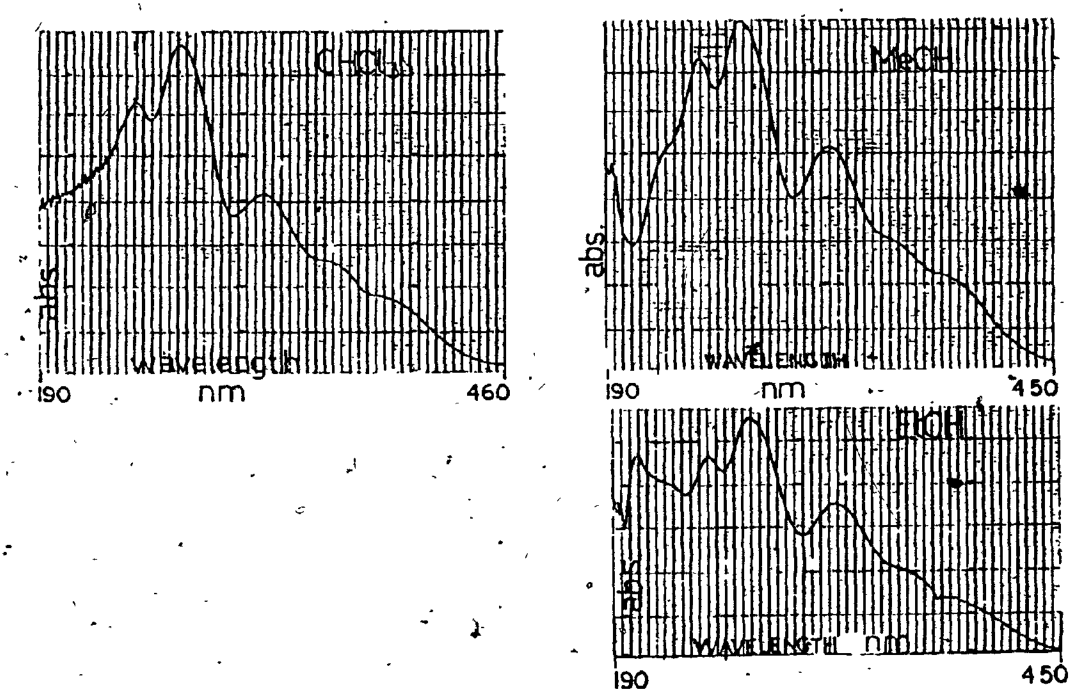
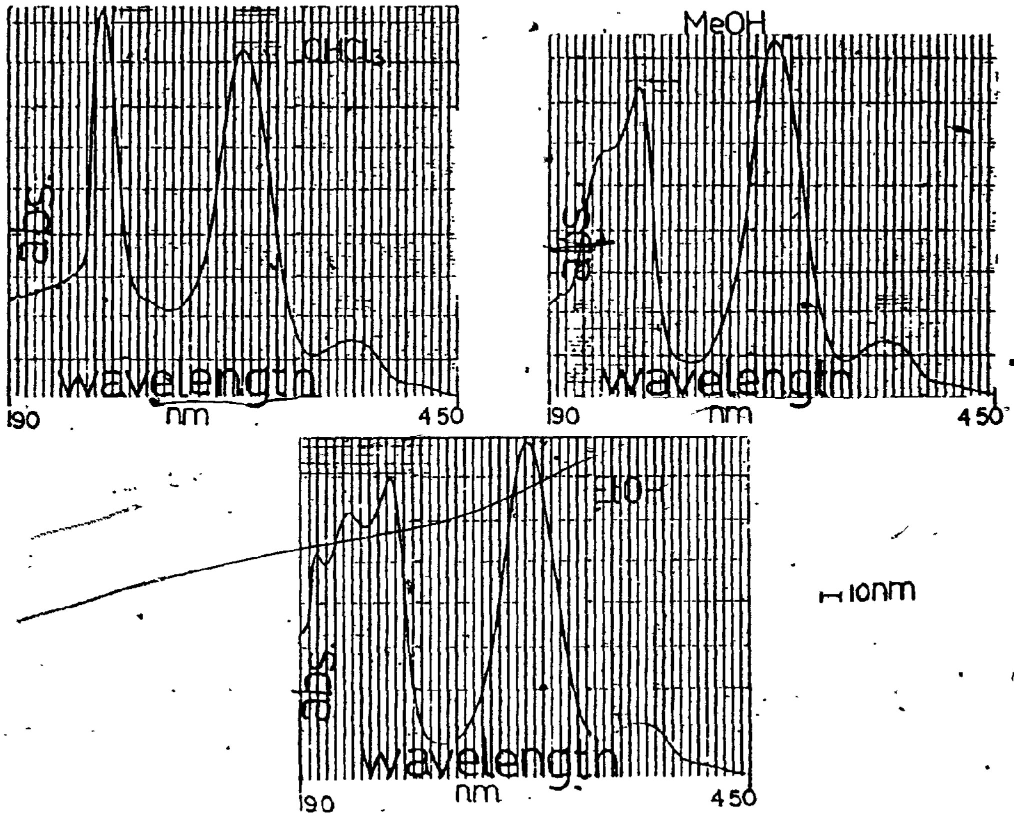


FIGURE 20(G)

UV SPECTRA OF Ni(DDC)$_2$ IN DIFFERENT SOLVENTS



as weak, solvent sensitive band at about 357 nm. It was suggested by Dingle that these bands are due to intraligand transitions (probably $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$). Nikolov et al. (87) empirically assigned bands II and III listed in Table X to the transition $\pi \rightarrow \pi$ and $n \rightarrow \pi^*$, respectively, for $Zn(DDC)_2$, $Cd(DDC)_2$ and $Hg(DDC)_2$. Transition metal chelates (Co, Ni and Fe) have additional bands in the visible range. They are believed to be due to transitions involving d-orbitals, but have not been assigned to a particular d-d transition.

TABLE X

UV ABSORPTION OF $M(DDC)_n$

Compound		Solvent						Literature Values	
		EtOH		MeOH		$CHCl_3$			
		λ_{max} nm	ϵ	λ_{max} nm	ϵ	λ_{max} nm	ϵ	λ_{max} nm ($CHCl_3$)	ϵ
$Ni(DDC)_2$	I	200.2	21,670						
	II	219.6	25,730	(220.0)*					
	III	244.0	28,800	243.5	28,484	244.6	33,700	246.9	33,700
	IV	322.0	32,100	320.8	32,480	325.2	30,100	327;322.6	30,100
	V	388.8	5,100	382.0	5,240	388.8	5,220	388	5,220
$Cu(DDC)_2$	I	202.0	31,450						
	II	223.0		218.7	5,620				
	III	268.4	32,320	268.6	30,280	269.0	29,927	269;270	30,000
	IV	287.2	17,300	286.8	15,603	288.0	17,284		

TABLE X (continued)

UV ABSORPTION OF $M(DDC)_n$

Compound		EtOH λ_{max} nm	EtOH ϵ	MeOH λ_{max} nm	MeOH ϵ	$CHCl_3$ λ_{max} nm	$CHCl_3$ ϵ	Literature Values λ_{max} ($CHCl_3$) nm	Literature Values ϵ
$Cd(DDC)_2$	I	200.8	12,000	200.6	15,335				
	II	(220)		220.4	12,300				
	III	258.4	9,530	258.7	27,600	263.0	42,500	265	45,000
	IV	280.5	5,560	279.8	14,700	284.0	22,307		
				(335)		(335.0)			
$Zn(DDC)_2$	I	201.6	23,457	213.6	3,800				
	II	260.2	18,457	259.0	16,076	265.0	32,692	260 (EtOH)	17,000
	III	(278)		(275.0)		281.0	20,709	285	21,200
	IV	(315)							
$Hg(DDC)_2$	I	206.7	45,700	211.6	29,500				
	II	(240.0)		(240.0)		243.0	24,280	243	13,183
	III	272.0	32,356	270.8	26,000	275.0	33,065	275	31,800;33,113
	IV					335.0	5,780	340	1,000

TABLE X (continued)

UV ABSORPTION OF M(DDC)$_n$

Compound		Solvent						Literature Values (CHCl$_3$)	
		EtOH		MeOH		CHCl$_3$			
		λ_{max} nm	ϵ	λ_{max} nm	ϵ	λ_{max} nm	ϵ	λ_{max} nm	ϵ
Pb(DDC)$_2$	I	201.3	29,060	203.8	24,000				
	II	228.4	21,280	(230)					
	III	258.5	22,000	259.3	34,200	260.0	40,298		
	IV	(298)	7,667	298.0	10,230	299.0	11,922	292	11.100
Co(DDC)$_3$	I	205.5	8,300						
	II	247.1	8,300	244.0	49,700	246.7	36,500		
	III	269.9	28,000	268.0	55,700	272.2	44,570		
	IV	322.8	6,300	319.0	35,000	319.8	24,300	323	23,300
	V	(360)		(360)		355.0	15,000	360	12,000
	VI	(390)		(390)		385.0	10,000	393	9,000

TABLE X (continued)

UV ABSORPTION OF M(DDC)$_n$

Compound		Solvent						Literature Values	
		EtOH		MeOH		CHCl$_3$		(CHCl$_3$)	
		λ_{max} nm	ϵ	λ_{max} nm	ϵ	λ_{max} nm	ϵ	λ_{max} nm	ϵ
Fe(DDC)$_3$	I	205.3	36,504	205.7					
	II	259.7	10,074	261.2	37,826	263.0	30,532		
	III			(347.2)	8,830	(343)	9,565	346	9,000
	IV					(389)	6,924	(389)	7,000
	V					(308)	10,011		

* Shoulders are in parenthesis.

11.2.0 Gas Chromatography of $M(DDC)_n$

11.2.1 Preliminary Experiments

Preliminary work was carried out with the three columns described in Table XI.

TABLE XI

Initial Columns Tested

Packing	Dimensions (L x O.D)	Tubing Material
5% OV-101 on CW-AW-DMCS	50 cm x $^1/_8$"	Stainless Steel
3% SE-30 on GC-HP	50 cm x $^1/_8$"	Stainless Steel
5% OV-101 + 5% QF-1 on GC-Q	60 cm x $^1/_8$"	Stainless Steel

These columns were used in order to:

(a) Find the conditions under which each $M(DDC)_n$ could be chromatographed most successfully.

(b) Establish the degree of linearity of plots of response (peak area) vs amount of $M(DDC)_n$ injected (ng or ug).

(c) Develop conditions for the separation of a mixture of a few $M(DDC)_n$.

The columns listed were the first selected because their use has been reported previously (15,17,18,32,34,35,37). They had been used successfully in the separation of a small number of some of the metal chelates of interest in this project (mainly, Ni, Cu and Zn chelates).

11.2.1 1.5% OV-101 on CW-AW-DMCS (50 cm x $^1/_8$" Stainless Steel, s.s.)

The results obtained using this column are given in Table XII for chelates injected individually. This data was used to select potentially useful temperatures for separation of mixtures.

Figs. 21A to 21B show that resolution was poor when separation was attempted of a mixture of Ni, Cu, Cd, Pb and Zn and was inadequate for a mixture of only Zn, Cu and Ni.

Fig. G-I and Fig. G-II (Apendix I) illustrate the detector response for injection of different amounts of sample. At the temperatures used good linearity was observed. In fact, on all the columns that were found to be useful for GC separation of $M(DDC)_n$, linearity of response was satisfactory. Linear correlation coefficients were usually found to be better than 0.99.

It was found that metal chelates like $Hg(DDC)_2$, $Pb(DDC)_2$ and $Cd(DDC)_2$ interacted with the column and decomposed. The first injection of the sample gave a distorted peak. As more injections were made peak shapes improved. This is shown in Fig. 22.

Attempts were made to analyze $Fe(DDC)_3$ and $Mn(DDC)_3$ but these compounds decomposed on the column. In fact, they were later found to decompose on all the columns that were studied. $Fe(DDC)_3$ probably reacted with the support or the

TABLE XII

RESULTS ON 5% OV-101 ON CW-AW-DMCS (50 cm x $^1/_8$")*

Compound	Ret. Time (min)	Col. Temp.	Sample Size (ug)	$Y_{int.}$ (mm^2)	Calibration Curve Regression Coefficients Slope(mm^2/ug)	Corr. Coefficient
$Ni(DDC)_2$	4.2	240°C	0.29-1.45	-129	724	0.997
$Cu(DDC)_2$	3.5	230°C	0.45-1.50	-203	700	0.997
$Zn(DDC)_2$	2.2	230°C	0.29-0.75	-81.5	400	0.996
$Pb(DDC)_2$**	4.4	245°C	2.04-5.10	-264	295	0.998
$Hg(DDC)_2$**	5.2	230°C	1.02-5.10	-252	363	0.998
$Cd(DDC)_2$**	4.3	235°C	0.65-1.60	-296	564	0.999
$Co(DDC)_3$	8.5	250°C	1.02-4.08	19.0	231	0.997

* Injector/detector temperature was 300°C.

** Some decomposition was observed for these compounds.

FIGURE 21(A)

SEPARATION OF Ni, Cu AND Zn ON 5% OV-101 ON CW-AW-DMCS (50 cm x 1/8" S.S.)

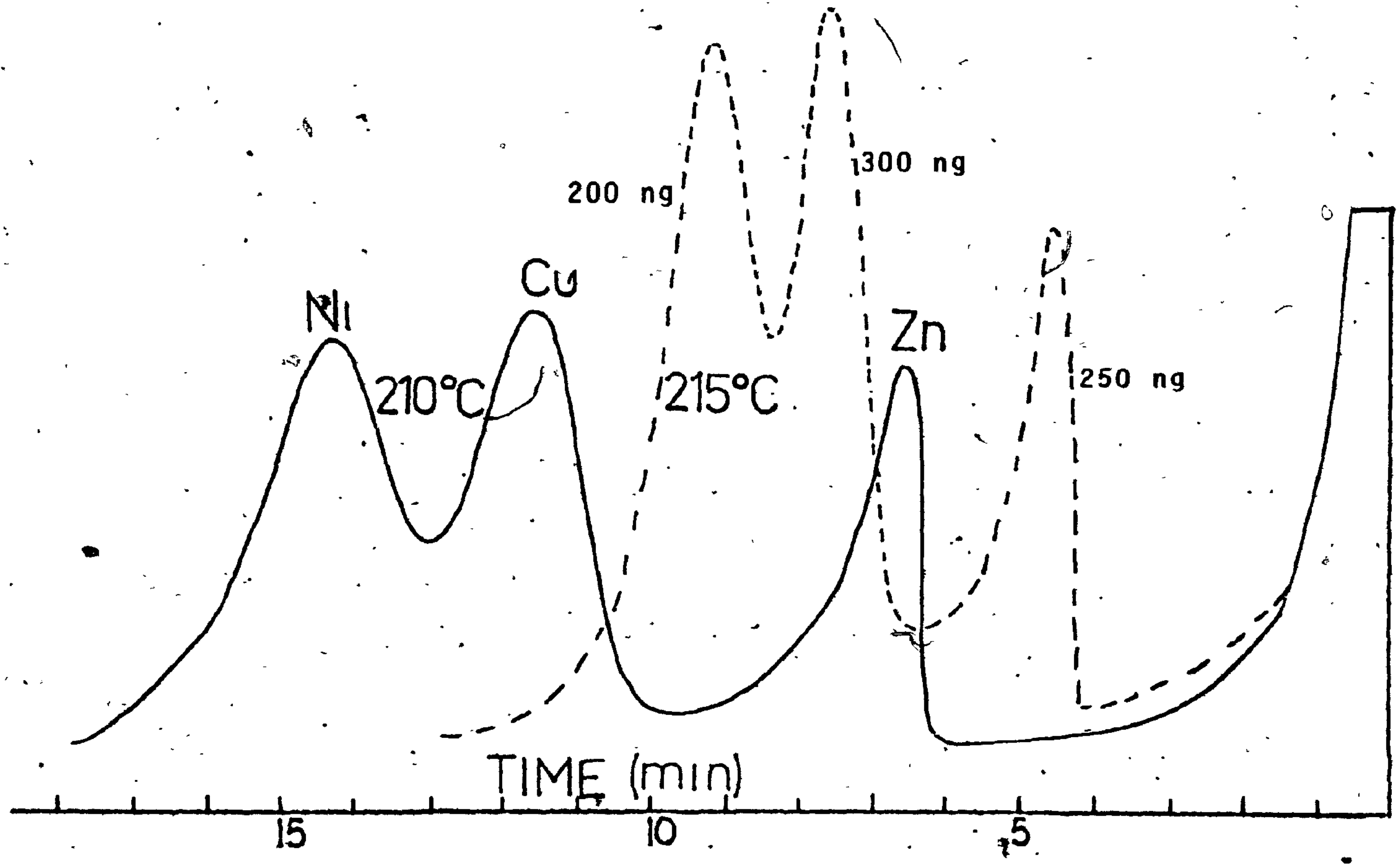


FIGURE 21(B)

SEPARATION ON 5% OV-101 ON CW-AW-DMCS (50 cm x 1/8" S.S.)

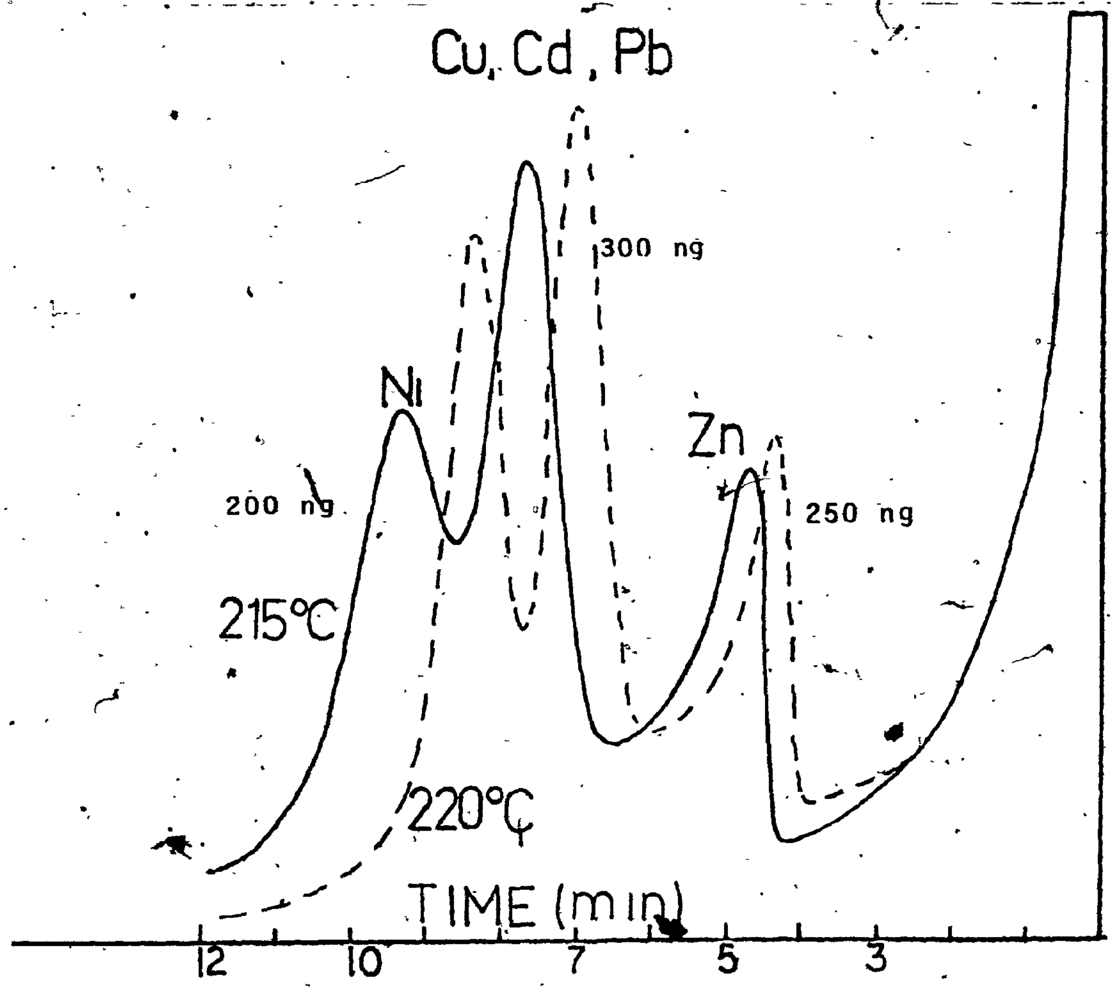
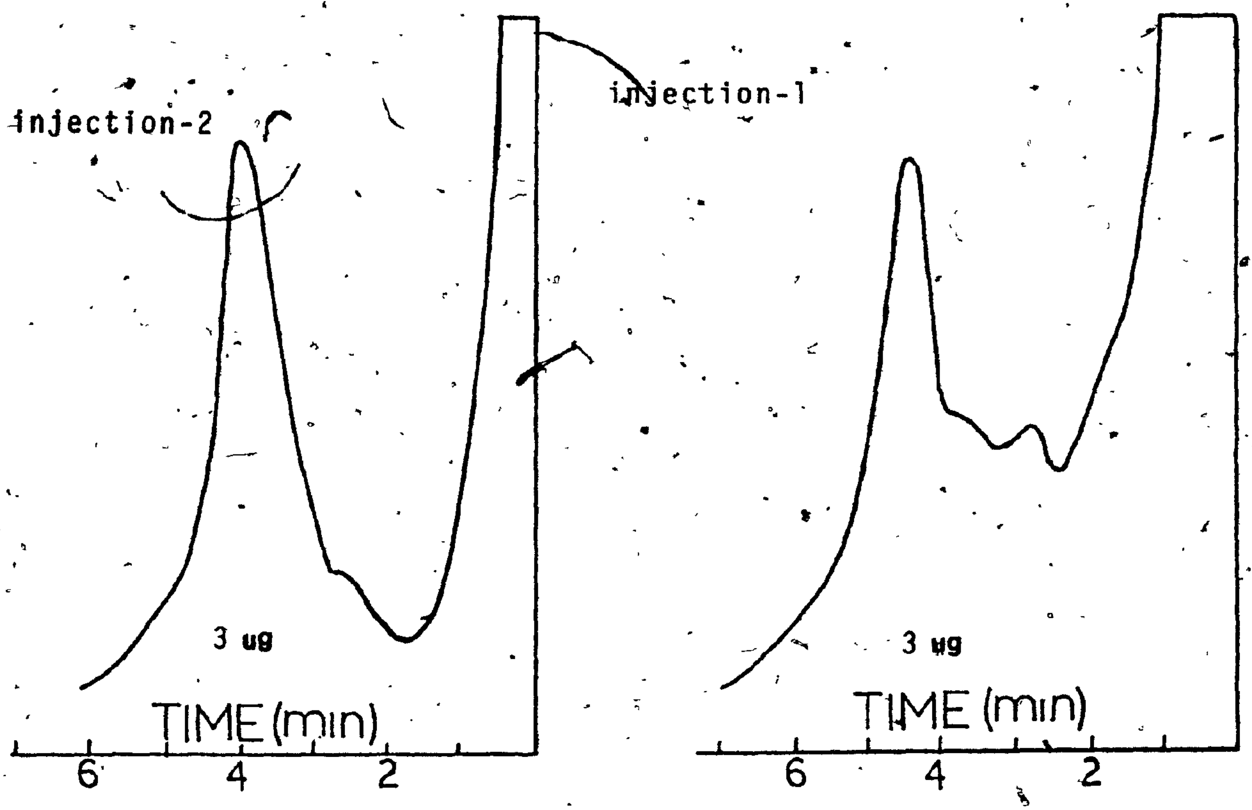


FIGURE 22

REPEATED INJECTIONS OF $Pb(DDC)_2$

5% OV-101 ON CW-AW-DMCS (50 cm x 1/8" S.S.)

245°C



metal surface of the tubing used. $Mn(DDC)_3$ decomposed even before GC was attempted since in most cases a precipitate was obtained when the sample in chloroform solution was stored at low temperatures, 0^oC to -5^o.

It is not surprising that at the column temperatures used, between 230^oC and 250^oC, and the injection port-detector temperature of 260^oC to 300^oC, decomposition occurred in some cases. It was to be expected based on the TGA results and Sceney et al.'s work (86). The fact that only one chromatographic peak ~~is~~ observed for most $M(DDC)_n$ chelates suggests that the decomposition products predicted by Sceney et al. (86) must be eluted with the solvent peak, or, are not volatile enough to be eluted from the column, or are not detected by FID. According to Sceney et al.,

$$2Cu(DDC)_2 \xrightarrow{\Delta} 3CS_2 + 2Et_2NH + (Et_2N)_2S + Cu_2S$$

CS_2, Et_2NH and $(Et_2N)_2S$ are all very volatile and would be expected to elute with the solvent peak. It is clear that such decomposition will not present a problem as far as separation is concerned but it will limit the minimum concentration of $M(DDC)_n$ that can be measured.

II.2.1.2 3% SE-30 on CG-HP (50 cm x $^1/_8$" Stainless Steel)

The results were similar to those obtained

TABLE XIII

DATA OBTAINED ON 3% SE-30 ON CG-HP (50 cm x $^1/_8$")*

Compound	Ret. Time (min)	Col. Temp °C	Sample Size (μg)	Calibration Curve Regression Coefficients $Y_{int.}$ (mm²)	Calibration Curve Regression Coefficients Slope mm²/μg)	Calibration Curve Regression Coefficients Corr. Coefficient
$Ni(DDC)_2$	4.0	245	0.25-1.16	-82.0	626	0.995
$Cu(DDC)_2$	3.2	245	0.50-2.04	-47.0	290	0.999
$Zn(DDC)_2$	2.1	245	0.60-1.20	-186	379	0.997
$Pb(DDC)_2$**	5.5	240	3.03-7.07	-268	198	0.999
$Hg(DDC)_2$**	3.7	245	1.04-4.08	-276	219	0.990
$Cd(DDC)_2$	2.9	245	1.15-3.45	-412	532	0.997
$Co(DDC)_3$	5.6	270	0.52-3.12	-140	467	0.999

* Injector/detector temperature was 300°C.

** Sample decomposition was observed for these compounds.

with 5% OV-101. This was reasonable since these liquid phases have similar polarities. Any differences would have been due to the nature of the support and chromatographic conditions, like column temperature, flow rate, etc. Results are summarized in Table XIII. Some decomposition occurred for $Pb(DDC)_2$ and $Hg(DDC)_2$ as is illustrated for $Pb(DDC)_2$ in Fig. 23.

Plots of response vs. amount injected gave linear relationships as shown on Figs. G-III to G-V (Appendix I).

An attempt at separation of synthetic mixtures of these chelates at 240°C failed because of poor resolution. At lower temperatures peaks were flat and exhibited tailing.

11.2.1.3 5% OV-101 + 5% QF-1 on Gas Chrom. Q (60 cm x $^1/_8$" Stainless Steel)

The results shown in Table XIV were obtained. On this column $Cd(DDC)_2$, $Pb(DDC)_2$ and $Hg(DDC)_2$ showed decomposition as shown in Fig. 24 for Hg and Pb. In the case of $Cd(DDC)_2$ and $Hg(DDC)_2$ the decomposition problem was not too serious. After a few repeated injections only one peak was obtained on a regular basis for each compound. $Pb(DDC)_2$, however, continued to give two peaks. This effect might have been due to the support or tubing or both.

Plots of peak area versus amount of sample injected were linear as shown in Figs. G-VI to G-VII (Appendix I).

FIGURE 23

DECOMPOSITION OF $Pb(DDC)_2$ ON 3% SE-30 ON CG-HP (3 INJECTIONS) AT 240°C (50 cm x 1/8" S.S.)

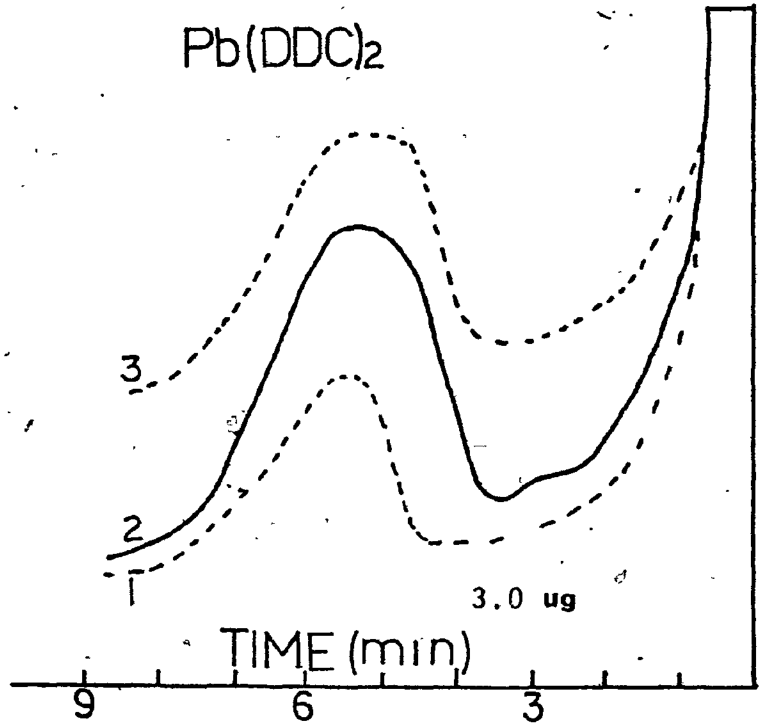


FIGURE 24

DECOMPOSITION OF $Pb(DDC)_2$ AND $Hg(DDC)_2$ ON 5% OV-101 + 5% QF-1 ON GC-Q (60 cm x 1/8" S.S.) AT 235°C

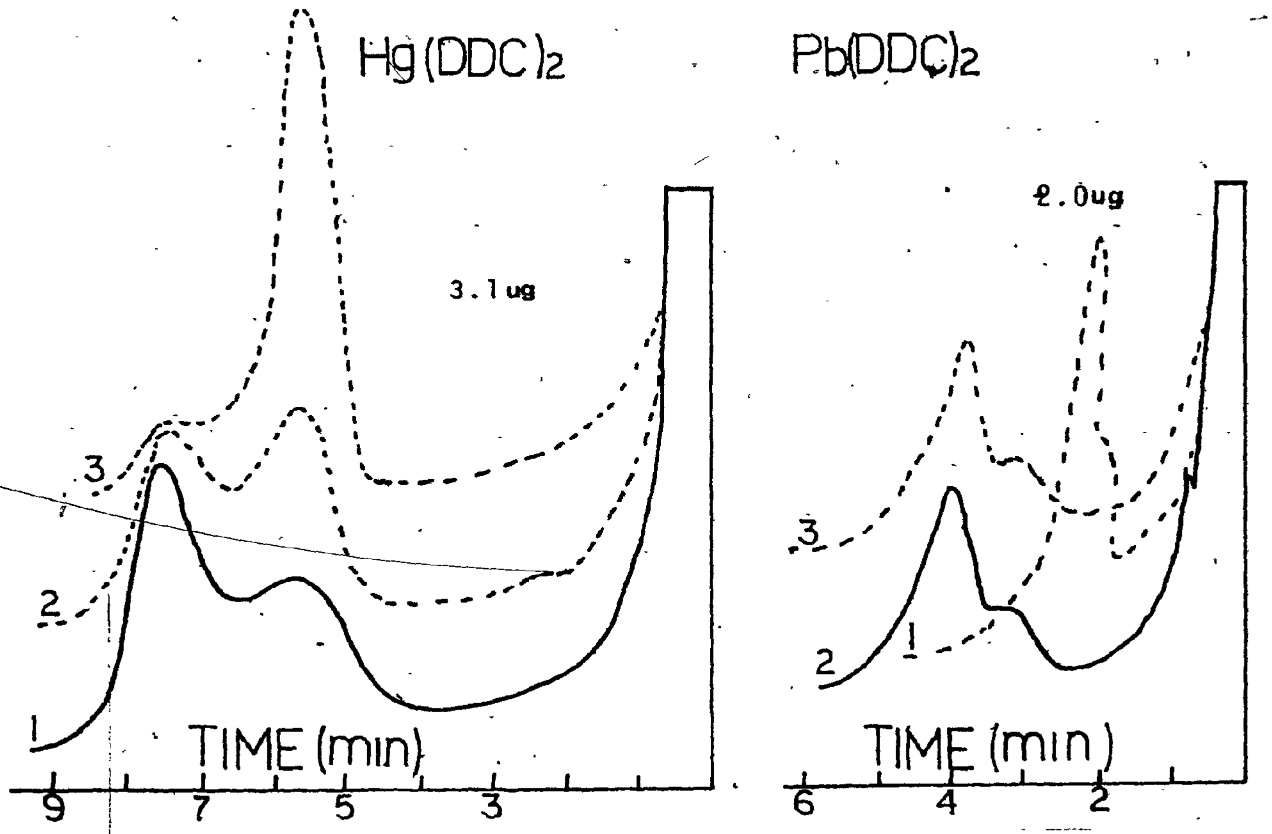


TABLE XIV

DATA ON 5% OV-101 + 5% QF-1 ON GAS CHROM-Q (60 cm x $^1/_8$")*

Compound	Ret. Time (min)	Col. Temp. (^oC)
Ni(DDC)$_2$	4.7	245
Cu(DDC)$_2$	3.5	245
Zn(DDC)$_2$	3.2	245
Cd(DDC)$_2$**	2.5 to 3.0	235
Pb(DDC)$_2$**	3.4 to 4.4	235
[illegible]g(DDC)$_2$**	3.4	235
Co(DDC)$_3$	13.6	235
	5.7	270

* Injector/detector temperature was 270^{o}C.

** Sample decomposition was observed.

Correlation coefficients were better than 0.990.

It was possible to separate a mixture of Ni(DDC)$_2$, Cu(DDC)$_2$ and Zn(DDC)$_2$ with good resolution on this column at 230°C (Fig. 25). If Co(DDC)$_3$ was added to the mixture a separation would still be possible using temperature programming. Attempts were made to separate a mixture of Ni, Hg and Pb chelates at 235°C but distortion of the Hg(DDC)$_2$ peak impaired the resolution as shown in Fig. 26. The resolution on this column was superior to anything reported in the literature. Although it was previously reported by Radecki et al. (37) that this mixture of liquid phases worked well it must be mentioned that in the present study modifications were made to their method of preparing the column packing. Radecki used a 1:1 mixture of 5% OV-101 on Gas Chrom Q and 5% QF-1 on Gas Chrom Q which were mixed together after preparation. This meant that if decomposition occurred with either of the packings alone under a particular set of chromatographic conditions, it would also occur when the 1:1 mixture of both packings was used. In this study a chloroform solution of OV-101 and QF-1 together was used to coat a support to give a 5% loading of each liquid phase. In this way it was anticipated that any active sites not eliminated by one liquid phase would be eliminated by the other. This appears to have in fact happened. Also, a 10% loading on the support was used in this work compared to only 5% by Radecki.

FIGURE 25

MIXTURE OF Ni, Cu AND Zn ON 5% OV-101 + 5% QF-1 ON GC-Q (60 cm x 1/8") AT 230°C

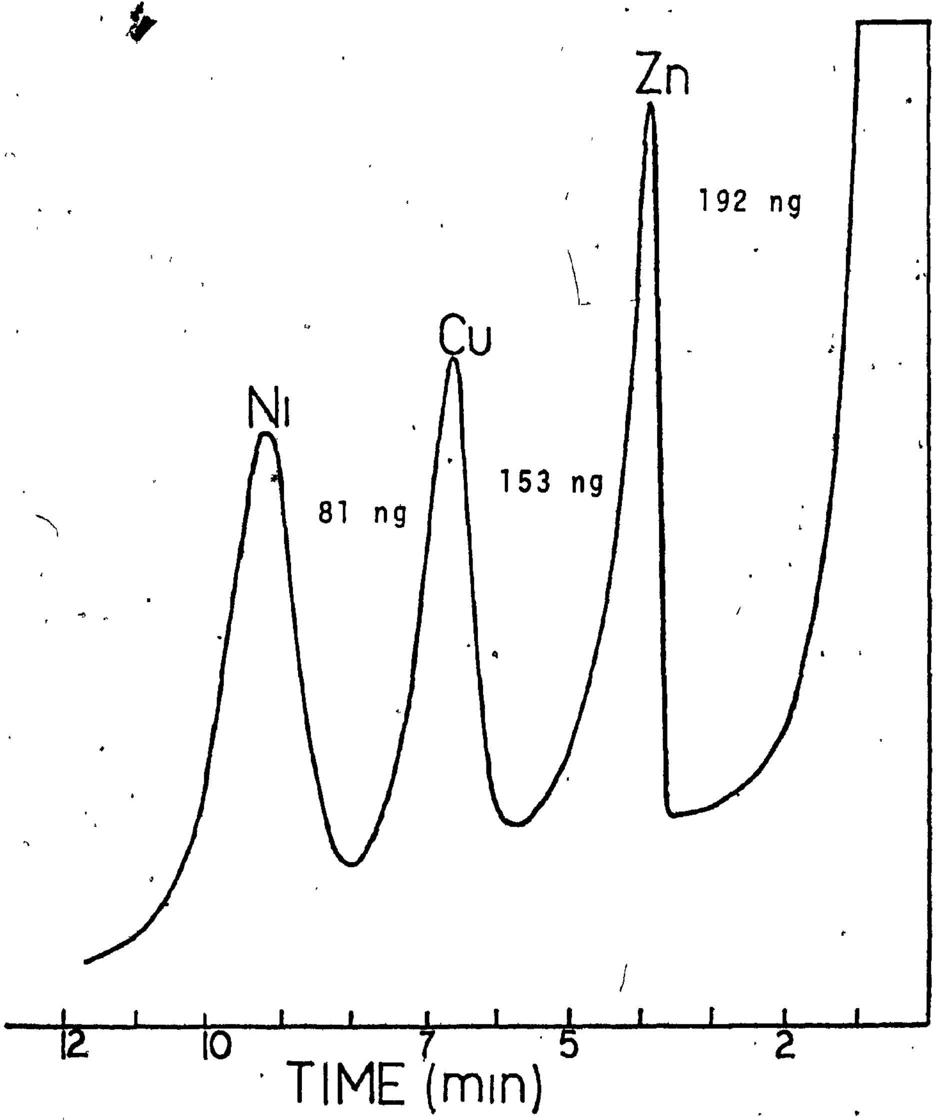
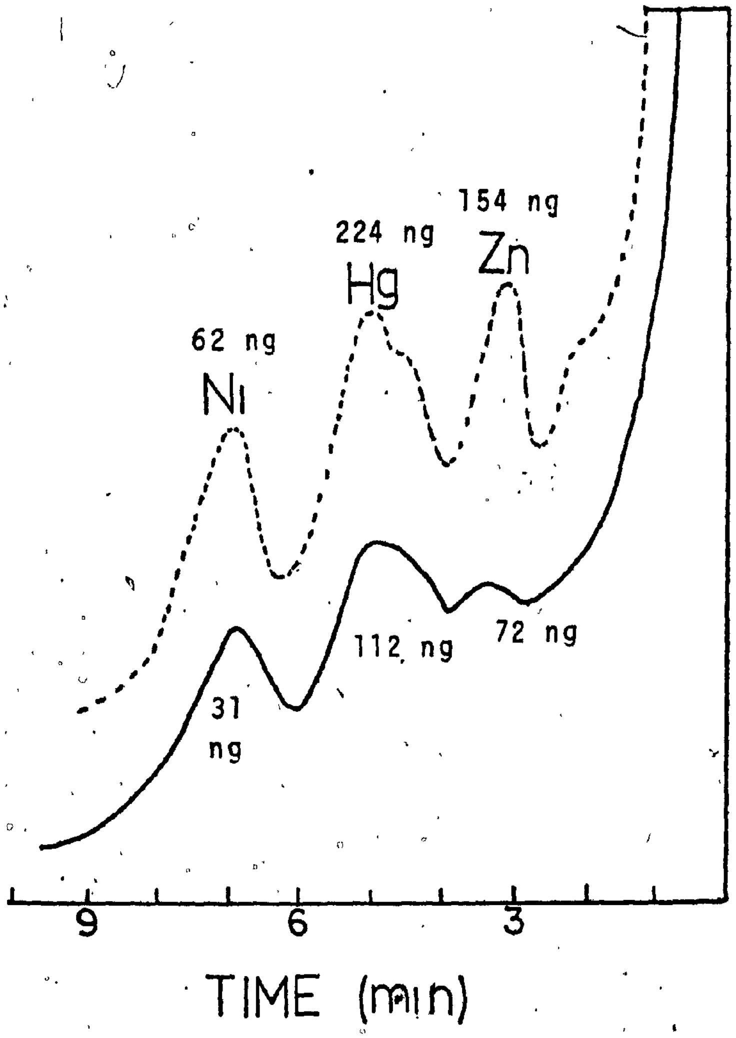


FIGURE 26

SEPARATION OF Ni, Hg AND Zn ON 5% OV-101 + 5% QF-1 ON GC-Q (60 cm x 1/8" S.S.) AT 235°C



11.2.1.4 Conclusions on the Basis of Tests with Above Columns.

It was concluded that:

(i) All three columns studied were suitable for individual detection of $Zn(DDC)_2$, $Ni(DDC)_2$, $Cu(DDC)_2$ and $Co(DDC)_3$.

(ii) $Pb(DDC)_2$, $Cd(DDC)_2$ and $Hg(DDC)_2$ presented problems due to decomposition on the column, probably by interaction with the support and/or metal tubing. These problems may perhaps be overcome.

(iii) $Mn(DDC)_3$ and $Fe(DDC)_3$ decomposed and could not be handled by GC.

(iv) Separation of more than three components was not possible under isothermal conditions on any of the columns.

(v) Only one column gave a separation with good resolution, i.e. 5% OV-101 + 5% QF-1 on GC-Q. It was more selective for mixtures than either one containing a single liquid phase.

(vi) The problem of decomposition has been noted by Krupcik et al. (34) in analyses of $Cd(DDC)_2$ and $Co(DDC)_3$ which they incorrectly reported to be $Co(DDC)_2$. The fact that decomposition of $Cd(DDC)_2$, $Hg(DDC)_2$ and $Pb(DDC)_2$ was observed may explain why these three columns have been used by other workers only for $Ni(DDC)_2$, $Cu(DDC)_2$ and $Zn(DDC)_2$ analyses. These appear to be, chromatographically, the best behaved metal chelates (32,35,37).

To further illustrate how resolution can be improved by the use of mixed liquid phases, a synthetic mixture of $Ni(DDC)_2$, $Cu(DDC)_2$ and $Zn(DDC)_2$ was analysed on three columns containing 5% OV-101, 5% QF-1 and 5% QF-1 + 5% OV-101, respectively, at three different temperatures. The results are shown in Figs. 27 to 29. On 5% OV-101 the $Ni(DDC)_2$ and $Cu(DDC)_2$ peaks overlapped, but there was good resolution between $Zn(DDC)_2$ and $Cu(DDC)_2$. On 5% QF-1 the reverse was true. When a mixture of both phases was used all three chelates were well resolved. There was reason to believe that this technique of mixed stationary liquid phases might be useful in achieving a separation of a more complex chelate mixture involving Cd, Pb, Hg and Co as well as Ni, Cu and Zn, if decomposition problems could be overcome.

It should also be noted that the lengths of the three columns studied up to this point were considerably shorter than what has been used by other workers and reported in the literature. For example, a column containing the mixed OV-101 + QF-1 packing as used by Radecki et al. (37) was 150 cm long and a separation of Ni, Cu and Zn chelates required 16 minutes at 240°C compared to 8 minutes for our 60 cm column. The choice of column length, usually 60 cm or less, was made to enable the use of lower column temperatures to

FIGURE 27

SEPARATION OF Ni, Cu AND Zn ON 5% OV-101 ON CW-AW-DMCS (50 cm x 1/8") AT 220°C

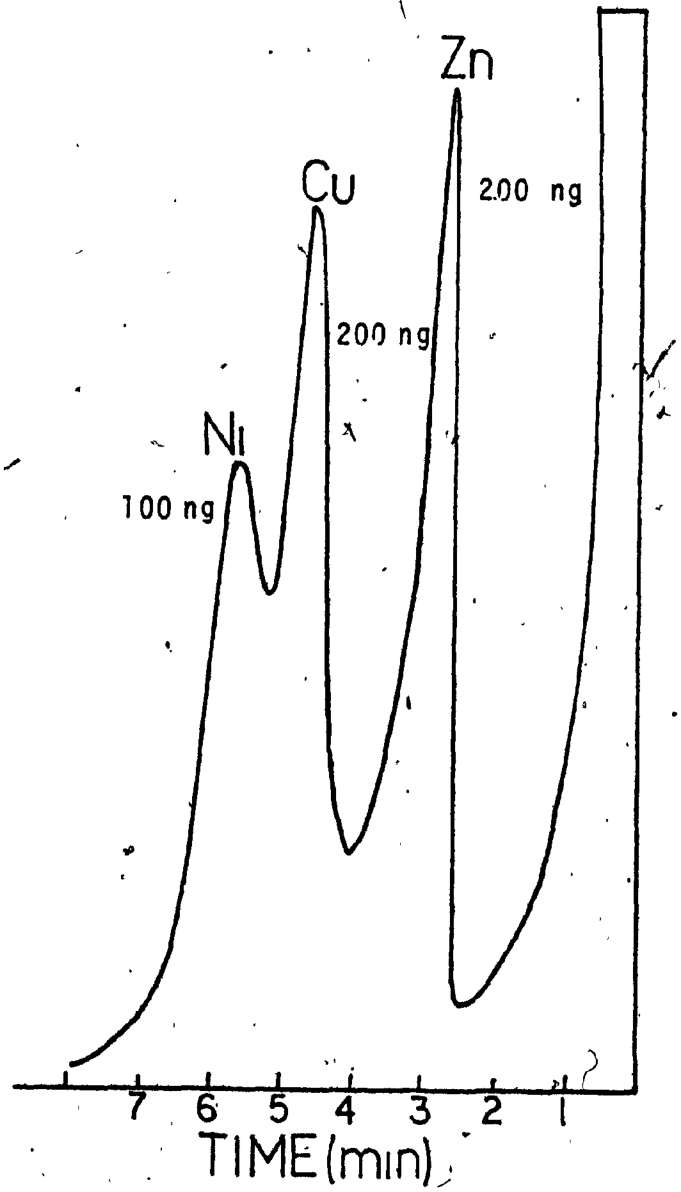


FIGURE 28

SEPARATION OF Ni, Cu AND Zn ON 5% QF-1 ON 5% QF-1 ON CW-AW-DMCS (60 cm x 1/8" S.S.) AT 240°C

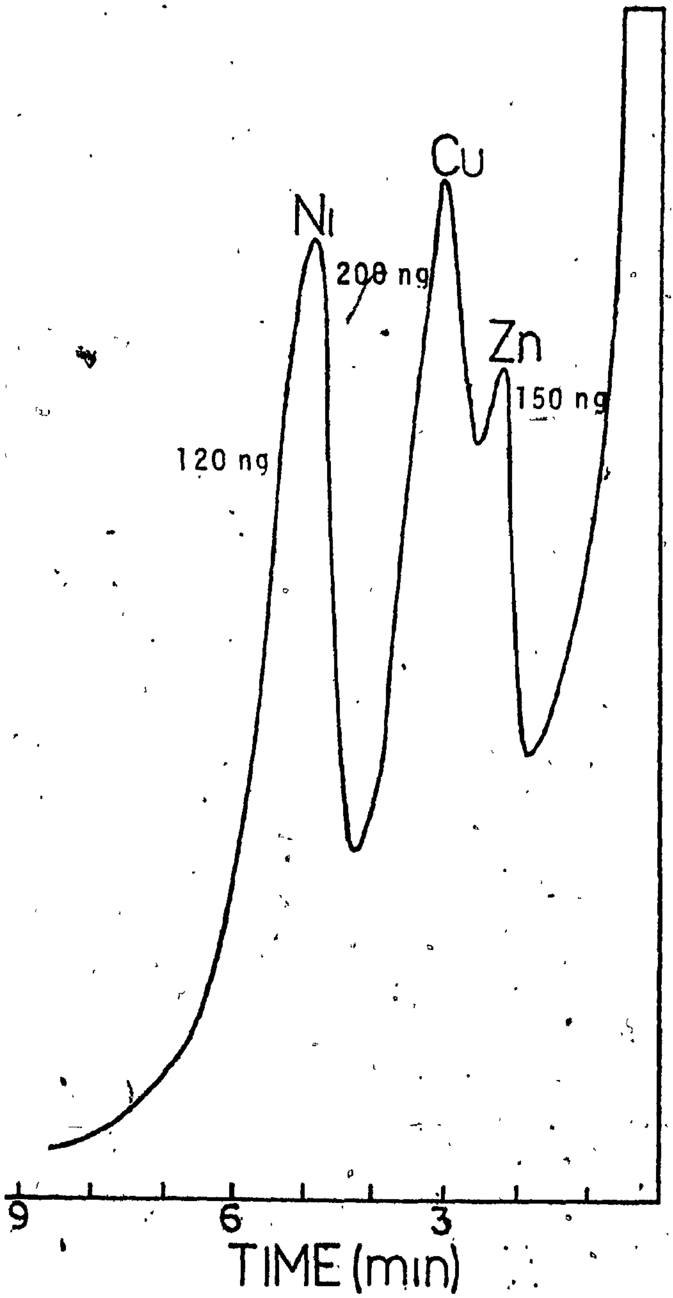
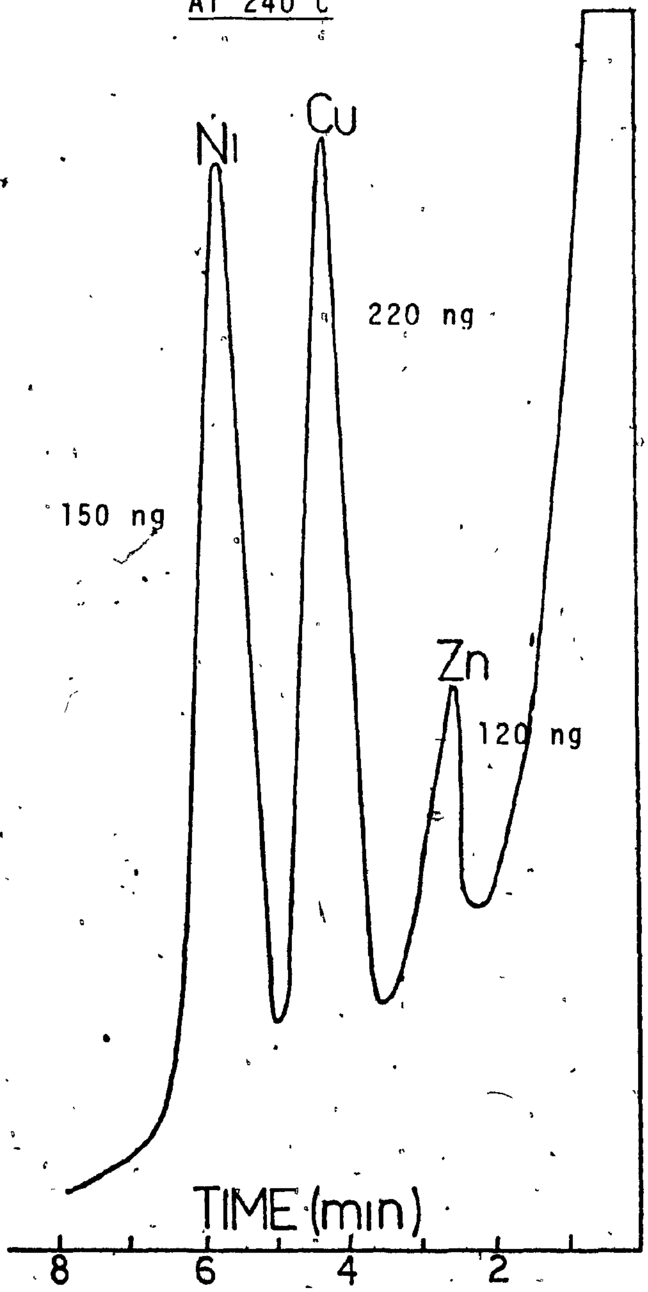


FIGURE 29

COMPARATIVE ANALYSIS OF Ni, Cu AND Zn
ON 5% OV-101 + 5% QF-1 ON GC-Q (60 cm x 1/8" S.S.)
AT 240°C



reduce retention times and thereby eliminate experimental conditions that could be conducive to sample decomposition. It is known that some $M(DDC)_n$ can decompose at high temperatures catalyzed by the metal surface of the tubing and/or the support.

11.2.2.0 Further GC Studies

The approach followed in the next part of this study to attempt improvement in $M(DDC)_n$ separations was the following:

(i) A number of columns were made with several types of supports (mainly Chromosorb W's and Gas Chrom-Q's) coated with different amounts of liquid phases such as OV-101, QF-1, SE-30 and OV-17.

(ii) Whenever a column was found to be satisfactory for the separation of a few $M(DDC)_n$ in a mixture, analyses of aqueous solutions of the metal ions in question were performed at the ppm level to establish whether the chelation was quantitative and to determine lower limits of detection.

(iii) The effect of tubing on resolution was studied, comparisons being made between stainless steel (s.s.) and glass.

The following coated supports, all packed in stainless steel tubing, were studied before undertaking tests with glass tubing. Also, uncoated polymer packings were studied.

11.2.2.1 Chromosorbs 104, 106 and 107 (60 cm x $^1/_8$")

These columns contained porous polymers as packing. Their temperature limit is 250°C to 275°C. Such polymers are predicted to be especially good for separation of S and N containing organic compounds (57) and, therefore, their application to $M(DDC)_n$ separations seemed promising. It was found, however, that in the temperature range of 150°C to 245°C no peaks for $M(DDC)_n$ could be eluted on any of these columns, perhaps due to their permanent adsorption on these supports. This being the case, polymer columns were not studied any further.

11.2.2.2 3% SE-30 on Chromosorb W-HP (60 cm x $^1/_8$" s.s.)

Figs. 30(A) to 30(C) show the separation obtained of some mixtures using this column. It differed from the SE-30 packing previously investigated in that CW-HP support was used in this case. The retention times of each sample studied at the different temperatures investigated are given in Table XV. Poor resolution was obtained for mixtures of Hg, Ni, Cd and Zn, of Ni, Cu and Zn, and of Zn, Pb, Cd and Hg chelates. Calibration curves were obtained on this column (Fig. G-VII and Fig. G-IX Appendix I).

$Hg(DDC)_2$ and $Pb(DDC)_2$ showed some decomposition. Their respective chromatograms are shown in Fig. 31.

FIGURE 30

SEPARATION OF $M(DDC)_2$ ON 3% SE-30 ON CW-HP (60 cm x 1/8") AT 210°C

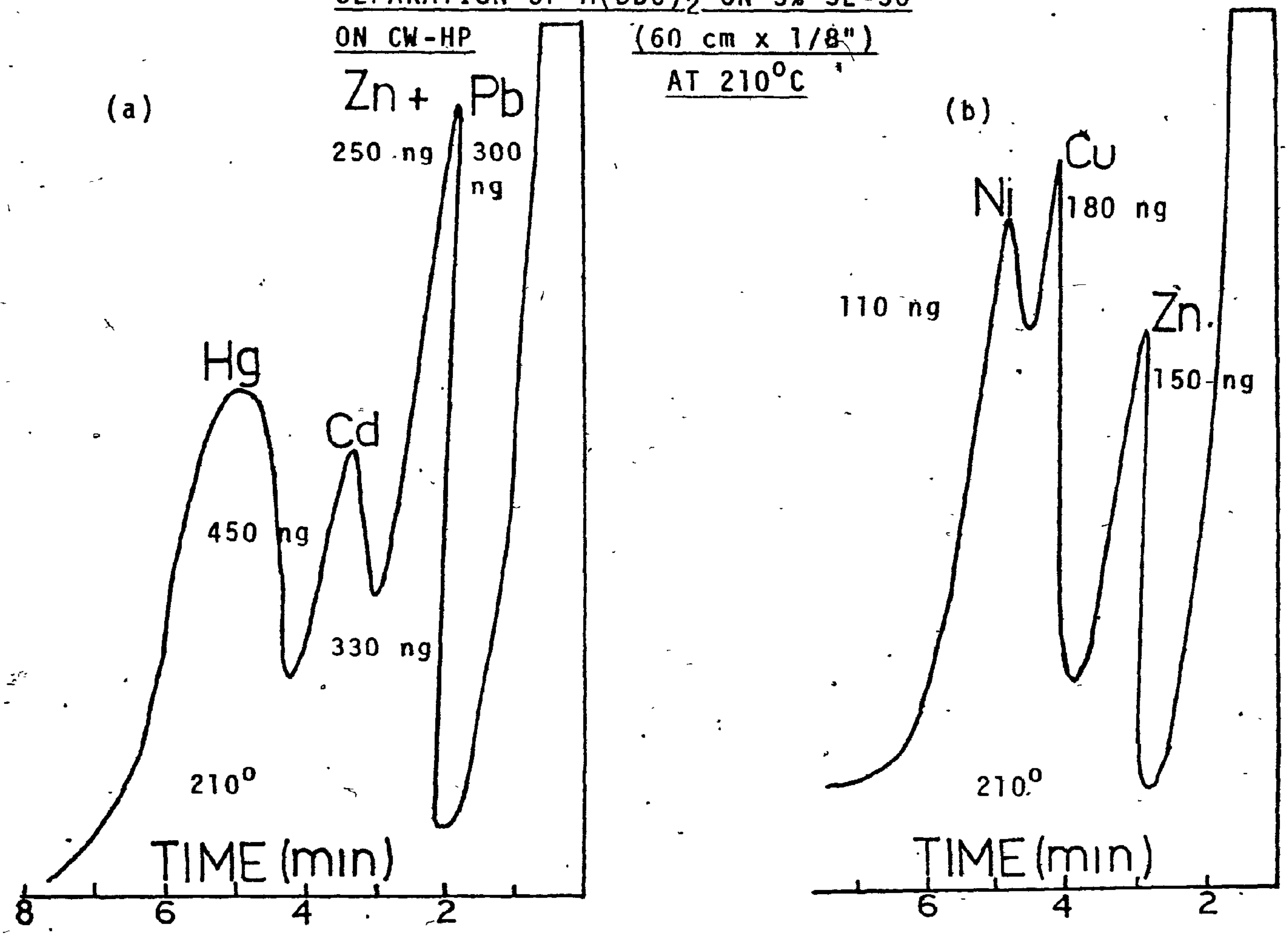


FIGURE 30(C)

SEPARATION OF $M(DDC)_n$ ON 3% SE-30 ON CW-HP (60 cm x 1/8" S.S.)

AT 185°C

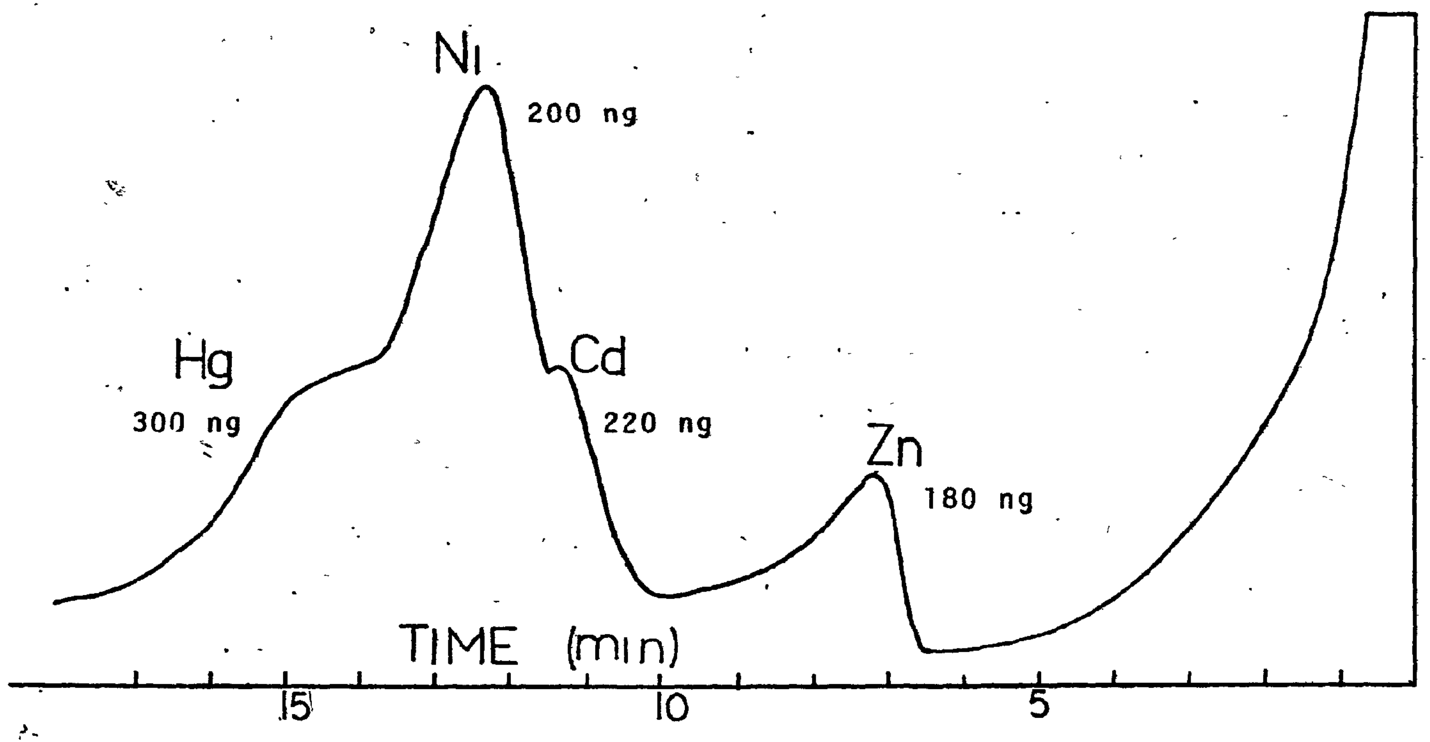


TABLE XV

RETENTION TIMES FOR $M(DDC)_n$ ON 3% SE-30 ON CW-HP* (60 cm x $^1/_8$" s.s.)

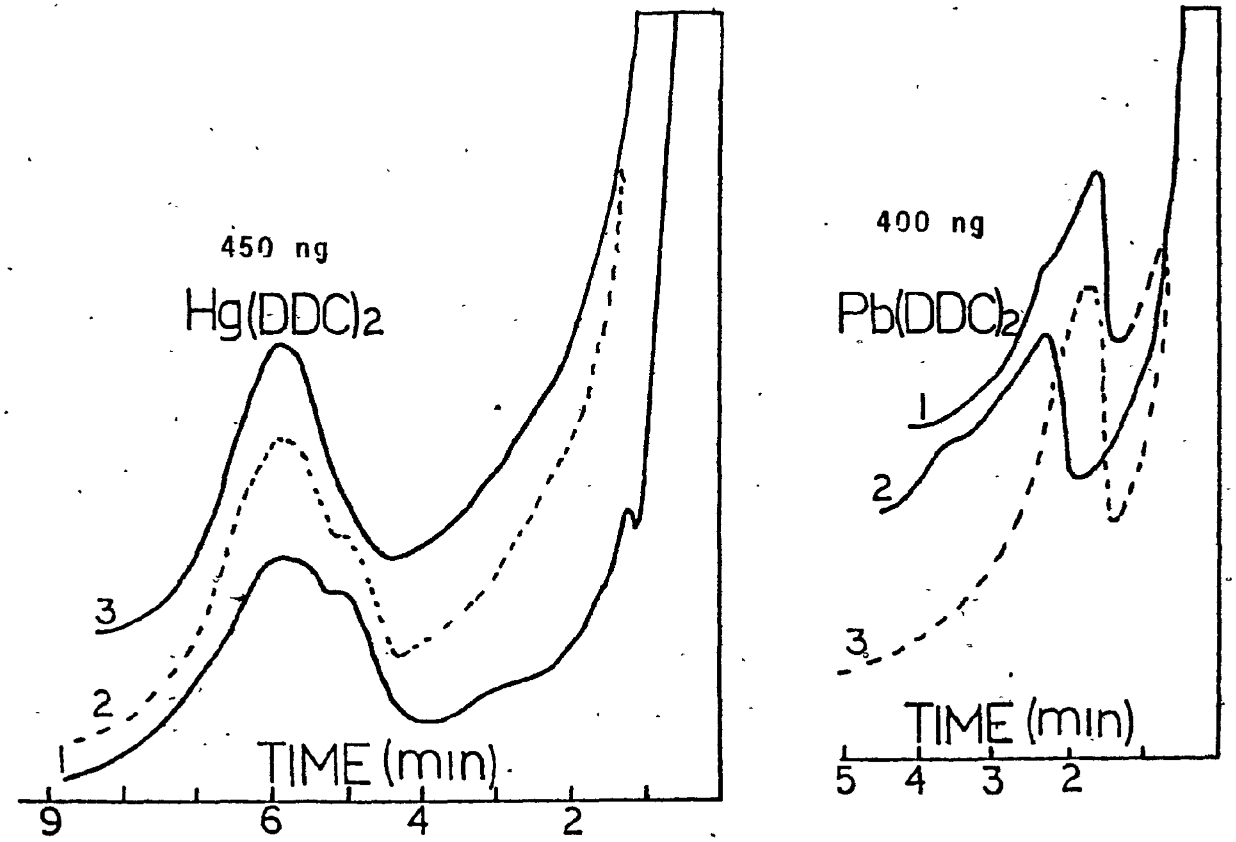
Compound	Retention Time (min.)						
	190°C	200°C	205°C	210°C	220°C	225°C	250°C
$Ni(DDC)_2$	10.7	6.7	5.4	4.2	-	-	-
$Cu(DDC)_2$	-	5.3	-	3.5	-	-	-
$Zn(DDC)_2$	5.1	3.1	2.6	2.2	1.5	-	-
$Cd(DDC)_2$	8.8	5.3	4.4	3.5	2.2	-	-
$Hg(DDC)_2$	-	8.9	-	5.5	3.5	3.1	-
$Pb(DDC)_2$	-	4.2	-	-	1.6	2.4	-
$Co(DDC)_3$	-	-	-	-	-	-	3.6

* Injector/detector temperature was 270°C.

FIGURE 31

ANALYSIS OF $Hg(DDC)_2$ AND $Pb(DDC)_2$ ON 3% SE-30 ON CW-HP (60 cm x 1/8")

AT 230°C



11.2.2.3 5% OV-101 on CW-HP (60 cm x $^1/_8$" s.s.)

Most of the chelates studied (Cd, Ni, Cu and Zn) showed tailing on this column which was similar to the OV-101 column tested before except for the nature of the support. Results were definitely poorer than on 5% OV-101 on CW-AW-DMCS (Fig. 32). The tailing made impossible the effective separation of more than two compounds at a time, and the retention times given in Table XVI are misleading since they do not take tailing into account.

Calibration lines were obtained for some chelates on this column. Responses were linear (Figs. G-X to G-XII, Appendix I) in the low microgram range. Table G-X in Appendix I shows linear regression parameters of calibration plots obtained for some $M(DDC)_n$ under the conditions used.

11.2.3.0 Quantitative Determinations of High ppm Concentrations of $M(DDC)_n$

During the synthesis of the metal chelates it was found that yields above 90% were obtained with all metals. It was necessary to confirm that this would still be the case starting with aqueous solutions containing metal ions in trace amounts only. Accordingly, a series of low concentration level metal ion solutions were prepared, the metal extracted as $M(DDC)_n$ as described in section 10.7.0, and the extracts analyzed on an OV-101 on CW-HP column.

FIGURE 32

PEAK SHAPES OF Cd, Ni, Cu AND Zn CHELATES

ON 5% OV-101 ON CW-HP (60 cm x 1/8")

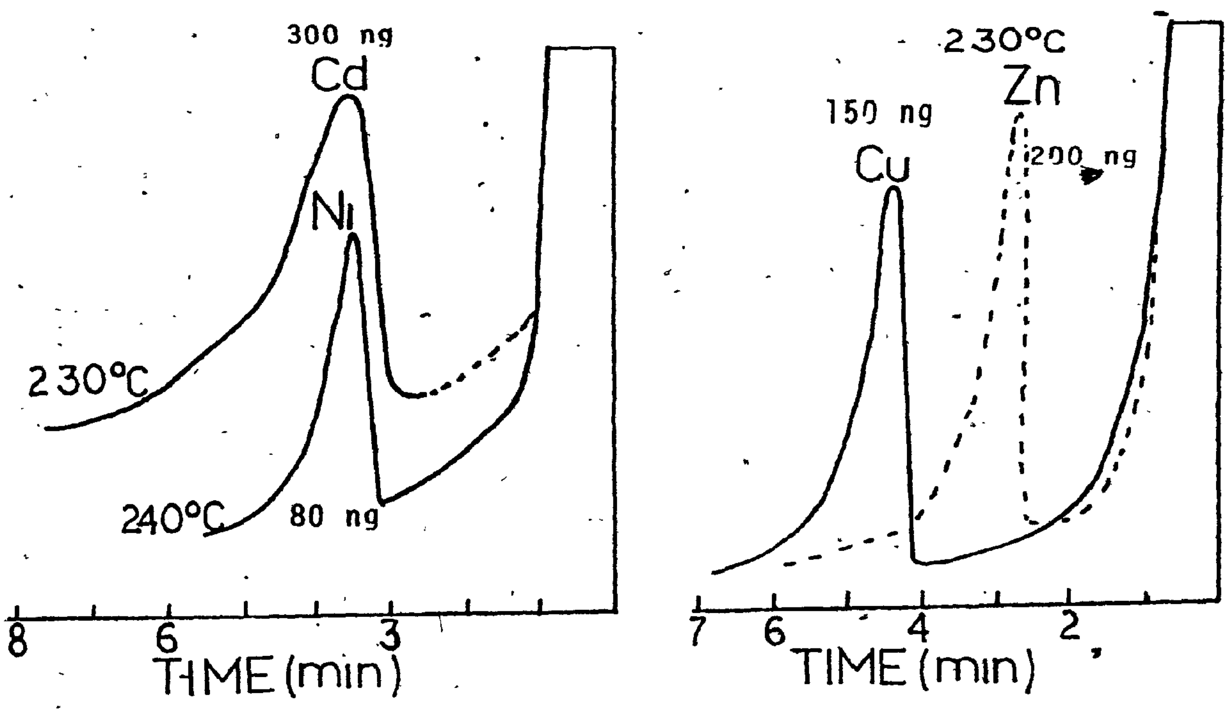


TABLE XVI

RETENTION TIMES ON 5% OV-101 ON CW-HP* (60 cm x $^1/_8$" s.s.)

Compound	Ret. Time (min)	Colm Temp. (°C)
$Ni(DDC)_2$	3.5	240
$Cu(DDC)_2$	4.5	230
$Zn(DDC)_2$	3.5	230
$Cd(DDC)_2$	3.8	230
$Hg(DDC)_2$	5.8	230
$Hg(DDC)_2$	(Decomposed)	

* Injector/detector temperature was 275°C.

The concentrations of metals in the prepared solutions were experimentally determined by comparison with calibration curves that were prepared and results were compared to theoretical values. The data obtained for chelates analyzed individually are shown in Table XVII for Ni, Cu and Zn solutions, and Table XVII(A) for Cd, Hg, Pb and Co analyzed on a 3% SE-30 on CW-HP column.

Examination of the data in these tables was very encouraging. Quantitatively acceptable results were obtained in all cases, the determined values never differing from theoretical values by more than 6% of what is generally acceptable in the ppm concentration range.

Figs. G-XII to G-XIV in Appendix I show the calibration curves on the two columns in question, plotted as response in mm^2 vs ppm of metal. In all cases plots were linear, which confirmed that reactions of metal ions with DDC were quantitative at the ppm level studied (7.0 to 100 ppm) as well as at high concentrations.

Note that at the high ppm concentrations studied, the metal chelates precipitate from aqueous solutions and extraction with chloroform is fairly easy. It was found in subsequent tests that at low ppm levels (1.0 to 10.0 ppm) no precipitation occurs as a rule, but the solution does become cloudy. The fact that at high concentrations the metal chelates precipitate from aqueous solutions may be used as a criteria for determining whether the sample needs

TABLE XVII

DETERMINATION OF ppm CONCENTRATIONS OF METAL IONS ON 5% OV-101 ON CW-HP (60 cm x $^1/_8$")*

	Concentration (ppm)		
Metal	Theoretical	Experimental	% Error
Cu(II)	5.0	5.0	0.0
	7.0	6.7	-2.9
	12.0	12.7	+5.8
	15.0	14.8	-1.3
Ni(II)	6.8	7.0	+2.9
	8.0	8.0	0.0
	8.5	8.4	-1.2
	11.0	11.1	+0.9
Zn(II)	5.0	5.2	+4.0
	9.0	9.4	+4.4
	10.0	9.4	-1.0
	13.0	13.2	+1.5

*Calibration lines shown in Fig. G-XII Appendix I

TABLE XVII(A)

DETERMINATION OF ppm CONCENTRATIONS OF METAL IONS ON 3% SE-30 ON CW-HP (60 cm x $^{1}/_{8}$")*

Metal	Concentration (ppm) Theoretical	Concentration (ppm) Experimental	% Error
Cd	11.0	11.1	+0.9
	18.0	18.5	+2.8
	27.0	26.8	-0.7
	14.0	14.0	0.0
Hg	18.0	18.4	+2.2
	40.0	40.0	0.0
	54.0	54.3	+0.6
	89.0	89.4	+0.5
Pb	50.0	50.8	+1.6
	75.0	74.5	-0.7
	110.0	110.0	0.0
Co	6.0	5.8	-3.3
	10.0	10.1	+1.0
	16.0	16.8	+5.0
	14.0	14.2	+1.4

*Calibration lines shown in Figs. G-XIII to G-XIV Appendix I.

dilution before GC analysis to ensure that results fall within calibration curve limits.

11.2.3.1 Quantitative Determination of Low ppm Concentrations of Metal Ions

Given the promising results obtained above, it was decided to study a series of synthetic aqueous solutions containing even lower ppm levels of metals, 1 to 10 ppm. This concentration range, as well as the ppb level, represents what would be most commonly encountered in real environmental and biological samples. It was necessary to establish whether mixtures of metals at these low levels in aqueous solutions could be determined quantitatively and simultaneously. Hence, the next series of tests, using the 5% OV-101 + 5% QF-1 On Gas Chrom Q column, was undertaken using a test solution containing Ni, Cu and Zn, each at the 2 ppm concentration level. Six 100 ml portions of this test solution were subjected to the analytical procedure described in Section 10.7.0.

The calculation of concentration of metal in ppm amounts in test solutions was simplified by using the following working equation which was developed:

$$\text{(Eq-9)} \qquad \text{Conc. in ppm (ng/ml)} = \frac{(\text{Av. Area} - Y_{Int})V_o \times \%M}{(\text{slope} \times V_i) \quad V_s \times 100}$$

<u>where</u>: Av. Area = average peak area for the $M(DDC)_n$

where: Y_{Int} = Y-intercept of regression line from a plot of peak areas (in mm^2) vs ng of $M(DDC)_n$ of standard solutions.

Slope = slope of the above regression line.

V_i = volume of chloroform extract injected, in ul (usually 1 to 5 ul).

V_o = volume of chloroform extract analyzed, in ml (from 5.0 to 25.0 ml).

V_s = volume of aqueous sample solution analyzed in ml (50 to 100 ml).

%M = percent of metal in the $M(DDC)_n$ being analyzed.

Depending on the column used, the volume of extract injected for GC analysis was varied from 1.0 to 5.0 ul to ensure that no column was overloaded. The volume of chloroform extract was varied depending on the detector sensitivity required, or on the concentration level at which the analysis was to be performed. The percent of metal ion (%M) was obtained from a knowledge of the molecular structure of the chelate. %M data is listed in Table XVIII for the chelates studied.

Calibration curves were prepared with solutions containing known amounts of $Ni(DDC)_2$, $Cu(DDC)_2$ and $Zn(DDC)_2$ (Fig. G-XV and Table G-XV, Appendix I). Using these lines the results in Table XIX were obtained.

TABLE XVIII

PERCENT OF METAL IN M(DDC)$_n$

Compound	M.W. (g/mole)	%M
Ni(DDC)$_2$	355.251	16.53
Cu(DDC)$_2$	360.08	17.65
Zn(DDC)$_2$	361.91	18.06
Cd(DDC)$_2$	408.94	27.49
Hg(DDC)$_2$	497.13	40.35
Pb(DDC)$_2$	503.73	41.13
Co(DDC)$_3$	503.62	11.70
Fe(DDC)$_3$	500.54	11.16
Mn(DDC)$_3$	499.75	10.99
NaDDC.3H$_2$O	225.3	10.20

TABLE XIX

SIMULTANEOUS ANALYSIS OF AQUEOUS SOLUTIONS CONTAINING 2.1, 2.0 AND 2.0 ppm OF Ni, Cu AND Zn RESPECTIVELY, ON 5% OV-101 + 5% QF-1 ON GC-Q (60 cm x $^{1}/_{8}$" s.s.)*

Sample No.	Ni (ppm)	Cu (ppm)	Zn (ppm)
1	1.8	1.8	1.9
2	1.8	1.6	1.7
3	2.0	2.0	2.0
4	1.8	1.8	2.0
5	1.8	1.7	2.0
6	1.8	1.7	2.0
Av. ±STD	1.8 ± 0.08	1.8 ± 0.1	1.9 ± 0.1
% error	-14.3%	-10.0%	-5.0%
Relative STD	4.4%	5.6%	5.3%

*Calibration lines shown in Fig. G-XV Appendix I

A sample calculation to illustrate the application of equation (Eq-9) is given below for the case of determination of ppm of Ni in sample 1 (Table XIX).

V_i = 5.0 ul $CHCl_3$ extract injected

V_o = 100.0 ml aqueous sample solution

V_s = 25.0 ml $CHCl_3$ extract

%M = 16.53% Ni

Average area of $Ni(DDC)_2$ = 888 mm^2

Y_{int} = -92.7 mm^2 (Table G-XV)

Slope = 4.48 mm^2/ng (Table G-XV)

Using this data the following result was obtained:

$$\text{ppm Ni} = \frac{(888\ mm^2 + 92.7\ mm^2)}{(4.48\ mm^2/ng \times 5.0\ ul)} \times \frac{25.0\ ml}{100.0\ ml} \times \frac{16.53}{100}$$

ppm Ni = 1.8 ppm.

All other ppm values were calculated in the same manner. For this method to work, the peak area of the sample analyzed must fall within the calibration curve range, as was the case in this study.

From Table XIX it can be seen that the standard deviations ranged from 4.4% to 5.6%, and the percent error ranged from 5.0% to 14.3%. These values were in the same range as those reported by Radecki et al. (37) in determination of the same metals but at higher ppm levels (10 to

40 ppm). It could, therefore, be concluded that Ni, Cu and Zn could be determined with adequate accuracy and precision at very low ppm levels on the 60 cm x $^1/_8$" 5% OV-101 + 5% QF-1 on GC-Q column. Further testing was carried out to establish whether other environmentally interesting metals could be determined at these same low levels.

Tests were undertaken with aqueous solutions containing Hg at the 5.1 ppm level. The calibration line on Fig. G-XVI (Appendix I) was obtained using standard solutions of $Hg(DDC)_2$ of known concentration. Five 100.0 ml portions of the aqueous test solution were treated according to the procedure in Section 10.7.0, and the concentration of Hg(II) in each portion was determined with the 5% OV-101 + 5% QF-1 on GC-Q (60 cm x $^1/_8$") column at 235°C. The results obtained are shown in Table XX. It should be noted that two portions of sample solutions were extracted with 10.0 ml of $CHCl_3$ and three with 25.0 ml. This had no significant effect on the accuracy of the results. It was found advantageous to inject 2 ul of extract rather than 4 ul to reduce interference of the solvent peak in calculation of $Hg(DDC)_2$ peak areas. Notice that the relative standard deviation was greater than for Cu, Ni and Zn. This was due to the fact that the peak shape of $Hg(DDC)_2$ was distorted as shown in Fig. 24, and its area, therefore, was more difficult to calculate by the peak height times peak width at one-half height method used.

TABLE XX

ANALYSIS OF 5.1 ppm Hg(II) AQUEOUS SOLUTIONS ON 5% QF-1 + 5% OV-101 ON GC-Q (60 cm x $^1/_8$")

Test Samples	Vol. $CHCl_3$ Used for Extraction	Experimental Conc.	% Error
1	10.0 ml	5.5 ppm	+7.8
2	25.0 ml	5.1 ppm	0.0
3	25.0 ml	4.7 ppm	-7.8
4	25.0 ml	5.6 ppm	+9.8
5	10.0 ml	5.5 ppm	+7.8
Av. ± STD		5.3 ± 0.38 ppm	3.5
Relative STD		7.2%	

Aqueous solutions of low ppm levels of Co were also investigated. This was of interest since on the 5% OV-101 + 5% QF-1 on GC-Q column at 260°C a retention time of 6.9 mins. was recorded and thereby Co could be separated from Ni, Zn and Cu or Hg when in a mixture. The results obtained with 2.0 ppm Co test solutions are given in Table XXI. Fig. G-XVII shows the calibration line used to calculate the results. The percent error of 1.0%, and relative standard deviation of 4.2%, is excellent for the low concentration of Co tested.

11.2.4.0 Further Testing of Other Column Packings for the Analysis of Mixtures Having Low ppm Concentrations of Metal Ions

While the results with low concentrations of metals were very encouraging up to this point, the major problem remained that with the 5% OV-101 + 5% QF-1 on Gas Chrom-Q column (60 cm x $^1/_8$") the only mixtures that could be separated successfully were those of Ni, Cu, Zn and Co, and Hg if Cu was not present. The only improvement here over the results reported by Radecki et al. (37) was that Co and in some cases Hg could be separated together with Ni, Cu and Zn, and that separation was achieved in a shorter time. The aim of this project, however, was to obtain separation of much more complex metal mixtures. Hence the search for more suitable column packings was resumed.

TABLE XXI

ANALYSIS OF 2.0 ppm Co SOLUTIONS ON 5% OV-101 + 5% QF-1 ON GC-Q (60 cm x $^1/_8$")*

AT 260°C

Test Solution	Experimental Conc. (ppm)	% Error
1	2.1	+5.0
2	2.0	0.0
3	2.0	0.0
4	2.1	+5.0
5	1.9	-5.0
Average ± STD	2.0 ± 0.08	1.0%
Relative STD	4.2%	

* Calibration line shown in Fig. G-XVII, Appendix I

11.2.4.1 5% OV-101 + 5% QF-1 on CW-HP (30 cm x 1/8" S.S.)

With this column a separation of Ni(DDC)$_2$, Cu(DDC)$_2$ and Zn(DDC)$_2$ was achieved in 7.0 minutes with good resolution at 225^{o}C which was 20^{o}C less than the temperature used with the 5% OV-101 + 5% QF-1 on Gas Chrom-Q (60 cm x 1/8") column, (Fig. 33). Co(DDC)$_3$ was eluted in 4.2 minutes at 255^{o}C which meant that it could be analyzed simultaneously with Ni, Cu and Zn using column temperature programming conditions. However, the problem of decomposition of Cd, Pb and Hg chelates and their interference with Cu and Zn peaks remained with this column. Because of the advantage of shorter retention times it was though worthwhile to determine the suitability of this column for the quantitative analysis of a synthetic aqueous solution containing Ni, Cu and Zn. Accordingly, six portions of sample solution were prepared containing 2.1 ppm of Ni, 2.0 ppm of Cu and 2.0 ppm of Zn. These sample portions were analyzed using the procedure in Section 10.7.0. The results are shown in Table XXII. The calibration curves prepared are shown in Fig. XVIII and Table G-XVIII (Appendix I). The percent error varied from 5.8% to 9.2%. The relative standard deviations ranged from 2.3% to 5.6%.

Cobalt by itself in aqueous solutions was analyzed at the 2.0 ppm level. The results obtained are shown in Table XXIII, with the calibration curve given in Fig. G-XIX (Appendix II). It can be seen that the average % error was

FIGURE 33

SEPARATION OF Ni, Cu AND $Zn(DDC)_2$ ON 5% OV-101 + 5% QF-1 ON CW-HP (30 cm x 1/8")

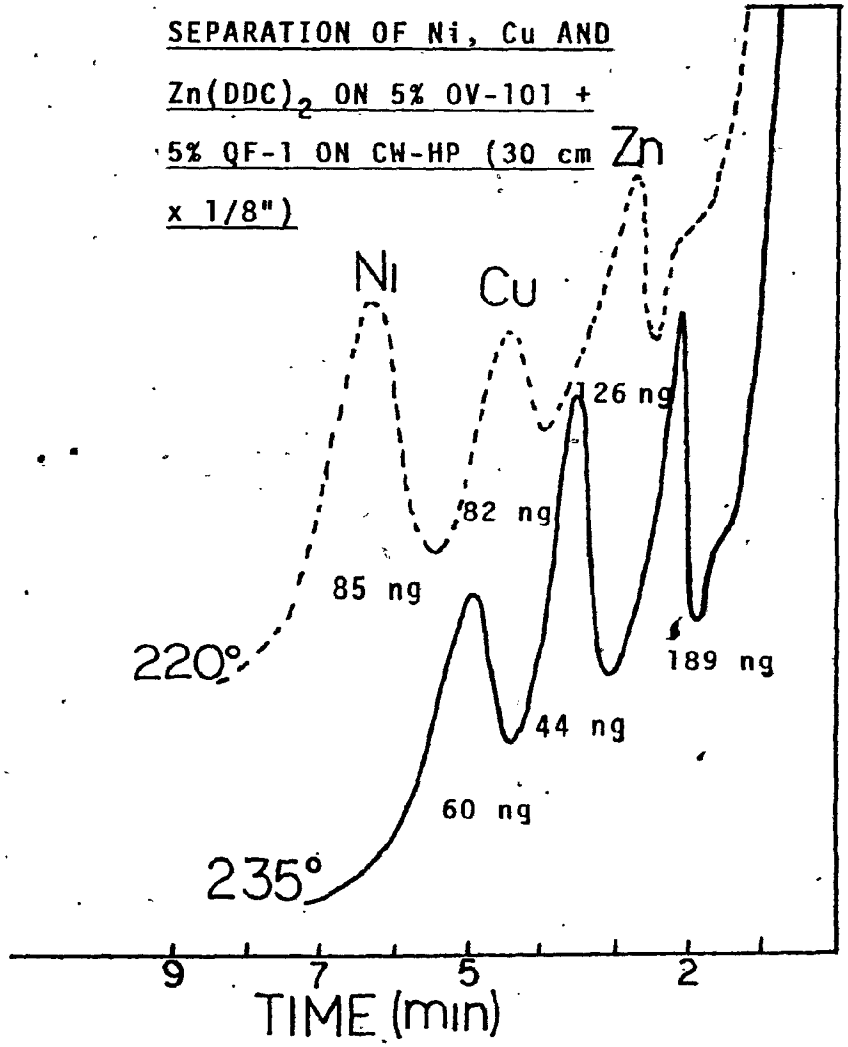


TABLE XXII

DATA FOR SOLUTIONS OF 2.1 ppm, 2.0 ppm AND 2.0 ppm OF Ni, Cu AND Zn, RESPECTIVELY, ON 5% OV-101 + 5% QF-1 ON CW-HP (30 cm x $^1/_8$") * AT 225°C

Sample No.	Zn ppm	Zn % Error	Cu ppm	Cu % Error	Ni ppm	Ni % Error
1	1.7	-15	2.1	+5.0	2.2	+4.8
2	1.9	-5.0	2.2	+10	2.3	+9.5
3	1.6	-2.0	2.1	+5.0	2.3	+9.5
4	1.8	-10	2.0	0.0	2.2	+4.8
5	2.0	0.0	2.2	+10	2.2	+4.8
6	1.9	-5.0	2.1	+5.0	2.2	+4.8
Av. ± STD	1.8±0.1	-9.2	2.1±0.08	+5.8	2.2±0.05	+6.4
Relative STD	5.6%		3.8%		2.3%	

* Calibration line in Fig. G-XVIII, Appendix I

TABLE XXIII

ANALYSIS OF 2.0 ppm Co ON 5% OV-101 + 5% QF-1 ON CW-HP (30 cm x $^{1}/_{8}$")* AT 255°C

Sample	Experimental Conc. (ppm)	% Error
1	1.8	-10
2	1.5	-25
3	1.6	-20
4	1.6	-20
5	1.9	-5.0
Av. ± STD	1.7 ± 0.16	16%
Relative STD	9.4%	

Ret. Time = 4.2 min.

* Calibration line shown in Fig. G-XIX (Appendix II)

higher (16%) than that obtained for Co with longer columns (1.0%).

11.2.4.2 2% SE-30 + 2% QF-1 on Gas Chrom-Q (30 cm x $^{1}/_{8}$" s.s.)

Tests were carried out with this column to obtain an indication of the effect of lowering the amount of liquid loading, and shortening the length of the column on the retention times and thereby on the column temperature required. As is shown in Fig. 34, separation of Ni, Cu and Zn was possible at 200°C but the Ni and Cu peaks were not completely resolved. At lower column temperatures attempted the Ni peak was very broad.

Analyses of a number of other $M(DDC)_n$ individually were attempted. Peak shapes obtained for Cd, Co, Ni and Cu chelates are shown in Fig. 35, at 220°C, 230°C and 240°C. All were eluted within 5.0 minutes. The metal chelate which gave the greatest problem was $Pb(DDC)_2$. It tailed appreciably at 195°C as is shown in Fig. 36, and the results were not reproducible.

The data obtained for each metal chelate under a particular set of conditions is summarized in Table XXIV. Consideration of the retention times suggested that simultaneous analysis of most of these metals in an aqueous mixture should be possible on this column.

It should be pointed out that for $Co(DDC)_3$ two

FIGURE 34

SEPARATION OF Ni, Cu AND Zn ON 2% SE-30 + 2% QF-1 ON GC-Q (30 cm x 1/8" S.S.)

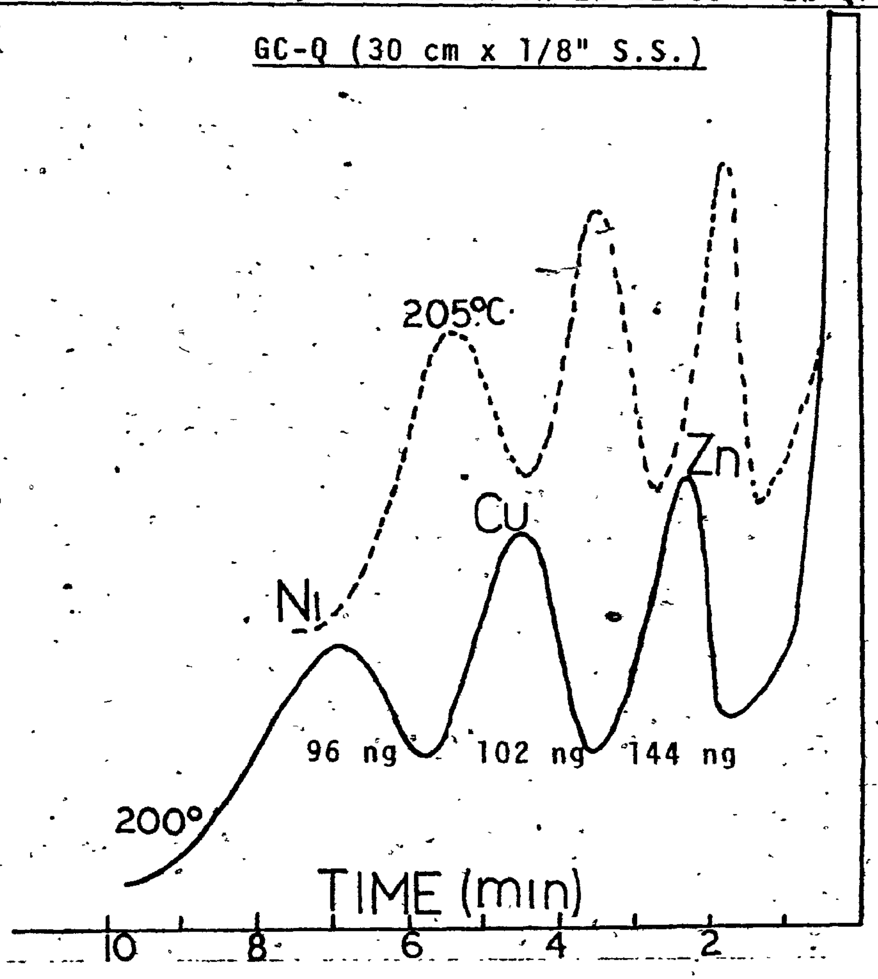


FIGURE 35

PEAK SHAPES ON 2% SE-30 + 2% QF-1 ON GC-Q

(30 cm x 1/8" S.S.)

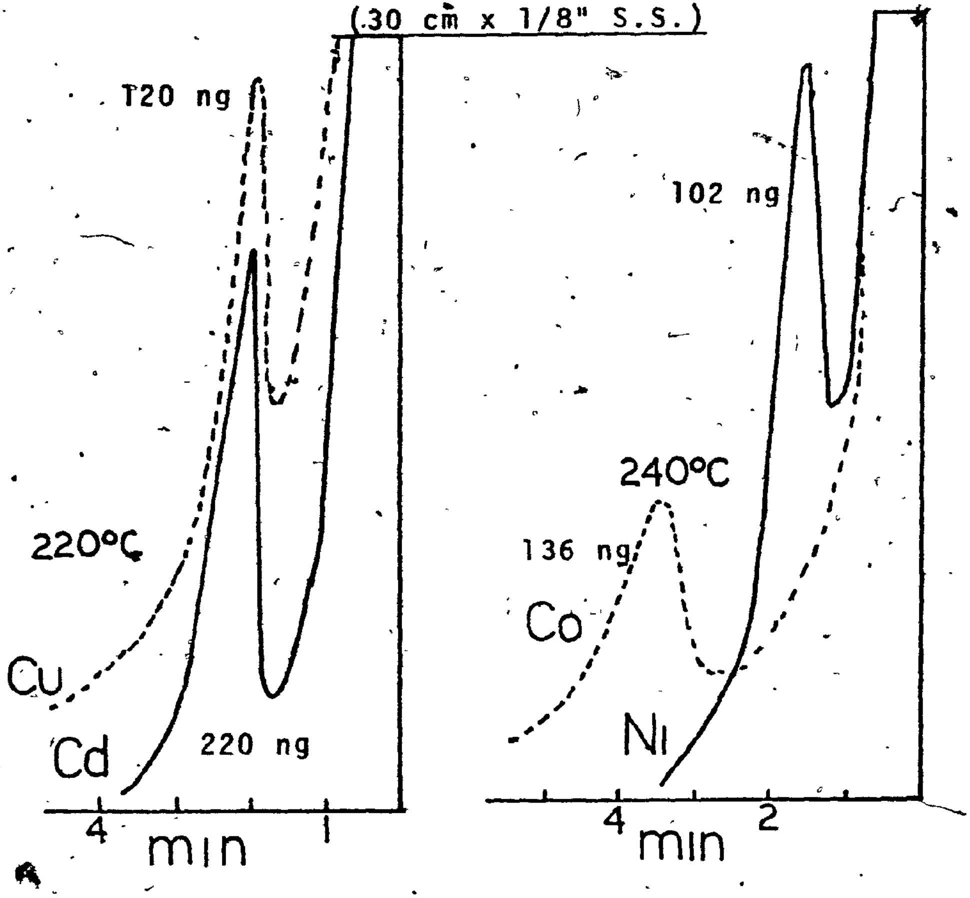


FIGURE 36

ANALYSIS OF Pb(DDC)$_2$ ON 2% SE-30 + 2% QF-1 ON GC-Q

(30 cm x 1/8" S.S.)

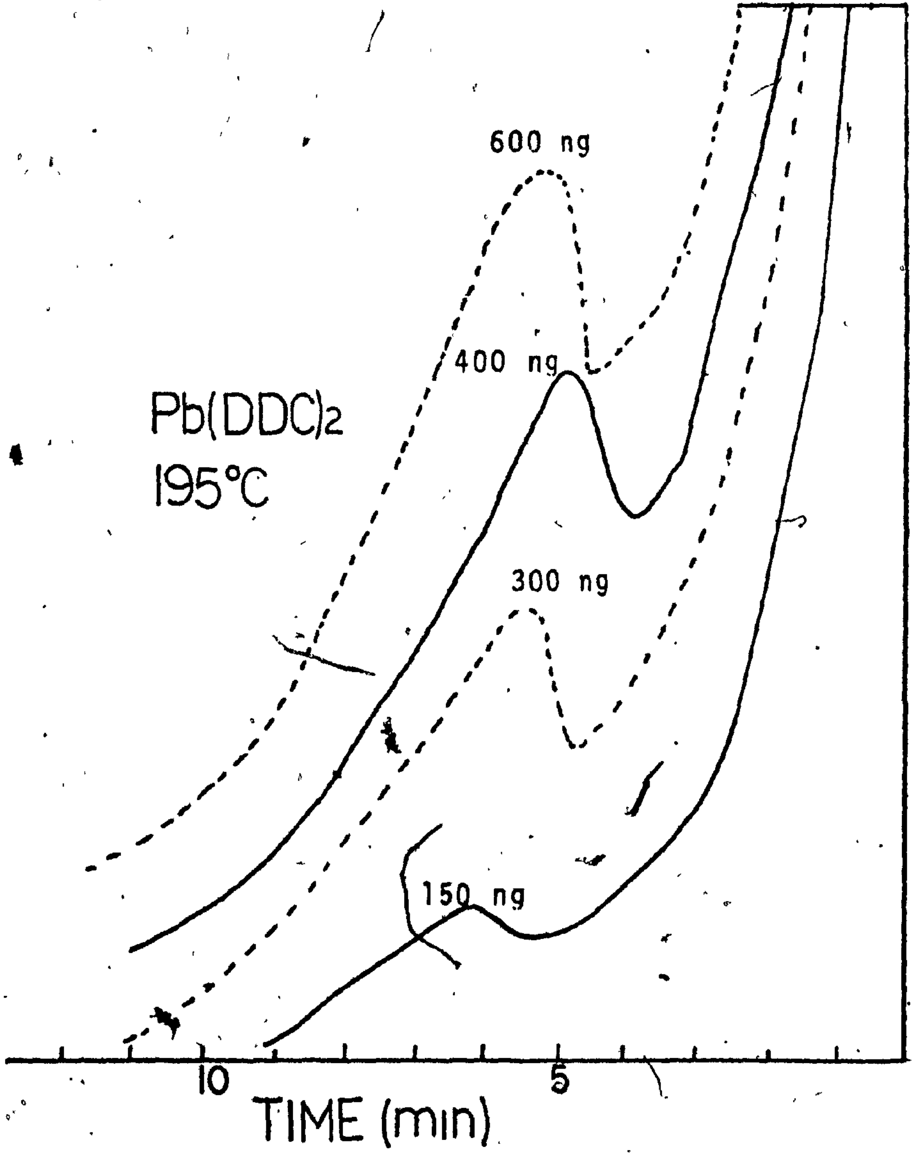


TABLE XXIV

DATA OBTAINED ON 2% SE-30 + 2% QF-1 ON GC-Q COLUMN* (30 cm x $^1/_8$")

Metal Chelate	Col. Temp. °C	Ret. Time (min)	Conc. Range for Calibration Lines (ng)	Regression Line Parameters Y-int. (mm²)	Slope (mm²/ng)	Corr. Coef.
$Cd(DDC)_2$	215	1.6	110-440	-342	2.73	1.000
$Zn(DDC)_2$	205	1.9	99-396	-283	3.78	.999
$Cu(DDC)_2$	215	2.3	71-284	-135	3.31	1.000
$Ni(DDC)_2$	220	2.7	42-168	-38.0	3.11	.999
$Co(DDC)_3$*	240	3.4	68-272	-110	3.00	1.000
$Co(DDC)_3$**	240	3.4	68-272	-149	3.76	1.000
$Pb(DDC)_2$	210	2.9	300-600	Not reproducible		
$Hg(DDC)_2$	230	1.5	244-610	-306	1.51	1.000

*, ** Calibration curves prepared on different days.

calibration lines were made on different days, but under the same conditions. Different results were obtained. This clearly demonstrated the requirement that analyses and calibrations had to be carried out at the same time for meaningful results to be obtained. Otherwise, an internal standard should be incorporated into the sample and standard solutions to eliminate variations in the system.

The results obtained upon analysis of ppm level concentrations of each of these metals individually are shown in Tables XXV and XXV(A). It can be seen in these Tables that the percent error in determinations ranged from 1.0% to 7.0% and the relative standard deviation (AV/STD x 100) ranged from 2.3% to 13.6%. These values are acceptable at these low ppm levels. The relative standard deviation may reflect non-reproducibility in the: (i) extraction, (ii) injection or (iii) peak area measurement techniques, and is most likely a combination of these effects. These values are in the range of those reported by Radecki et al. (37) in determination of Ni, Cu and Zn.

11.2.4.3 <u>3.5% OV-17 on CW-HP (40 cm x $^1/_8$" s.s.)</u>

Poor resolution of mixtures of Ni, Cu and Zn was obtained with this column at 240°C and 230°C. A long time was required for separation at 240°C (12.0 mins.). This packing was not studied any further because reduction of

TABLE XXV

ANALYSIS OF INDIVIDUAL ppm SOLUTIONS OF Cd, Zn, Cu AND Ni ON 2% SE-30 + 2% QF-1 ON GAS CHROM-Q (30 cm x $^1/_8$")

Sample	Cd (3.4 ppm)		Zn (1.1 ppm)		Cu (1.0 ppm)		Ni (1.0 ppm)	
	Expt (ppm)	% Error	Expt (ppm)	% Error	Expt (ppm)	% Error	Expt (ppm)	% Error
1	3.4	0.0	1.0	-9.1	1.1	+10	1.1	+10
2	3.4	0.0	1.0	-9.1	1.1	+10	0.87	-13
3	3.4	0.0	1.1	0.0	1.1	+10	0.82	-18
4	3.6	+5.9	1.1	0.0	1.0	0.0	1.1	10
5	3.6	+5.9	1.1	0.0	1.1	+10	1.0	0.0
6	3.4	0.0	1.1	0.0	1.0	0.0		
Av.± STD	3.5±0.08	2.0	1.1±0.05	-3.0	1.1±0.05	6.7	1.0±0.1	-2.2
Rel. STD	2.3%		4.5%		4.5%		10%	

TABLE XXV(A)

INDIVIDUAL ANALYSIS OF ppm SOLUTIONS OF Co AND Hg ON 2% SE-30 + 2% QF-1 (30 cm x $^1/_8$")

Sample	Co (0.67 ppm) Expt. (ppm)	Co (0.67 ppm) % Error	Hg (10.6 ppm) Expt. Conc. (ppm)	Hg (10.6 ppm) % Error
1	* 0.55	-15.0	10.9	+2.8
2	* 0.59	-10.6	10.8	+1.9
3	* 0.59	-10.6	10.0	-5.7
4	** 0.73	+9.0	10.9	+2.8
5	** 0.76	+13.0	10.8	+1.9
6	** 0.72	+5.0	11.0	+3.8
Av. ± STD	0.66 ± 0.09	-0.8	10.7 ± 0.37	1.3
Relative STD	13.6%		3.5%	

* First calibration line on Table XXIV was used for $Co(DDC)_3$.

** Second calibration line on Table XXIV was used for $Co(DDC)_3$.

retention times would require raising of temperature to values above 240^{0}C where decomposition may occur.

11.2.4.4 2% OV-17 + 2% SE-30 on CW-HP (40 cm x $^1/_8$")

This column did not show any advantage in terms of resolution as far as the separation of more than two components was concerned. Fig. 37 shows the results obtained when attempts were made to separate mixtures of three chelates using temperature programming. Results were not as good as what had already been achieved with OV-101 + QF-1 packings.

11.2.5.0 Tests Using Glass Tubing Packed Columns

The next step of this project was to determine the effect of column tubing on the separation of $M(DDC)_n$. Little effect of tubing was expected since Cardwell and Desarro (32) reported that glass and stainless steel tubing gave the same results for different $M(DDC)_n$ chelates.

Figs. 38 and 39 compare the resolution of a mixture of $Ni(DDC)_2$, $Cu(DDC)_2$ and $Zn(DDC)_2$ obtained using three columns: one, a stainless steel column (30 cm x $^1/_8$"), the second a glass column (60 cm x 2 mm); and the third a glass column (60 cm x 5 mm). All were packed with the same material, 2% SE-30 + 2% QF-1 on Gas Chrom-Q.

The resolution was better with both glass columns,

FIGURE 37

SEPARATION OF $M(DDC)_2$ ON 2% SE + 2% OV-17 ON CW-HP (40 cm x 1/8")

TEMP. PROG. 200 TO 235°C

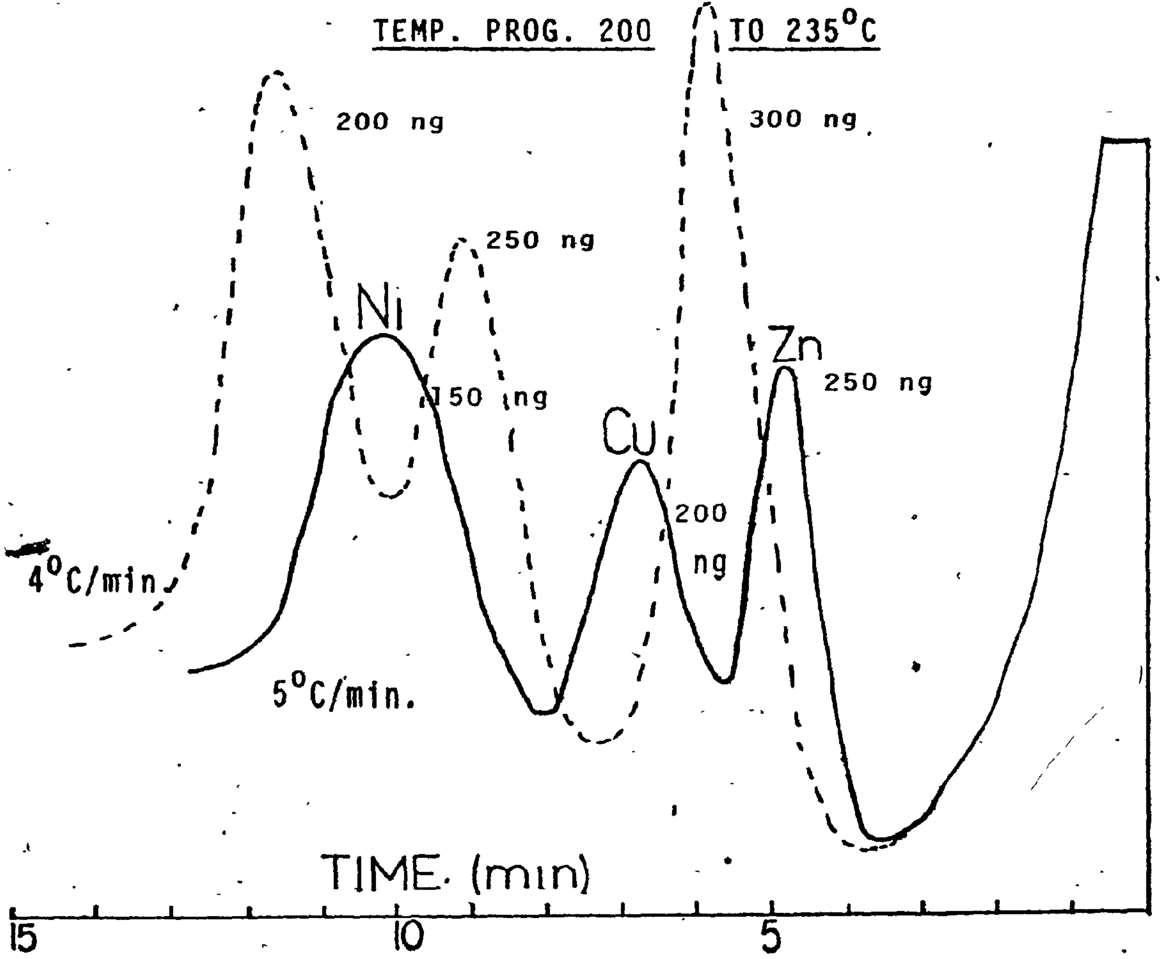


FIGURE 38

COMPARISON OF TUBING

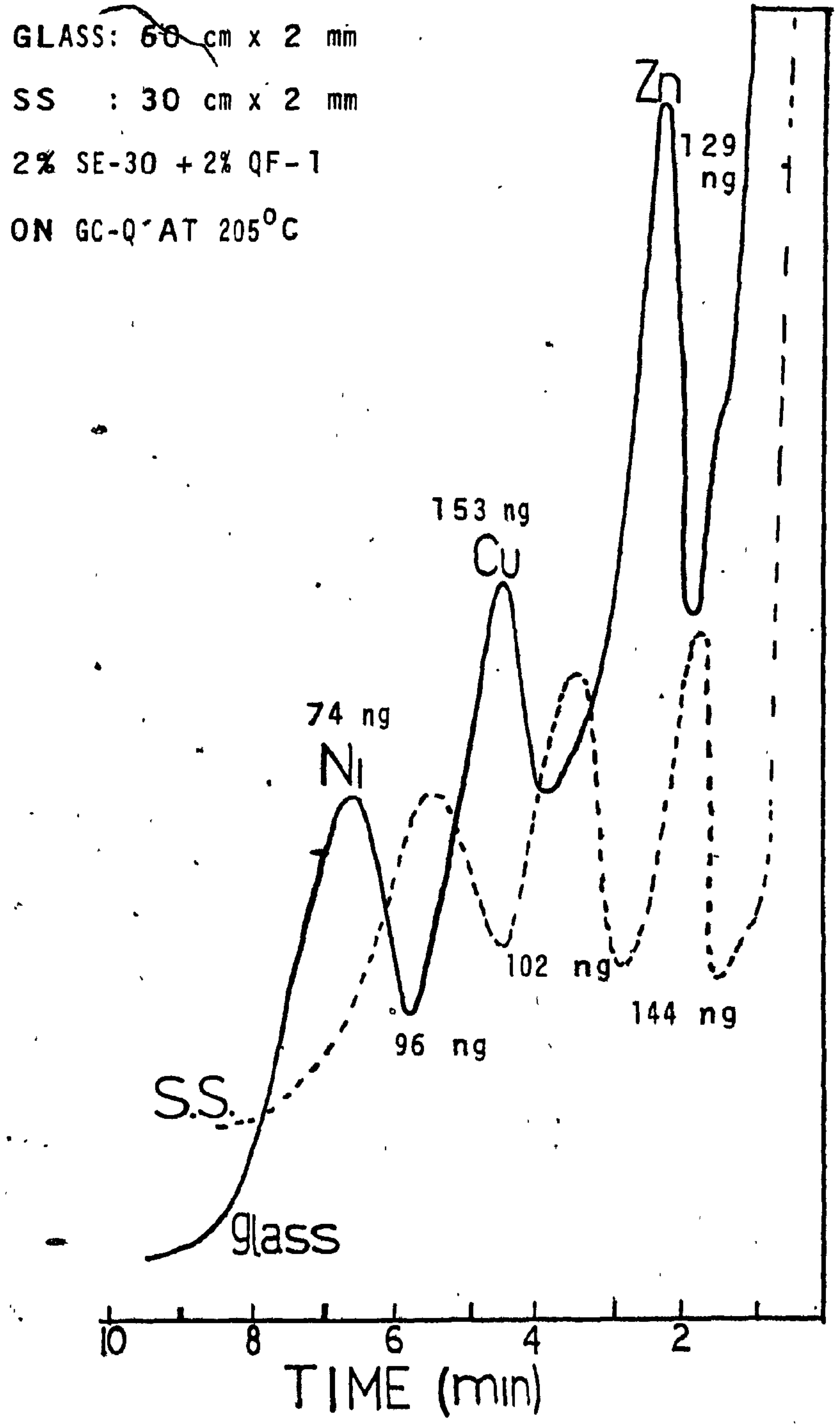
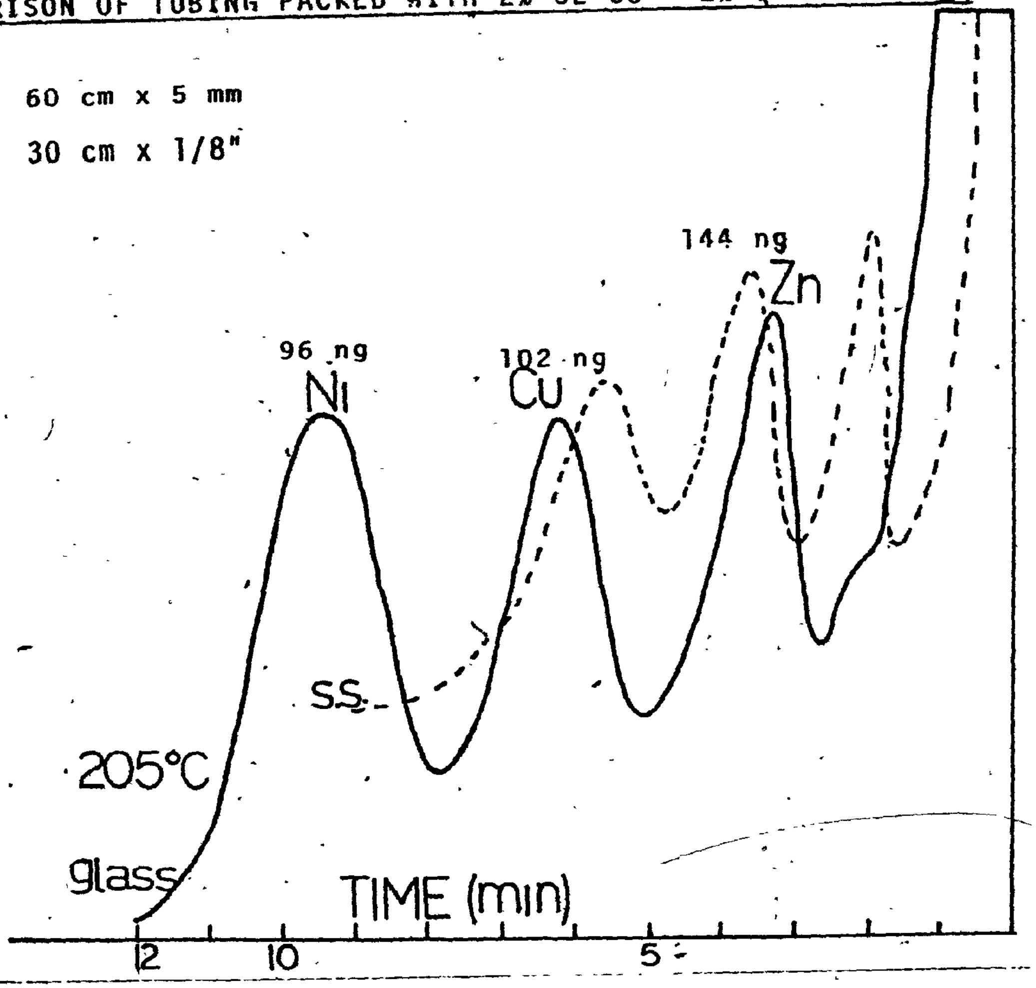


FIGURE 39

COMPARISON OF TUBING PACKED WITH 2% SE-30 + 2% QF-1 ON GC-Q

GLASS: 60 cm x 5 mm

S.S.: 30 cm x 1/8"



compared to the stainless steel column, but tailing of the solvent peak was greater with glass columns. Although it may be argued that the glass column was longer than the metal column and hence this accounted for the improvement in resolution, it must be pointed out that the use of longer metal columns, 60 cm, usually increased the retention times drastically, leading to flat peaks that impaired resolution.

An important advantage of using glass tubing columns was that no degradation of Pb, Cd and Hg was observed. Their peaks did, however, show some tailing (Fig. 40). These results were promising enough to justify analysis of these metals, individually, present in ppm amounts in aqueous test solutions by the procedure in Section 10.7.0. The results are shown in Table G-XXVI. The calibration lines used to obtain these results are shown in Fig. G-XX and Table GXX (Appendix I). Very satisfactory quantitation was achieved for these metals.

Excellent resolution of Ni, Cu and Zn was obtained using glass columns packed with 5% QF-1 + 5% OV-101 on CW-HP (60 cm x 5 mm or 2 mm). Results are shown in Figs. 41 and 42.

Table XXVII contains a comparison of resolution and retention times obtained on glass and stainless steel tubing columns containing the same packing and at the same temperature. Resolutions of 1.8 and 2.7 on the 2 mm i.d.

FIGURE 40

PEAK SHAPE OF Pb, Cd and Hg on 2% SE-30 + 2% QF-1 (60 cm x 2 mm) ON GC-Q GLASS

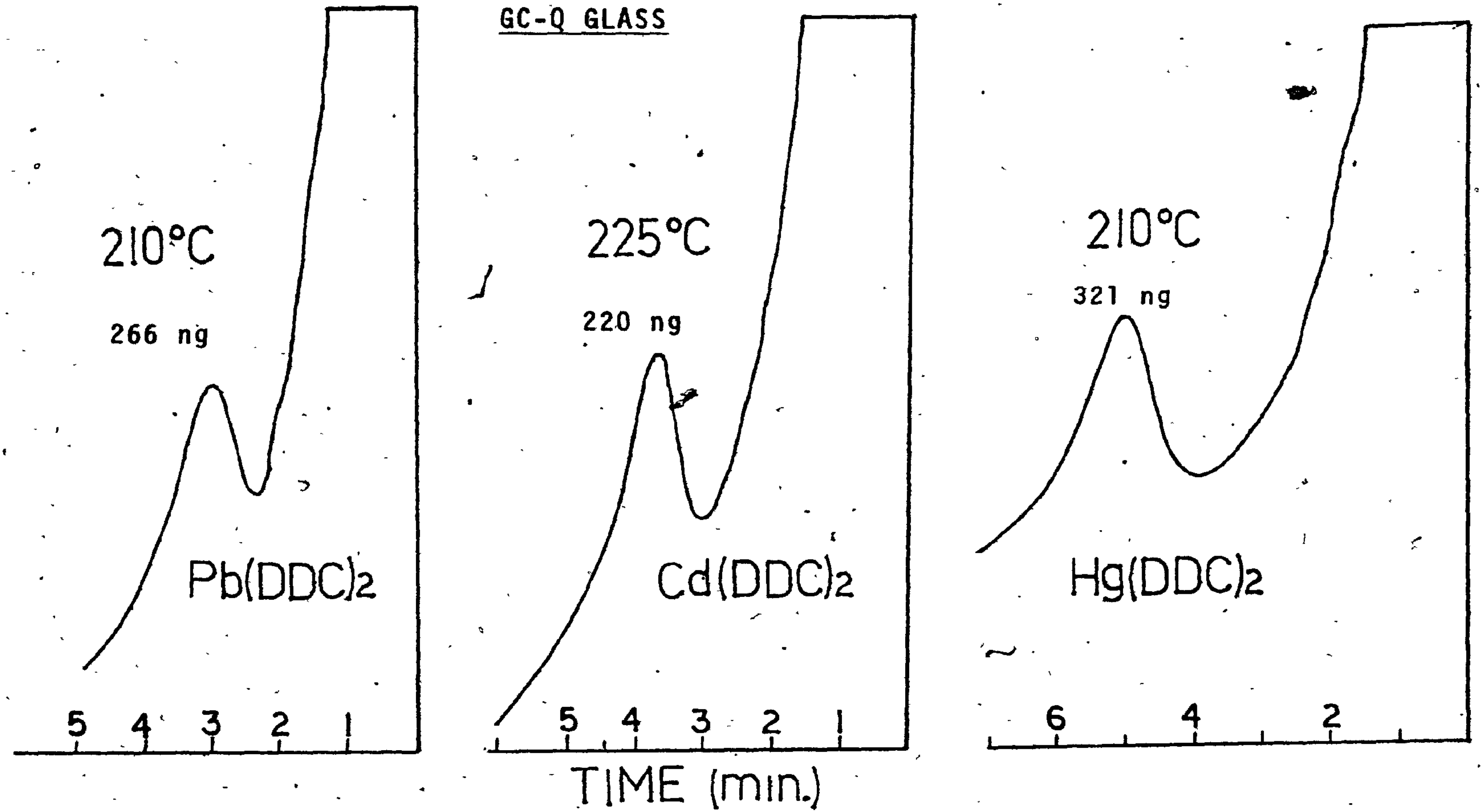


TABLE XXVI

ANALYSIS OF ppm SOLUTIONS OF Pb, Cd AND Hg ON 60 cm x 5 mm GLASS PACKED WITH 2% SE-30 + 2% QF-1 ON GC-Q*

	Cd (ppm)			Hg (ppm)			Pb (ppm)	
Theor.	Expt.	% Error	Theor.	Expt.	% Error	Theor.	Expt.	% Error
5.1	5.0	-2.0	7.2	7.1	-1.4	5.1	4.7	-7.8
	5.2	+2.0		6.7	-6.9		4.9	-3.9
	5.1	-2.0		7.5	+4.2		5.1	0.0
Av. ± STD	5.1±0.08	-0.7		7.1±0.37	-1.4		4.9±0.2	-3.9
Rel. STD	1.6%			5.2%			4.1%	
3.1	3.1	0.0	12.3	12.0	-2.5	10.3	10.4	+1.0
	3.1	0.0		12.1	-1.6		10.7	+3.9
	2.7	-12.9		12.5	+1.6		10.6	+2.9
	2.7	-12.9						
Av. ± STD	2.9±0.25	-6.5		12.2±0.24	0.8		10.6±0.15	2.6
Rel. STD	8.6%			2.0%			1.4%	

* Calibration lines on Fig. G-XX, Appendix I.

FIGURE 41

SEPARATION OF Ni, Cu AND Zn ON GLASS AND STAINLESS STEEL COLUMNS AT 220°C

5% QF-1 + 5% OV-101 ON CW-HP

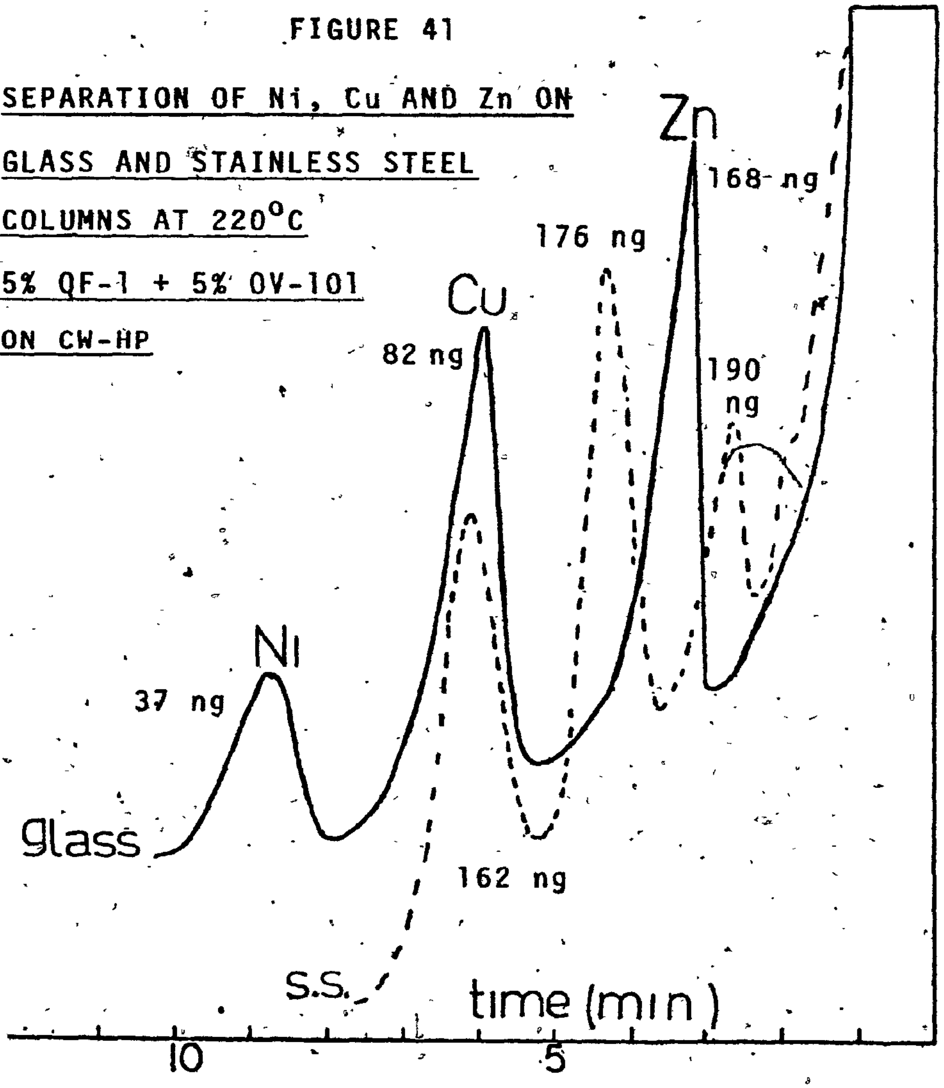


FIGURE 42

SEPARATION OF $M(DDC)_2$ ON 5% OV-101 + 5% QF-1 ON CW-HP GLASS TUBING (60 cm x 2 mm) AT 220°C

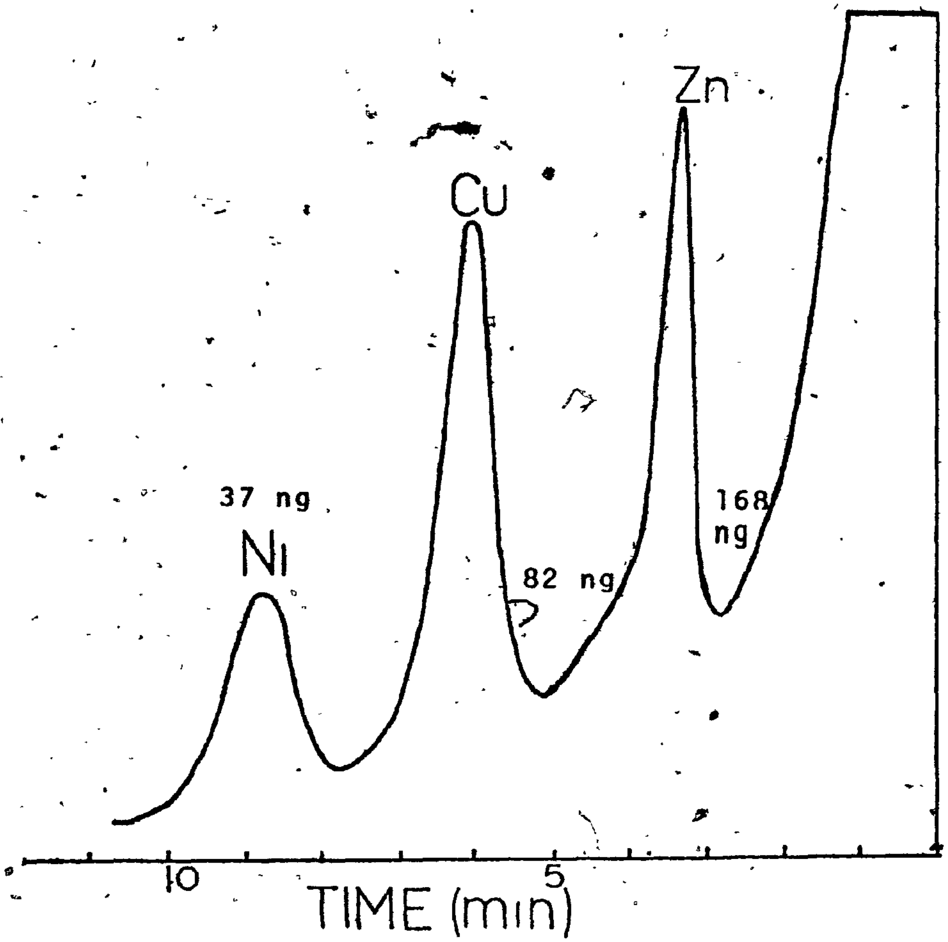


TABLE XXVII

RESOLUTION AND RETENTION TIMES ON 5% QF-1 + 5% OV-101 ON CW-HP AT 220°C

Compound	Glass (60 cm x 2 mm)		Stainless Steel (30 cm x 2 mm)	
	Ret. time (min.)	Resolution	Ret. time (min.)	Resolution
$Ni(DDC)_2$	8.8		5.9	
		1.8		1.4
$Cu(DDC)_2$	6.1		4.1	
		2.7		1.6
$Zn(DDC)_2$	3.4		2.6	

glass column are very significant. It can be shown that for two gaussian peaks of the same width, a Resolution of 1.5 represents 99.98% effective separation (50,69,71). L.S. Ettre (69) has pointed out that for resolution values greater than R=2.0, (R-1) additional peaks can be placed between the two peaks in question and a separation will still be obtained. This being the case, it should be possible to analyze for a metal whose retention time is between that of Cu and Zn at the same time as Zn, Cu and Ni are determined. To verify this hypothesis, separation was attempted of mixtures containing Ni, Cu, Zn and Cd, and of Hg, Cu, Zn and Cd. The results are shown in Fig. 43. The resolution was acceptable. Also, $Co(DDC)_3$ could be added to either of the above mixtures and a separation obtained by using column temperature programming. The best results were obtained when the column was maintained initially at 210°C for 10 minutes, followed by temperature programming at 10°C/min. up to 250°C, or by having the column initially at 210°C for 9 minutes and then programming at 20°C/min. to 250°C (Figs. 44 and 45). The limitation of this 5% OV-101 + 5% QF-1 packing is that as a temperature of 250°C is reached, QF-1 starts bleeding and the recorder base line rises appreciably under temperature programming conditions. It was thought that this problem could be eliminated by decreasing the amount of liquid phase on the support which would also reduce the time required for

FIGURE 43

SEPARATIONS ON 5% OV-101 + 5% QF-1

ON CW-HP GLASS (60 cm x 2 mm)

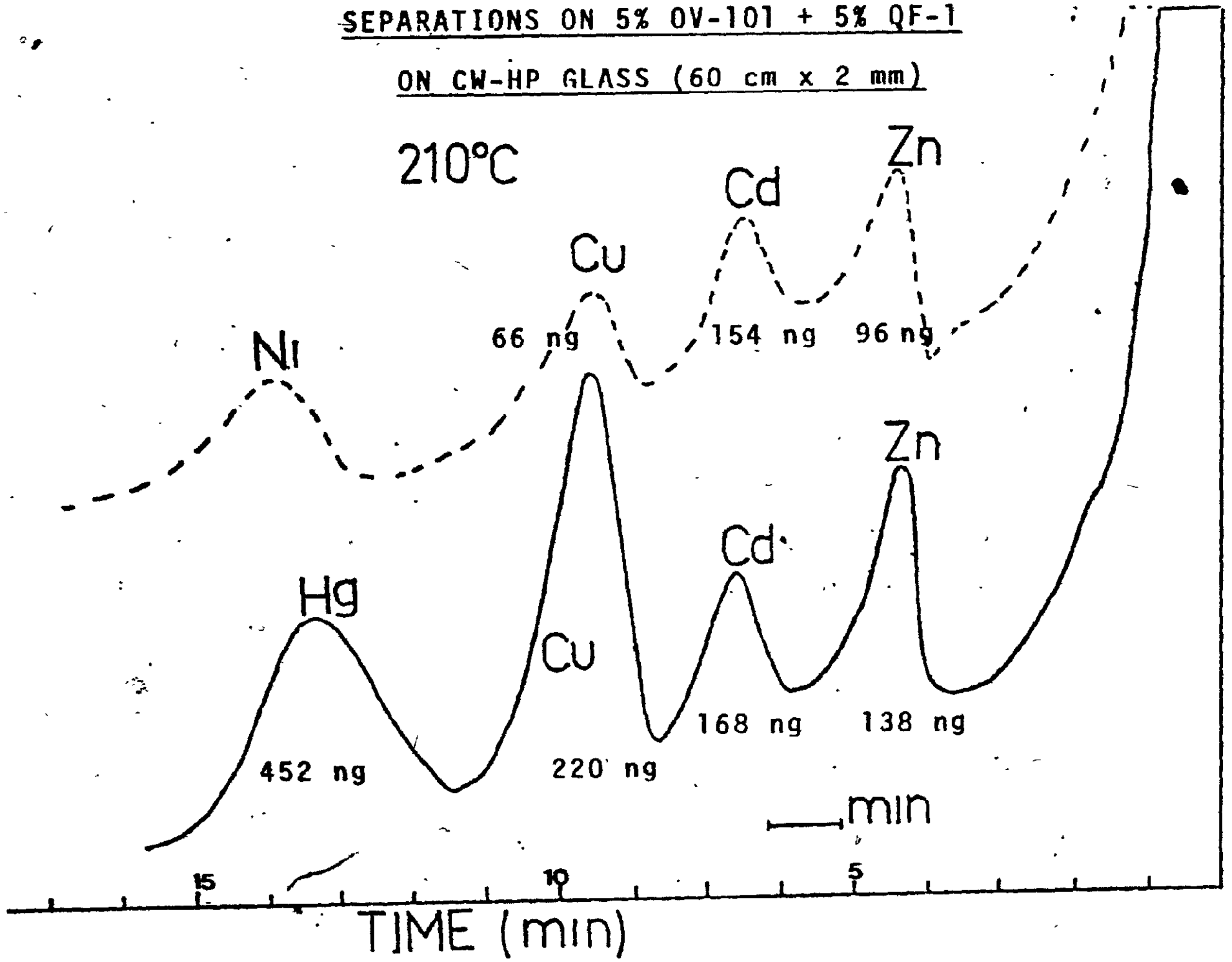


FIGURE 44

SEPARATION OF M(DDC)$_n$ ON 5% OV-101 + 5% QF-1 ON CW-HP (GLASS), 210° FOR 10 MIN., THEN PROG. AT 10°/MIN. TO 250°C

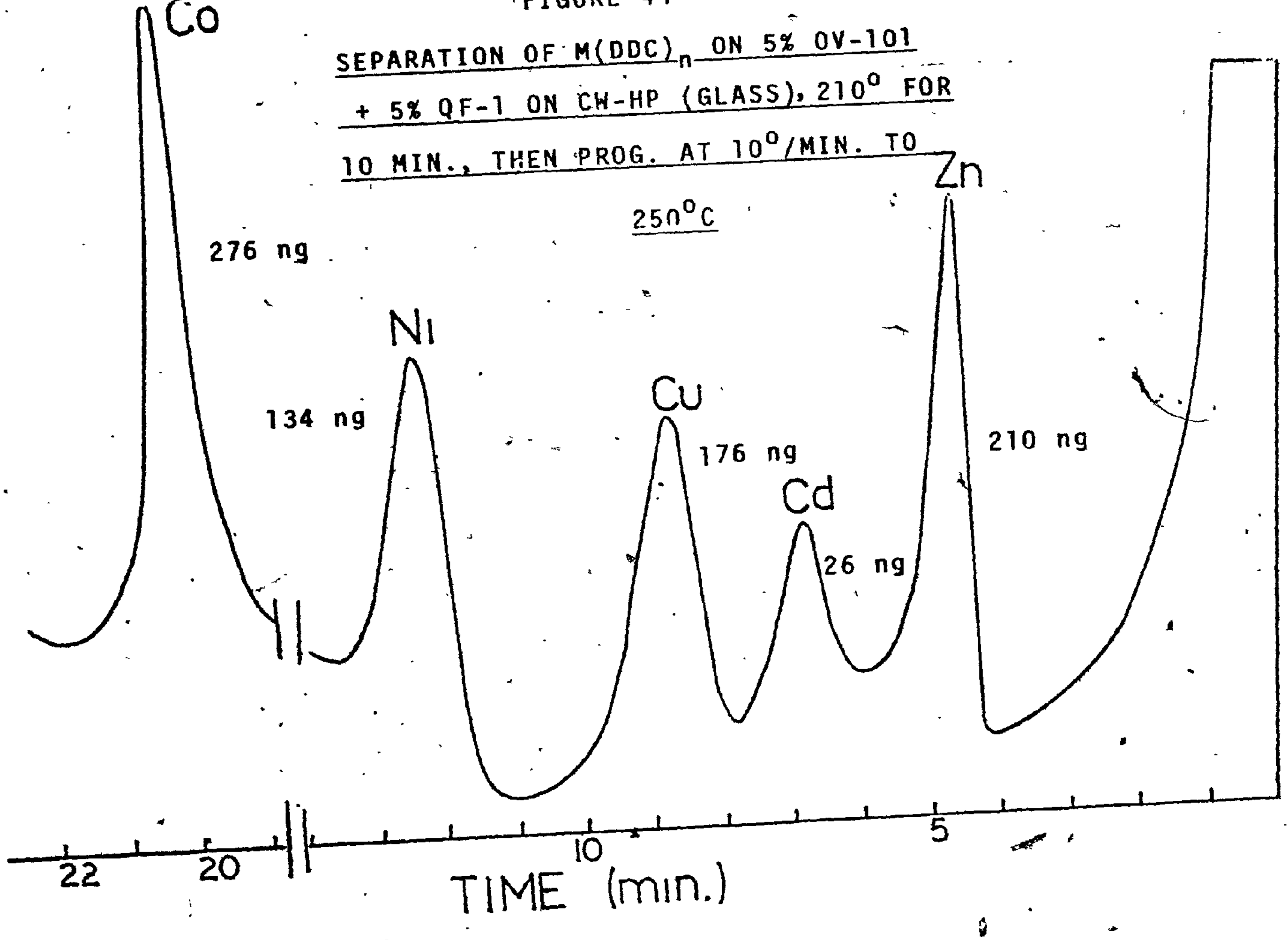
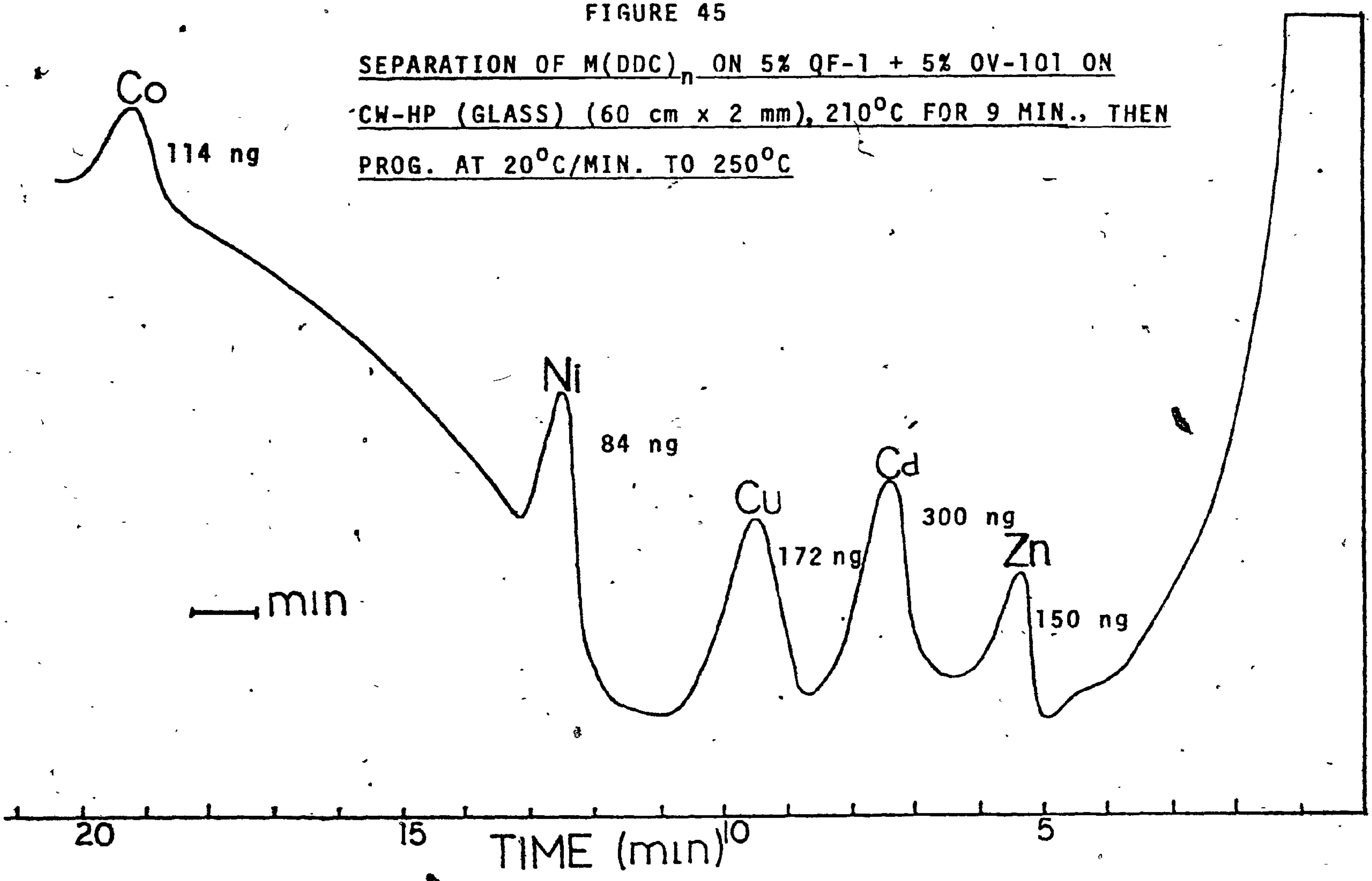


FIGURE 45

<u>SEPARATION OF M(DDC)$_n$ ON 5% QF-1 + 5% OV-101 ON CW-HP (GLASS) (60 cm x 2 mm), 210^{o}C FOR 9 MIN., THEN PROG. AT 20^{o}C/MIN. TO 250^{o}C</u>



analysis below 22 minutes. However, another problem that existed with this column was that of decomposition of $Pb(DDC)_2$ which gave two peaks that overlapped the peak for Cu. Linearity of peak area vs. ng plots using the 60 cm x 2 mm glass tubing packed with 5% QF-1 + 5% OV-101 on CW-HP are shown in Figs. G-XXI and G-XXI(A) and Table G-XXI (Appendix I). These plots were obtained by simultaneous analysis of the five metal chelates in a chloroform solution.

Using the above calibration lines, portions of a synthetic aqueous mixture containing Ni, Cu, Zn, Cd and Co in ppm amounts were analyzed as described in Section 10.7.0. The results obtained are given in Table XXVIII. It is interesting to note that the relative standard deviations and the percent errors ranged from 4.4% to 7.7% and 3.2% to 11.0%, respectively, which is reasonable. What was not acceptable was that 20 minutes was required for an analysis of a mixture including Co which eluted only after 18.7 mins. This places a major limitation on the calibration line method, since 3 to 4 hours is required to prepare the calibration lines. The solution to this problem would be to reduce retention times or to use the internal standard method and thereby eliminate the need for daily preparation of calibration lines. The latter method has its advantages and disadvantages. The approach followed in this project was to attempt reduction of retention times (and thereby analysis time).

TABLE XXVIII

RESULTS FROM SIMULTANEOUS ANALYSES OF ppm LEVEL SOLUTIONS OF METALS ON 5% QF-1 + 5% OV-101 ON CW-HP (GLASS TUBING*, 60 cm x 2 mm)**

	Zn (3.1 ppm)		Cd (5.1 ppm)		Cu (2.1 ppm)		Ni (2.1 ppm)		Co (2.0 ppm)	
	Expt. ppm	% Error	Expt. ppm	% Error	Expt. ppm	% Error	Expt. ppm	% Error	Expt. ppm	% Error
	3.4	9.7	4.5	-9.8	2.3	+9.5	1.8	-14.3	2.2	10.0
	3.3	6.5	5.0	-2.0	2.4	+14.3	2.0	-4.8	2.4	20.0
	3.1	0.0	4.9	-3.9	2.2	+4.8	2.0	-4.8	2.2	10.0
	3.1	0.0	5.0	-2.0	2.2	+4.8	2.0	-4.8	2.3	15.0
	3.1	0.0	5.0	-2.0	2.1	0.0	2.0	-4.8	2.0	0.0
Av.±STD	3.2±0.1	+3.2	4.9±0.2	-3.9	2.2±0.1	6.7	2.0±0.1	-6.7	2.2±0.1	11.0
Rel.STD	4.4%		4.5%		5.0%		4.5%		7.0%	

* Column temperature: 210°C for 9.0 min. then programmed at 20°C/min. to 250°C.

** Calibration lines shown in Fig. G-XXI and G-XXI(A), Appendix I.

11.2.5.1 Other Packings in Glass Tubing (60 cm x 2 mm)

In order to attempt to decrease analysis time, decrease liquid phase bleeding, and at the same time, to improve resolution, a number of packings were prepared where the amount of liquid phase was reduced from 5% QF-1 + 5% OV-101 to the following values: 2.5%, 1.5%, and 1.0% each of OV-101 and QF-1.

Separations are shown for mixtures of: Zn, Cd, Cu, Ni and Co chelates on: 2.5% QF-1 + 2.5% OV-101 on CW-HP (Fig. 46); Zn, Cd, Pb, Hg and Co on 1.5% OV-101 + 1.5% QF-1 on CW-HP (Fig. 47); and Zn, Cd, Ni, Cu and Co on 1% OV-101 + 1% QF-1 on Gas Chrom-Q (Fig. 48). Analysis time with these columns was reduced to about 15 minutes.

The second mixture, that of Zn, Cd, Co, Hg and Pb, was of much interest because its separation had not been accomplished before in this study. Therefore, quantitation was attempted even though resolution was only fair (Fig. 47). Aqueous solutions having these metals in ppm amounts were analyzed with the results obtained shown in Table XXIX. The calibration lines for each of these metal chelates are given on Fig. G-XXII and Table G-XXII (Appendix I). The highest percent error was obtained for Cd, 12%, along with a relative standard deviation of 8.3%. This high error for Cd is due to its peak being overlapped on both sides, the front by $Zn(DDC)_2$ and the tail by $Pb(DDC)_2$. This poor resolution made

FIGURE 46

2.5% QF-1 + 2.5% OV-101 ON CW-HP (60 cm x 2 mm)

TEMP. PROG. 200-240°C AT 5°C/MIN.

SEPARATION OF $M(DDC)_n$

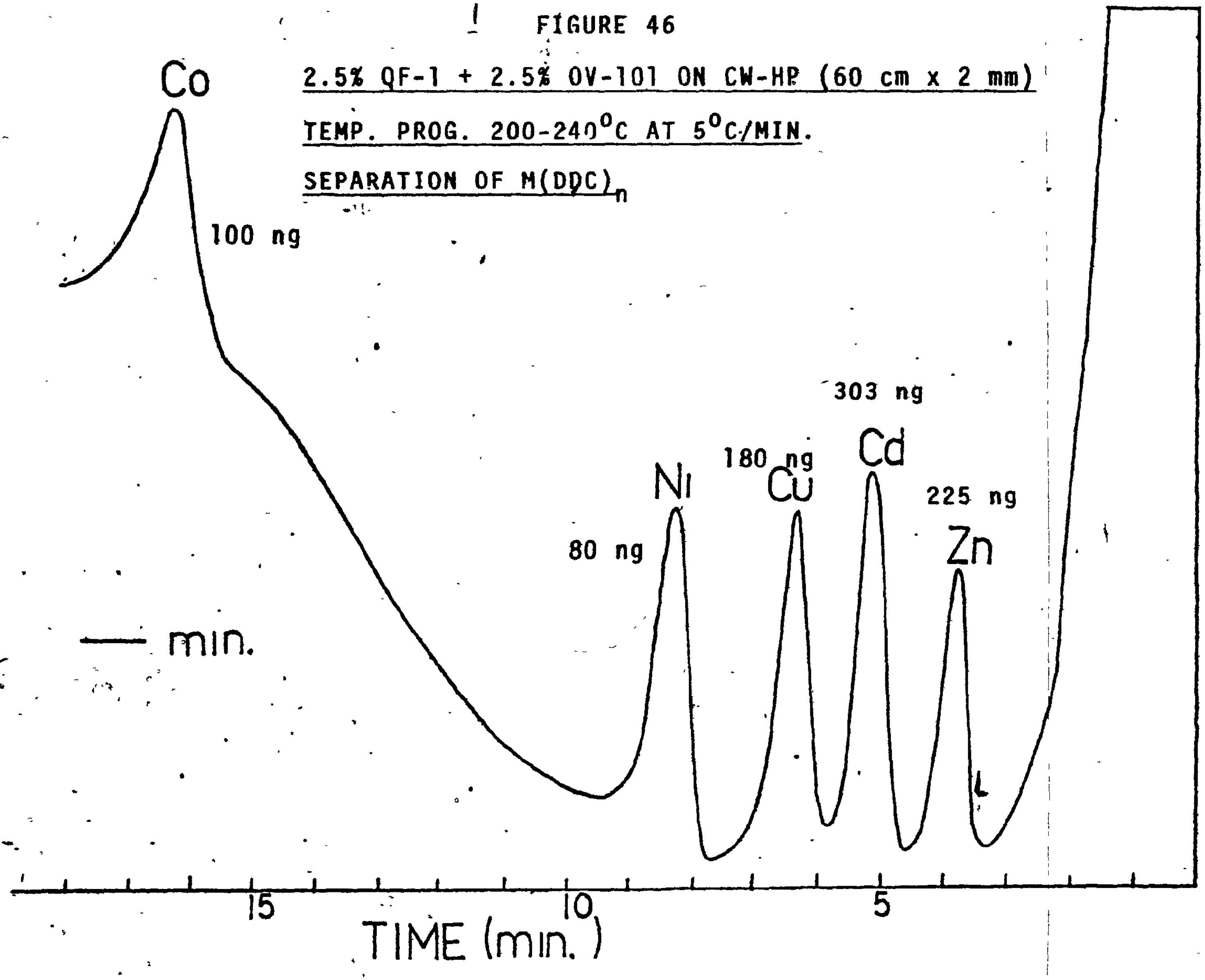


FIGURE 47

SEPARATION OF $M(DDC)_n$ ON 1.5% OV-101 + 1.5% QF-1 ON CW-HP (60 cm x 2 mm) 205°C FOR 8 MIN. AND PROG. AT 20°C/MIN. TO 245°C

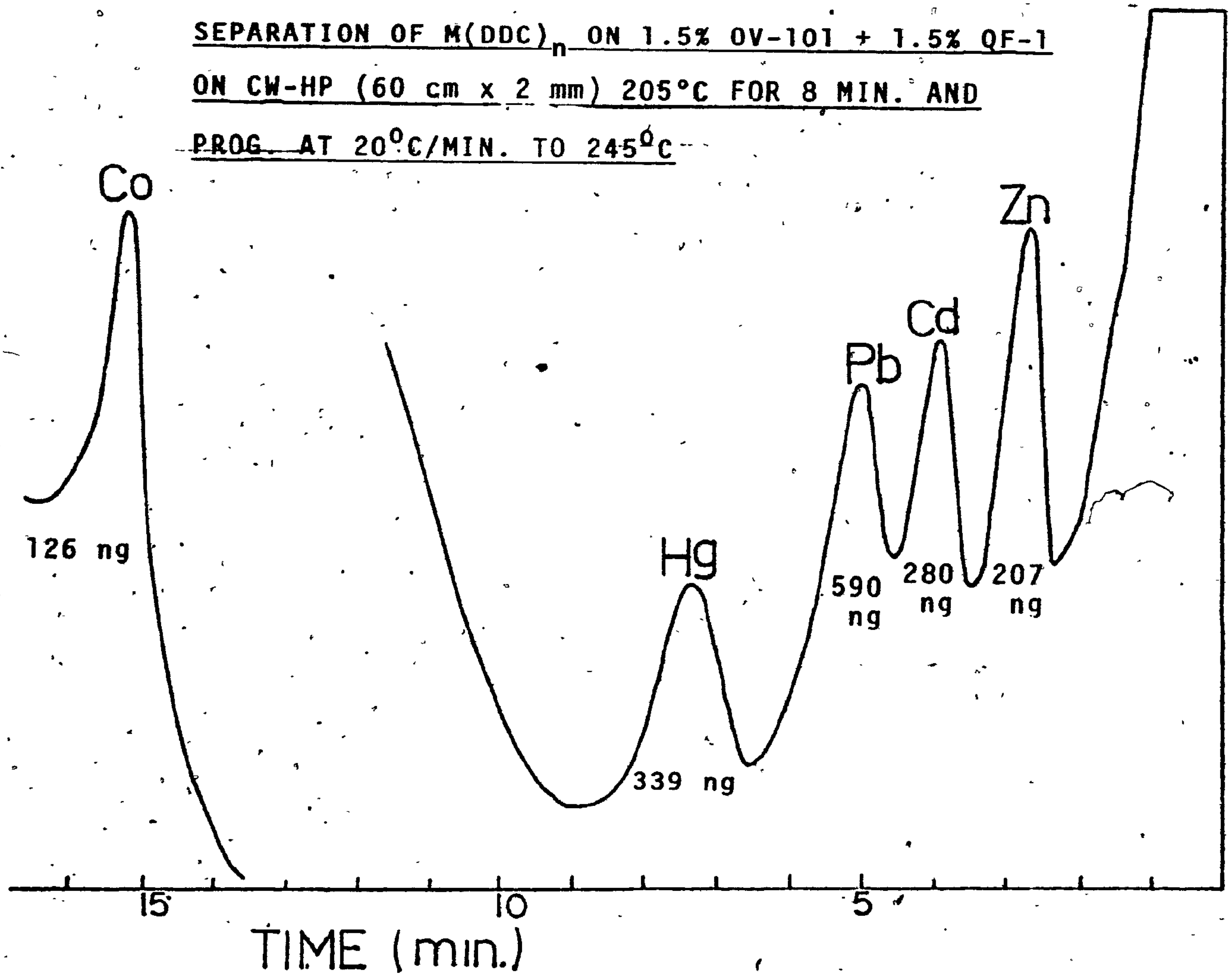


FIGURE 48

SEPARATION OF M(DDC)$_n$ ON 1% QF-1 + OV-101 ON GC-Q (60 cm x 2 mm), 190°C FOR 7 MIN., THEN PROG. AT 20°C/MIN. TO 245°C

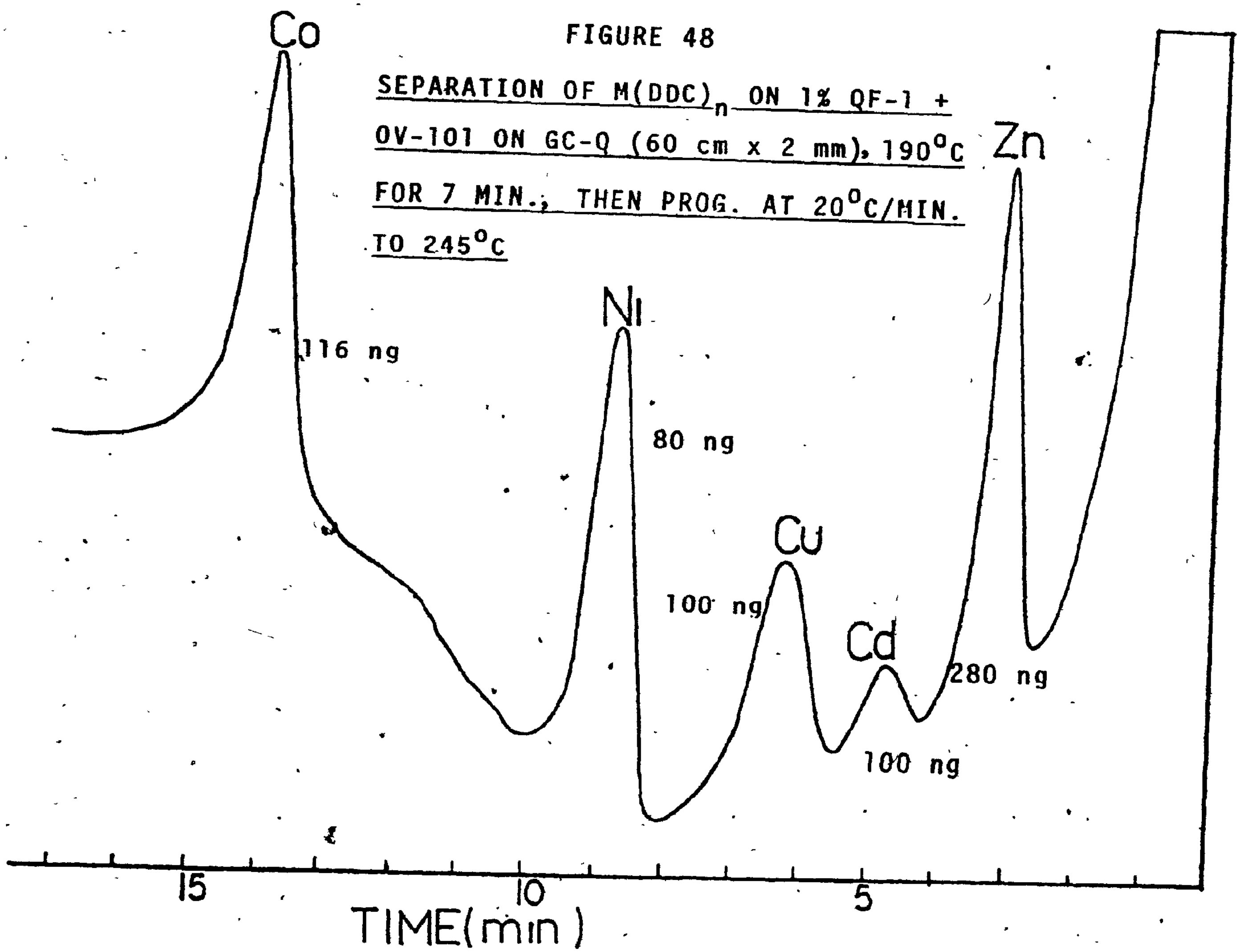


TABLE XXIX

ANALYSIS OF ppm MIXTURES OF Zn, Pb, Cd, Hg AND Co ON

1.5% QF-1 + 1.5% OV-101 CW-HP (GLASS TUBING 60 cm x 2mm)

	Zn (2.0 ppm)		Cd (2.0 ppm)		Pb (8.1 ppm)		Hg (5.1 ppm)		Co (1.0 ppm)	
	Expt. ppm	% Error	Expt. ppm	% Error	Expt. ppm	% Error	Expt. ppm	% Error	Expt. ppm	% Error
	2.0	0.0	1.6	-2.0	8.2	+1.2	5.2	+2.0	1.0	0.0
	1.9	-5.0	1.9	-5.0	8.3	+2.5	5.3	+3.9	1.0	0.0
	2.0	0.0	1.9	-5.0	8.0	-1.2	4.9	-3.9	1.1	+10.0
	1.9	-5.0	1.8	-10	7.7	-4.9	4.8	-5.9	1.1	+10.0
	1.8	-10	1.6	-2.0	7.8	-3.7	5.1	0.0	1.0	0.0
Av.±STD	1.9±0.1	-4.0%	1.8±0.15	-12.0%	8.0±0.3	-1.2%	5.1±0.2	0.8%	1.0±0.05	4.0%
Rel.STD	5.3%		8.3%		3.8%		3.9%		5.0%	

* Temperature: 205°C for 8 min., then programmed at 20°C/min. to 235°C.

** Calibration lines shown in Fig. G-XXII, Appendix I.

difficult the determination of peak area for Cd(DDC)$_2$. All other metals were determined with an accuracy no worse than 4.0%. Relative standard deviations were in the same range as those obtained with the previous columns.

Aqueous mixtures containing known ppm amounts of Ni, Cu, Zn, Cd and Co were analyzed using the 1% OV-101 + 1% QF-1 on GC-Q packing (60 cm x 2 mm) to determine the degree to which accuracy and precision are improved when a mixture is well resolved and bleeding from the column is reduced (Fig. 48). The results of these analyses are shown in Table XXX. The calibration lines used to calculate these results are shown in Fig. G-XXIII and Table G-XXIII (Appendix I). The percent error for each metal was less than 8% and the relative standard deviations were less than 4.5%. This indicated that good resolution improved accuracy and reproducibility of results but not by all that much.

11.2.5.2 Some Conclusions Regarding GC Results

It has been established that synthetic aqueous mixtures containing up to five metals can be separated quantitatively. In fact, glass tubing (60 cm x 2 mm) packed with 1.5% QF-1 + 1.5% OV-101 on CW-HP (or 2.5% QF-1 + 2.5% OV-101 on CW-HP) can be used to analyze mixtures of the following compositions:

(i) Ni, Cu, Cd, Co and Zn (Fig. 49)

TABLE XXX

ANALYSIS OF AQUEOUS MIXTURES CONTAINING ppm AMOUNTS OF Ni, Cu, Zn, Cd AND Co on 1.0% OV-101 + 1% QF-1 ON GC-Q (60 cm x 2 mm)

	Zn (5.1 ppm)		Cd (3.1 ppm)		Cu (2.1 ppm)		Ni (2.1 ppm)		Co (2.0 ppm)	
	Expt. ppm	% Error	Expt. ppm	% Error	Expt. ppm	% Error	Expt. ppm	% Error	Expt. ppm	% Error
	4.7	-7.8	2.9	-6.5	2.1	0.0	2.1	0.0	1.9	-5.0
	4.9	-3.9	3.0	-3.2	2.2	4.8	2.3	9.5	1.9	-5.0
	4.8	-5.9	3.1	0.0	2.1	0.0	2.2	4.5	2.0	0.0
	4.6	-9.8	3.1	0.0	2.2	4.8	2.1	0.0	2.1	5.0
	4.7	-7.8	3.0	-3.2	2.1	0.0	2.1	0.0	1.9	-5.0
Av±STD	4.7±0.1	-7.0%	3.0±0.08	-2.6%	2.1±0.05	1.9%	2.2±0.09	2.8%	2.0±0.09	-2.0%
Rel.STD	2.1%		2.7%		2.4%		4.1%		4.5%	

* Column temperature (190°C for 7 mins..then programmed at 20°C/min. to 250°C).

** Calibration lines shown in Fig. G-XXIII, Appendix I.

(ii) Hg, Pb, Cd, Zn and Co (Fig. 50)
(iii) Zn, Cd, Cu, Hg and Co (Fig. 51)
(iv) Ni, Pb, Cd, Co and Zn

A major unresolved problem is that resolution of mixtures appears to be poor whenever Pb is present. Mixture (iv) listed above was not actually analyzed in this study, but the separation predicted should be possible since $Hg(DDC)_2$ and $Ni(DDC)_2$, and $Pb(DDC)_2$ and $Cu(DDC)_2$, have very similar retention times under the same GC conditions.

The order of elution of the metal chelates and the possible decomposition of some of them may be related to their ionic radii and metal-sulphur bonding characteristics. A hypothesis is given in Appendix II to explain these effects.

11.2.6.0 Lower Limits of Detection

In order to establish the limitations of the methodology developed here for analysis of metals by FID-gas chromatography, the minimum amounts of metals that could be detected had to be determined. Typical detection limits for each metal chelate studied were evaluated for both glass and stainless steel columns and are listed in Table XXXI.

It should be noted that lower limits of detection were obtained with the glass tubing. This suggests some loss of the metal chelates on the surface of stainless steel because of adsorption and/or degradation. Also, detection limits

FIGURE 49

SEPARATION OF $M(DDC)_n$ ON 1.5% QF-1 + 1.5% OV-101 ON CW-HP (60 cm x 2 mm, GLASS). TEMPERATURE PROG. FROM 200°C to 230°C AT 5°C/MIN. AND MAINTAINED AT 230°C

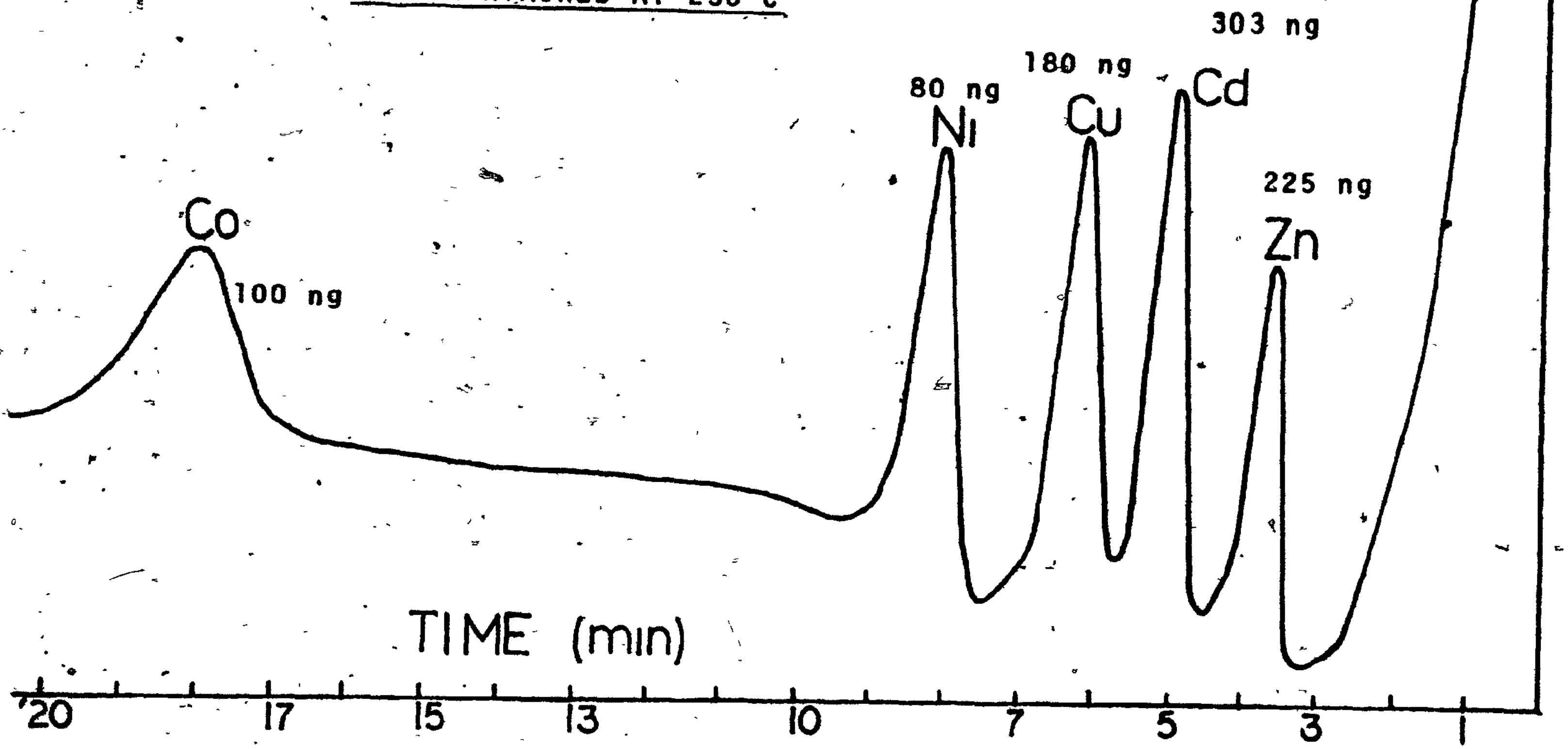
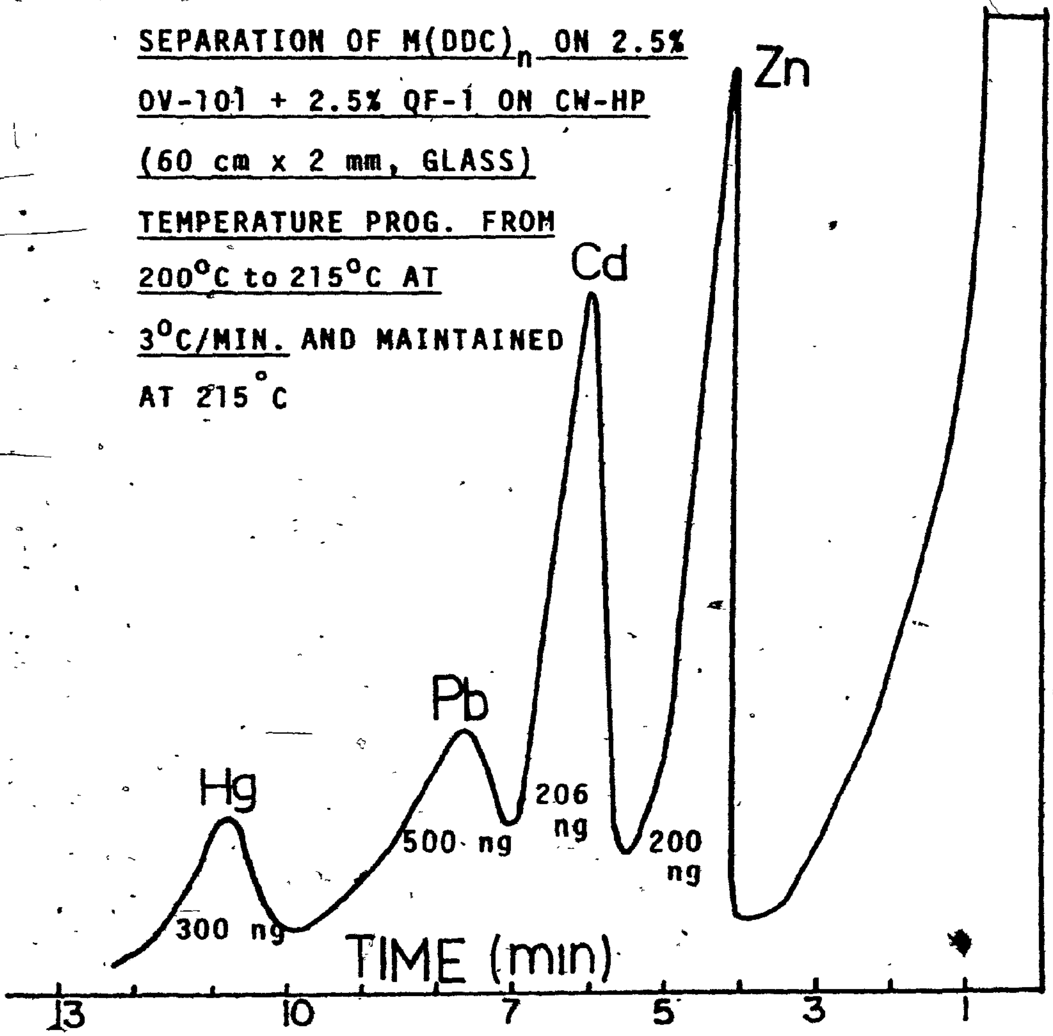


FIGURE 50

SEPARATION OF $M(DDC)_n$ ON 2.5% OV-101 + 2.5% QF-1 ON CW-HP (60 cm x 2 mm, GLASS) TEMPERATURE PROG. FROM 200°C to 215°C AT 3°C/MIN. AND MAINTAINED AT 215°C



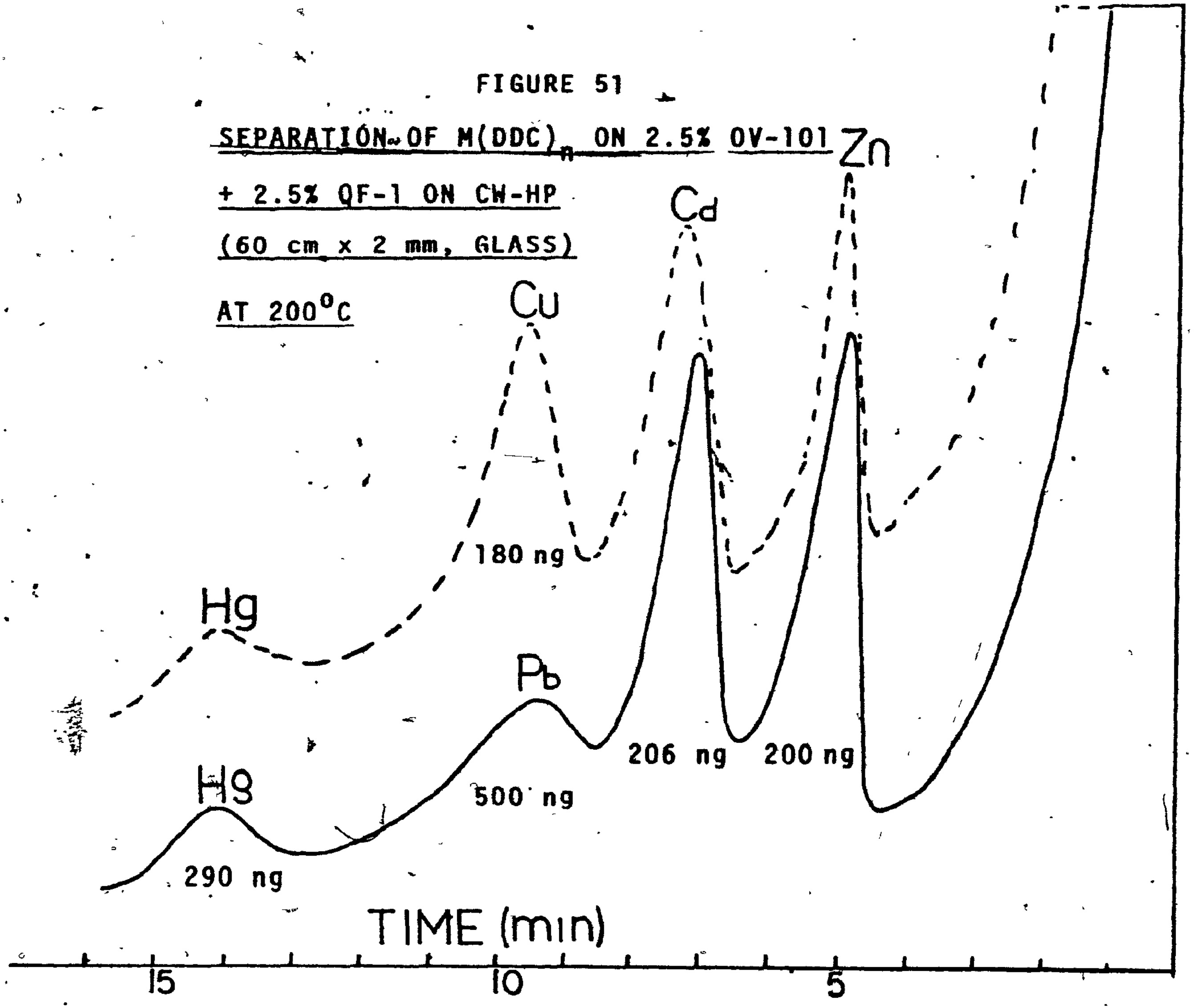


FIGURE 51

SEPARATION OF M(DDC)$_n$ ON 2.5% OV-101
+ 2.5% QF-1 ON CW-HP
(60 cm x 2 mm, GLASS)
AT 200°C

TABLE XXXI

FID DETECTION LIMITS FOR A SIGNAL/NOISE RATIO = 3

Metal Chelate	Chelate (ng)		Metal (ng)		Min. Conc. of Metal Detectable (ppb)
	Glass Tubing*	Stainless Steel**	Glass Tubing*	Stainless Steel**	Glass
Ni(DDC)$_2$	20	30	3.3	5.0	17
Cu(DDC)$_2$	40	70	7.1	12.4	35
Zn(DDC)$_2$	70	100	12.6	18.1	63
Cd(DDC)$_2$	56	110	15.4	30.2	77
Hg(DDC)$_2$	100	150	40.4	60.5	202
Pb(DDC)$_2$	150	220	61.7	90.5	310
Co(DDC)$_3$	30	30	3.5	3.5	18

* Packed with 1.5% QF-1 + 1.5% OV-101 on CW-HP. Column temperature - 190°C for 5 mins., then programmed to 250°C at 20°C/min.

** Packed with 2% SE-30 + 2% QF-1 on CW-HP. Column temperature - 210°C, except for Co(DDC)$_3$ at 250°C.

depended on the amount of metal present in each chelate. For example, smaller amounts of Co and Ni chelates could be detected than of Pb and Hg chelates. This was observed with both glass and metal tubing columns, and was dependent on the fact that FID-detector does not respond to the metal part of the chelate, but only to the organic fraction.

In practical terms, the meaning of these detection limits is as follows. For example, for the case of $Ni(DDC)_2$, if 20 ng is the detection limit, then a solution containing 5 ng/ml of $Ni(DDC)_2$ (or 0.8 ng/ml Ni) can be detected if 4.0 ul of sample is injected for GC analysis. (Injection of more than 4 μl is unlikely to be feasible since the solvent peak would most likely overlap the $Ni(DDC)_2$ peak.) If the aqueous sample solution containing Ni is of a volume of 50.0 ml, and is extracted with a 1.0 ml volume of chloroform, then it should be possible to detect as little as 17 ppb of Ni in the aqueous sample. Similarly, Pb amounts as little as 0.3 ppm could be determined with the FID. It can be predicted that using the ECD even lower concentrations should be detectable. For example, Tavlaridis and Neeb (33B) reported detection of amounts as small as 20 pg of $Ni(DDC)_2$ (3.3 pg of Ni). By using non-electron affinitive extraction solvents to isolate the $M(DDC)_n$ it should be possible to inject samples considerably greater than 4 μl without affecting the operation of the ECD, and without solvent peak overlapping of the sample peak, hence enabling lower levels of detection.

11.2.7.0 HPLC of Mixtures of $M(DDC)_n$

There have been reports in the literature describing the use of HPLC for separation of mixtures of $M(DDC)_n$ chelates. Separation of about seven metal chelates has been claimed, but in fact, resolution was poor using either HPLC or reversed phase HPLC (41,42,42A).

The possibility of using HPLC for separation of mixtures of $M(DDC)_n$ prepared in this study was of interest since it was hoped that by avoiding the use of elevated temperatures, as is required in GC, degradation problems observed with, for example, Hg and Pb, could be eliminated. Accordingly, to compare the effectiveness of liquid chromatography relative to the GC method developed in this project, HPLC was used to attempt separation of a number of mixtures.

A stainless steel column, 20 cm long and 0.46 cm inside diameter, packed with a silica type adsorbent LiChrosorb-C, of particle size 10 µm was used. LiChrosorb-C is a porous type material with a surface area of about 300 m^2/g. This particular packing has been claimed to be selective for compounds close to one another in polarity. A number of trials were carried out. Two different solvent systems were used as mobile phases, 2% ethylacetate in cyclohexane, and

2% chloroform in cyclohexane. Both of these solvent systems have been reported to be useful in the separation of diethyldithiocarbamates (41).

The best results were obtained using 2% ethylacetate in cyclohexane (v/v). The maximum number of compounds that could be separated was only four; $Co(DDC)_3$, $Ni(DDC)_2$, $Cu(DDC)_2$ and $Hg(DDC)_2$ (Figs 52 and 53). The retention times and detection limits of the chelates tested individually are shown in Table XXXII under the conditions reported in Table VI, Section 10.8.0.

It should be noted that the retention times were shorter when ethylacetate was used as mobile phase rather than chloroform. This indicated that ethylacetate has more affinity for the adsorbent than does chloroform. This may be attributed to the ability of ethylacetate to form hydrogen bonds with the hydroxyl groups on the surface of the adsorbent. Another point that should be noted is that $Fe(DDC)_3$ could not be analyzed by HPLC. It gave three peaks even under room temperature conditions used. The retention times of $Ni(DDC)_2$, $Zn(DDC)_2$, $Pb(DDC)_2$ and $Cd(DDC)_2$ were very similar. This rendered unfeasible attempted separation of mixtures including more than any one of these compounds.

The detection limits were in the same range as those for GC-FID, except for $Ni(DDC)_2$ where 4.2 ng could be detected, compared to 20 ng by GC-FID.

FIGURE 52

SEPARATION OF $M(DDC)_2$ BY HPLC, 2% $CH_3COOC_2H_5$ IN CYCLOHEXANE, LICHROSORB-C (20 cm x 0.46 cm s.s.)

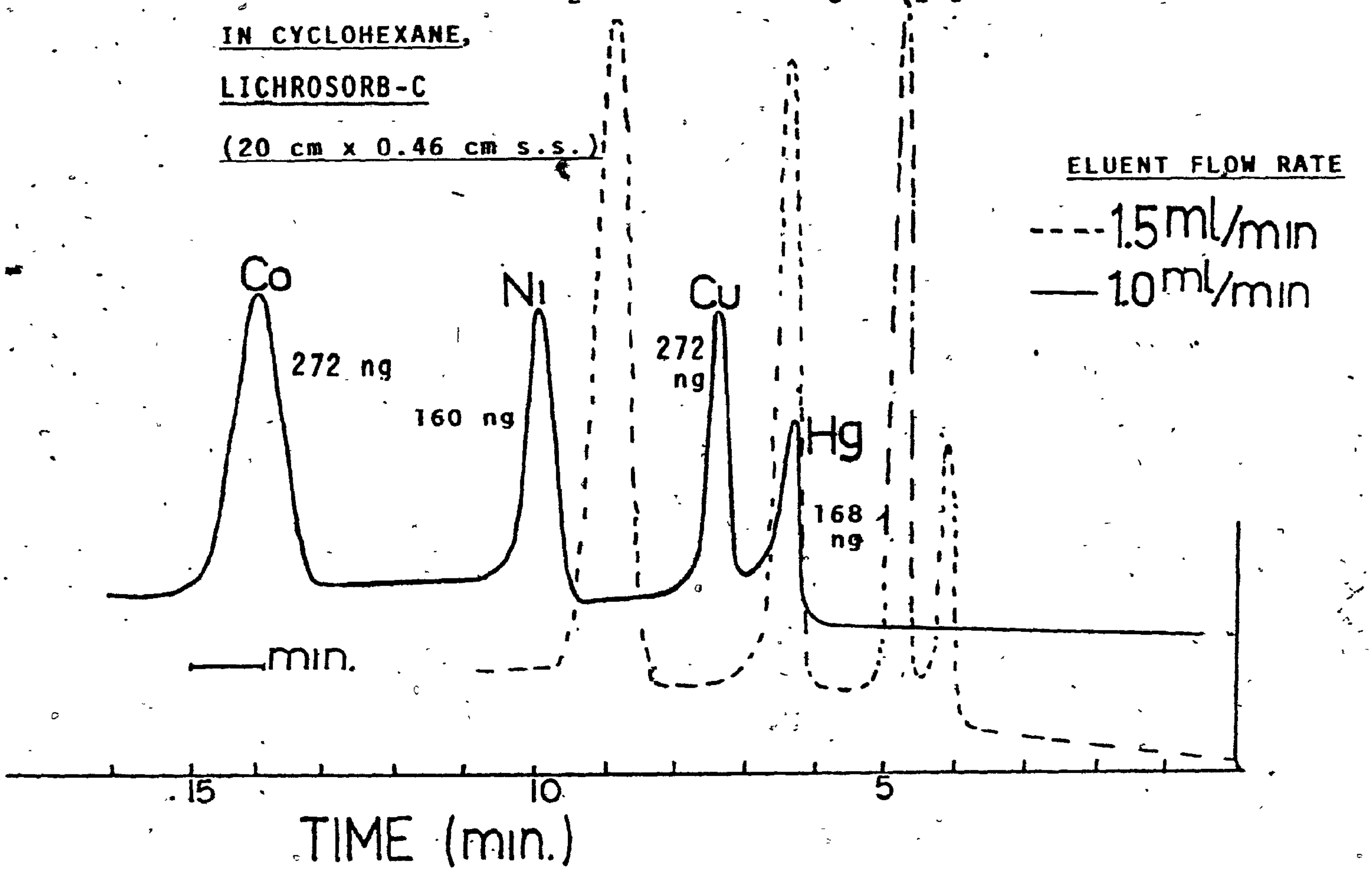


FIGURE 53

SEPARATION OF M(DDC)$_n$ BY HPLC,

2% CHCl$_3$ IN CYCLOHEXANE,

LICHROSORB-C (20 cm x 0.46 cm)

FLOW RATE 2.0 ml/min.

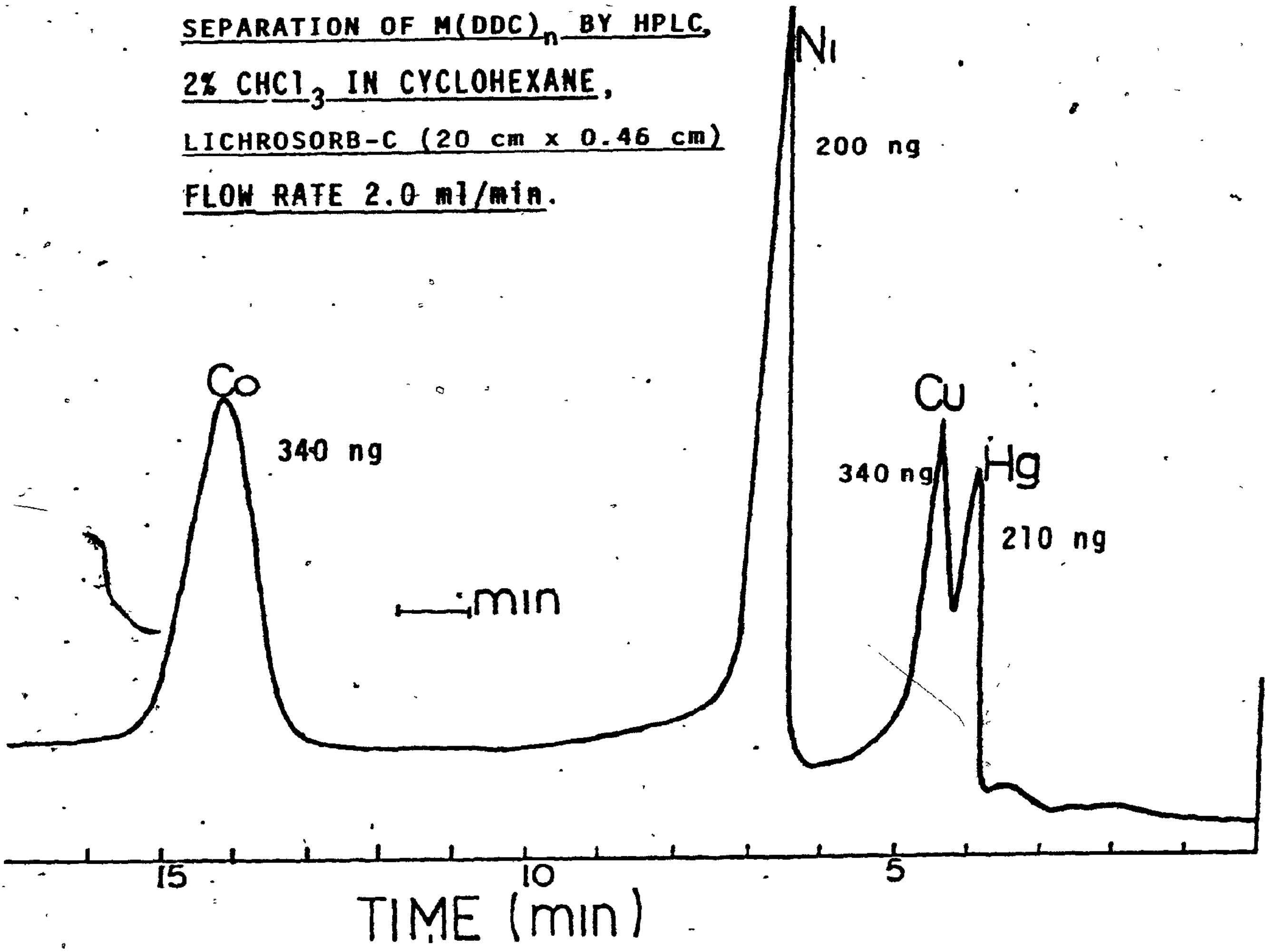


TABLE XXXII

Sample	Retention Time (mins.) Mobile Phase Flow Rate (2% Chloroform in Cyclohexane)			Detection Limit (ng)
	2.0 ml/min.	1.5 ml/min.	1.0 ml/min.	
$Hg(DDC)_2$	3.1	5.5	8.1	107
$Cu(DDC)_2$	4.5	8.1	8.8	40
$Co(DDC)_3$	14.9	19.1	24.5	34
$Ni(DDC)_2$	7.5	9.1	13.5	4.2
$Cd(DDC)_2$	7.7	9.2	13.7	103
$Zn(DDC)_2$	7.8	9.5	13.8	75
$Pb(DDC)_2$	7.0	9.0	13.0	133
$Fe(DDC)_3$	(6.8,7.2,9.1)			

TABLE XXXII (continued)

Sample	Retention Time (mins.) Mobile Phase Flow Rate (2% Ethylacetate in Cyclohexane)			Detection Limit (ng)
	2.0 ml/min.	1.5 ml/min.	1.0 ml/min.	
$Hg(DDC)_2$	-	4.1	6.5	-
$Cu(DDC)_2$	-	4.7	7.5	-
$Co(DDC)_3$	-	8.7	14.7	-
$Ni(DDC)_2$	-	6.3	10.3	-
$Cd(DDC)_2$	-	6.6	11.0	-
$Zn(DDC)_2$	-	6.5	10.3	-
$Pb(DDC)_2$	-	6.6	12.4	-
$Fe(DDC)_3$	-	(7.0,9.1,10.5)		-

The order of elution, Hg, Cu, Ni and Co (Fig. 53), may be related to the softness or hardness of the respective acids (metal chelates) from the point of view of the Hard-Soft-Acid-Base theory. The first metal chelate eluted is $Hg(DDC)_2$, a soft acid, and the last metal chelate eluted is $Co(DDC)_3$, a hard acid. The adsorbent being a hard base (due to -Si-OH on the surface) should have more affinity for hard acids than for soft acids and this indeed appears to have been the case. This hypothesis has been elaborated upon in Appendix II.

Moriyasu and Hashimoto (41) reported being able to separate seven metals, including $Hg(DDC)_2$, $Cu(DDC)_2$, $Pb(DDC)_2$, $Ni(DDC)_2$, $Co(DDC)_3$ and $Bi(DDC)_3$, but with very poor resolution. In actual fact, only the metal chelates of Cu, Ni, Hg and Co are well separated in chromatograms. This was in line with our findings. The order of elution that they reported is consistent with the Hard-Soft-Acid-Base (HSAB) theory.

12.0.0 Conclusions

A general method was developed for the synthesis of $M(DDC)_n$ in good yields. Elemental analysis, DTA, TGA and UV-spectroscopy confirmed that the procedure gave compounds pure enough to be used as standards for analyses of metals at the ppm level.

New UV spectroscopic data was obtained for many of the chelates studied. Molar extinction coefficients were determined in solvents such as methanol, ethanol and chloroform. Most of the data in alcohols has not been reported before. Also UV spectra were recorded for all the compounds studied.

It was found possible to separate with good resolution mixtures of up to five metals present in ppm amounts by gas chromatography. Mixtures of metals such as $Ni(DDC)_2$, $Cu(DDC)_2$, $Co(DDC)_3$, $Cd(DDC)_2$ and $Zn(DDC)_2$, or $Zn(DDC)_2$, $Cd(DDC)_2$, $Pb(DDC)_2$, $Hg(DDC)_2$ and $Co(DDC)_3$ could be separated using glass tubing (60 cm x 2 mm) packed with mixed phase OV-101 + QF-1 coated on CW-HP. Separation of the second of these mixtures was possible also if $Cu(DDC)_2$ was present instead of $Pb(DDC)_2$ and if $Ni(DDC)_2$ was present instead of $Hg(DDC)_2$. All five component mixtures required the use of column temperature programming GC to reduce time of analysis since $Co(DDC)_3$ is eluted only slowly under isothermal conditions suitable for separation of other metal chelates in the mixtures.

Accuracy and precision of analyses were good. It was found that the relative standard deviations were generally well below 10% and averaged 5% which is comparable with values reported by others in the literature.

FID detection limits were in the order of 20 to 150 ng for the $M(DDC)_n$. Detectability in the picogram range should be feasible using ECD.

Compounds such as $Mn(DDC)_3$ and $Fe(DDC)_3$ could not be analyzed by GC due to decomposition during their preparation or on the column. $Fe(DDC)_3$ appears to decompose even under HPLC conditions which involved room temperature.

While this study was restricted to synthetic samples only it should be applicable to the analysis of marine samples in general after adequate clean-up of the samples.

13.0.0 Suggestions for Further Research

In this research it was found that the order of elution in the periodic group $Zn(DDC)_2$, $Cd(DDC)_2$ and $Hg(DDC)_2$ seemed to depend on the ionic radii of the metal ion. Also, in the periodic series $Co(DDC)_3$, $Ni(DDC)_2$, $Cu(DDC)_2$ and $Zn(DDC)_2$ it was found that the order of elution appeared to depend on the effect of the metal on the π-electron cloud of the ligand. It would be interesting to establish whether these properties would account for the order of elution of other $M(DDC)_n$ as well. If this is the case, then it should be possible to predict potential separation of any mixture of metals. As a start, the mixture, $Ni(DDC)_2$, $Pb(DDC)_2$ and $Pt(DDC)_2$, would be an interesting one to study.

Another suggestion for further research would be to do analysis, of the compounds successfully separated in this study, by using ECD. In this case, non-electron affinitive liquid phases should be tried to eliminate effects of any bleeding of stationary phase on the sensitivity of the ECD.

It was seen in this study that when a stainless steel column was used chelates that contained soft acids were more sensitive to decomposition than those that contained hard acids. It would be worthwhile to determine whether by using non-silanized glass tubing (hard base surface) decomposition occurs for hard or intermediate acids (Co(III), Ni(II), etc. to a greater extent than for soft acids Cd(II), Hg(II)).

Further studies should be carried out to find GC or HPLC conditions for resolution of a more complex mixture of metals of marine interest. Reversed phase HPLC and capillary GC are worth investigating. If such efforts are not entirely successful work should be initiated on developing a chromatographic method including preliminary chemical or ion-exchange separation procedures to selectively remove interfering metals from samples before GC analysis.

Finally, comparative studies of accuracy and precision of chromatographic and spectroscopic methods for $M(DDC)_n$ mixture analyses are required.

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APPENDIX I

FIGURE G-I

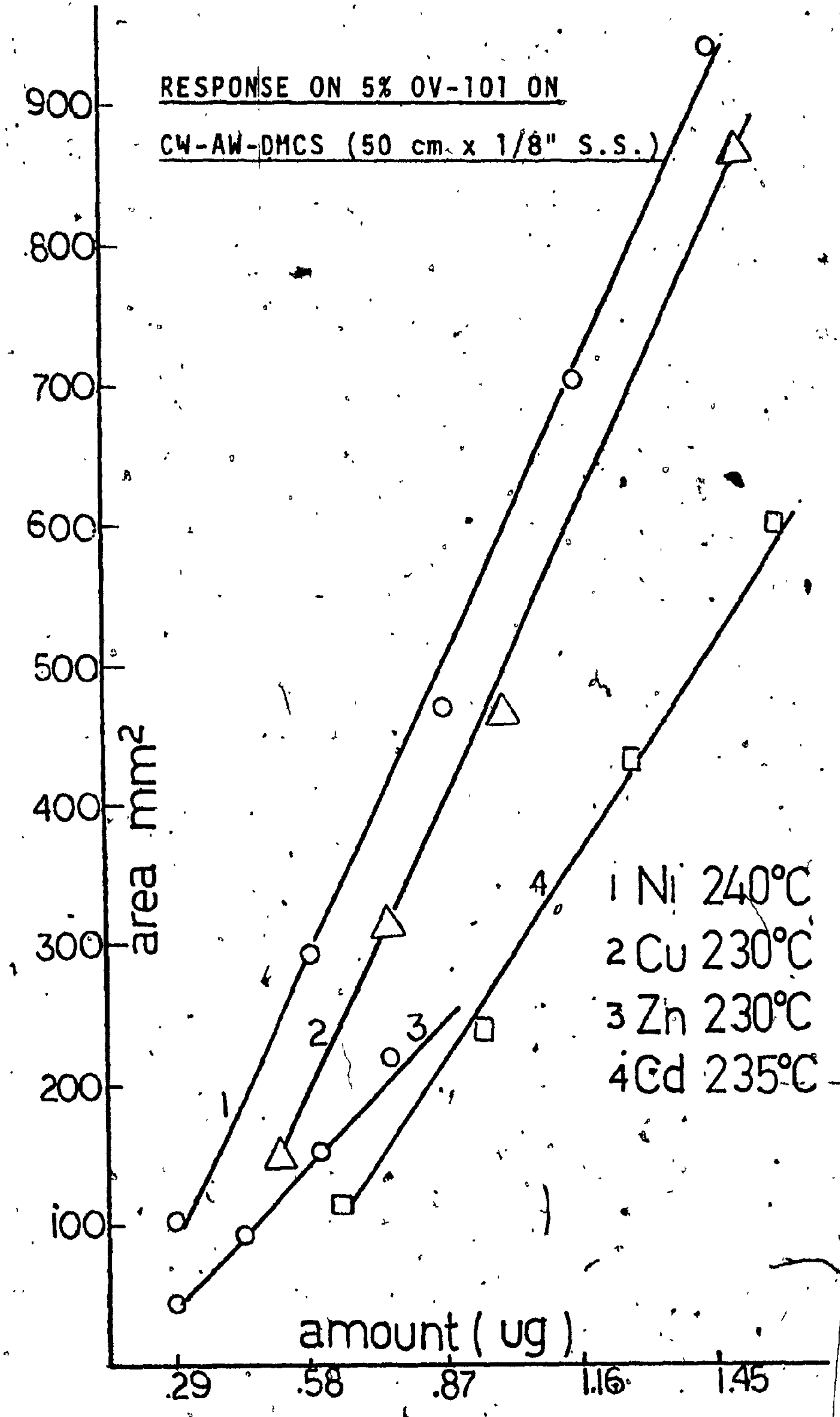

RESPONSE ON 5% OV-101 ON
CW-AW-DMCS (50 cm x 1/8" S.S.)
900
800
700
600
500
400
300
200
100
area mm²
amount (ug)
.29
.58
.87
1.16
1.45
1
2
3
4
1 Ni 240°C
2 Cu 230°C
3 Zn 230°C
4 Cd 235°C

FIGURE G-II

RESPONSE ON 5% OV-101 ON CW-AW-DMCS (50 cm x 1/8" S.S.)

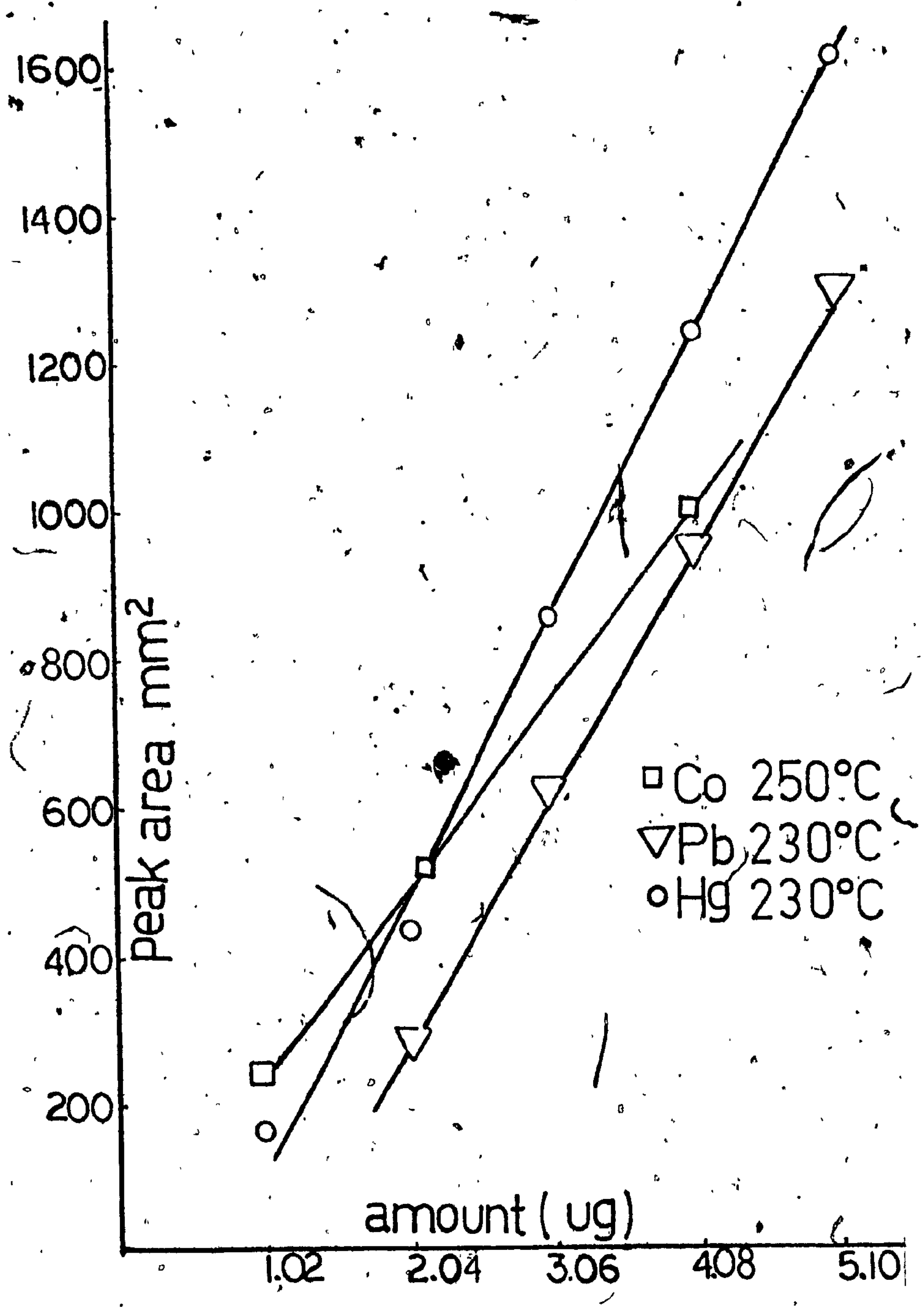


FIGURE G-III

RESPONSE ON 3% SE-30 ON

CG-HP (50 cm x 1/8" S.S.)

AT 245°C

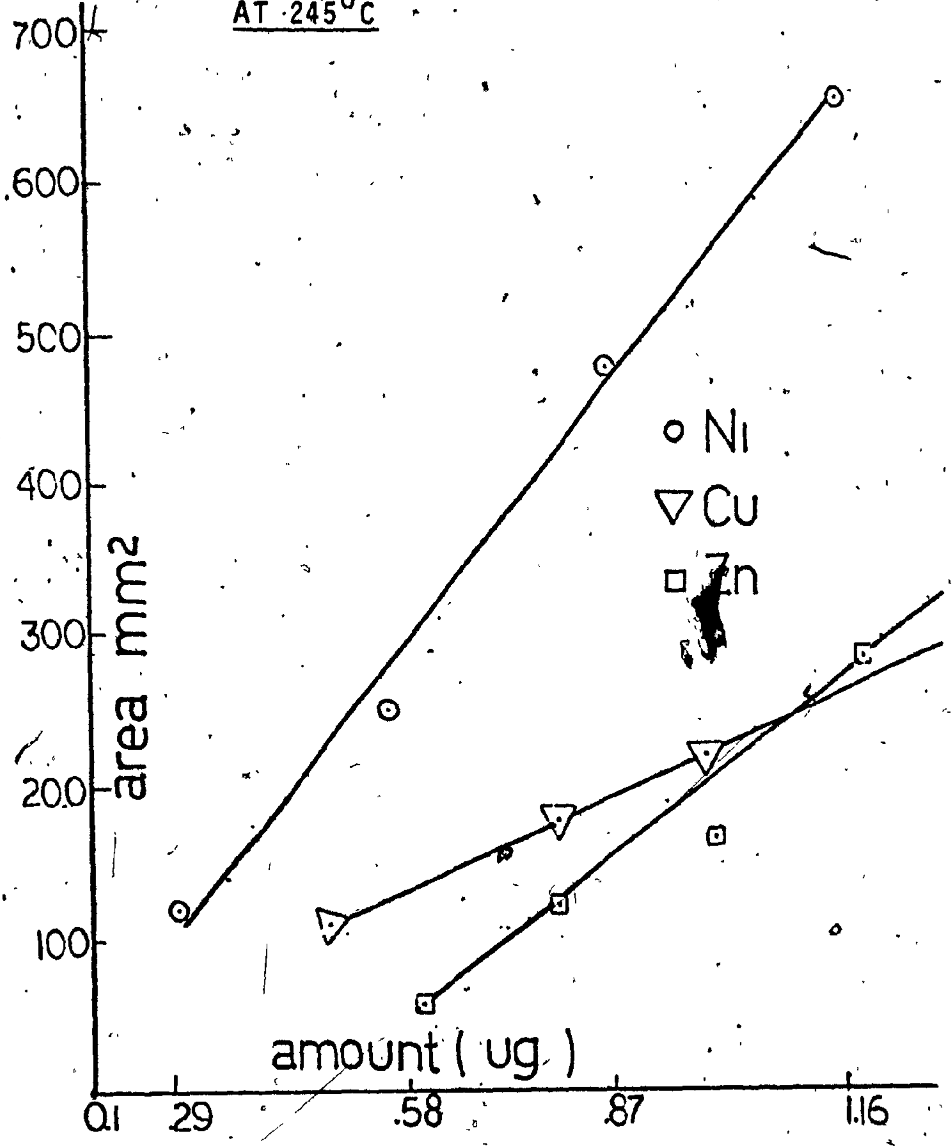


FIGURE G-IV

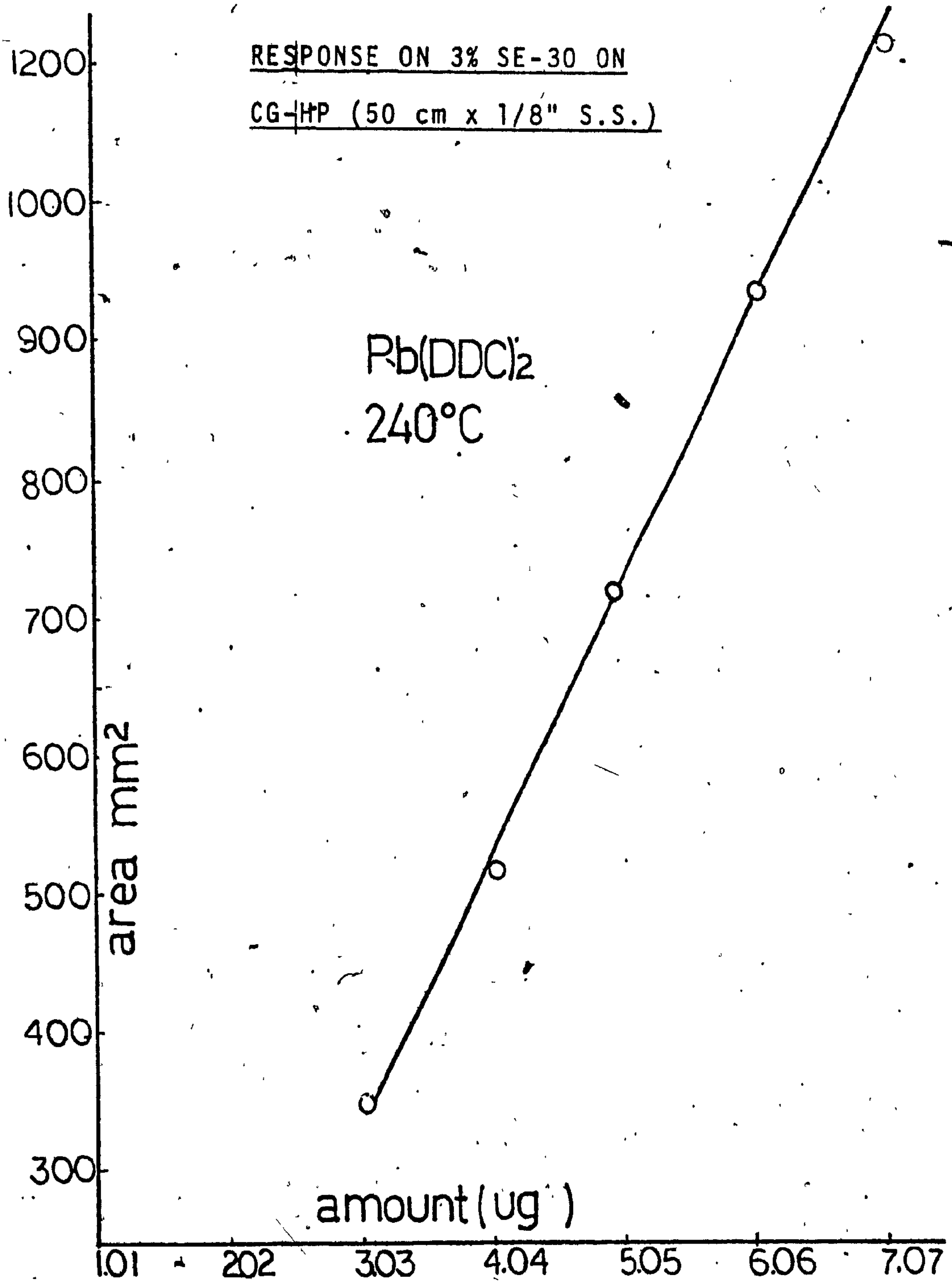

RESPONSE ON 3% SE-30 ON
CG-HP (50 cm x 1/8" S.S.)
Pb(DDC)2
240°C
area mm2
amount (ug)
1200
1000
900
800
700
600
500
400
300
1.01
2.02
3.03
4.04
5.05
6.06
7.07

FIGURE G-V

RESPONSE ON 3% SE-30 ON

CG-HP (50 cm x 1/8" S.S.)

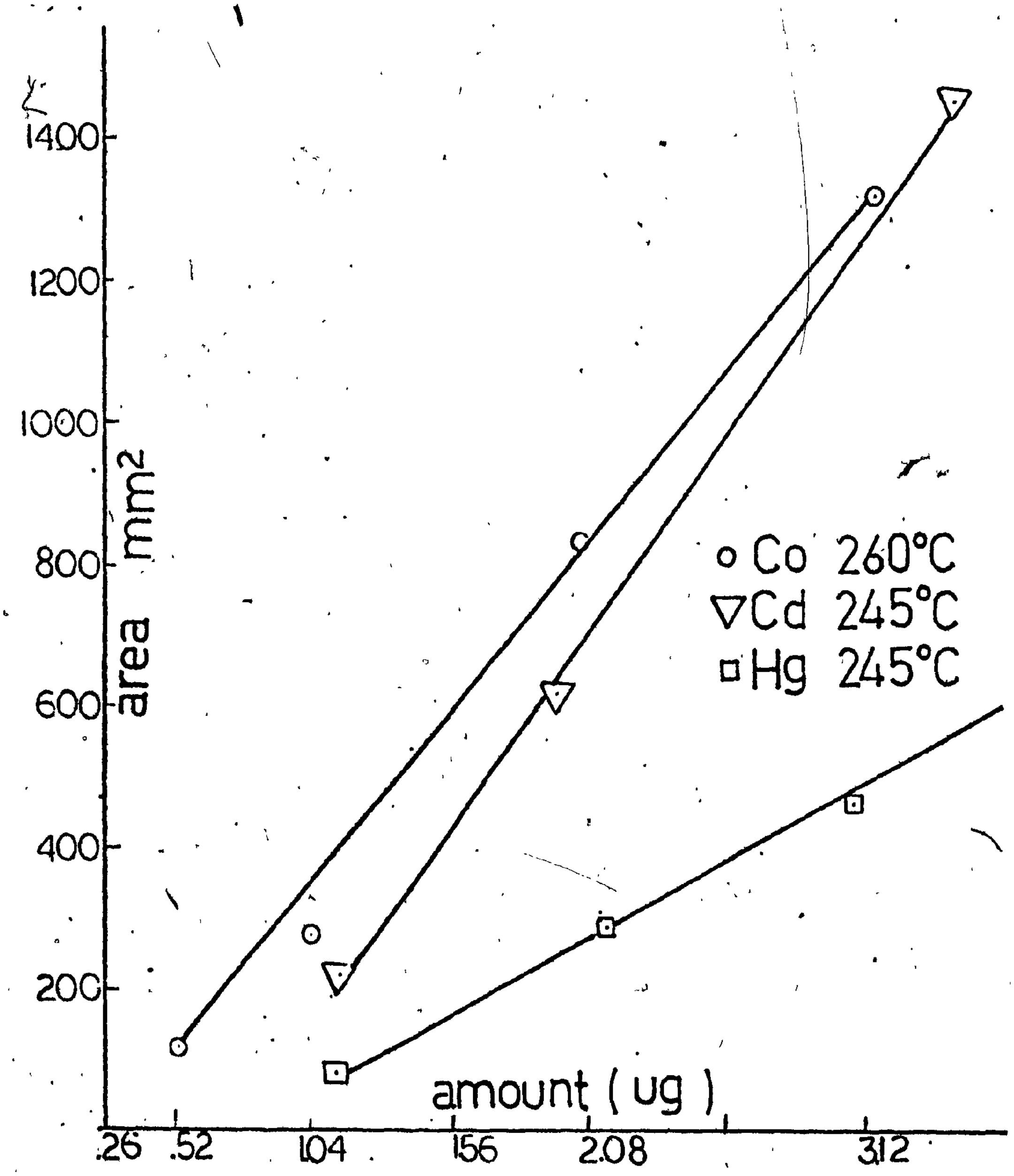


FIGURE G-VI

RESPONSE ON 5% OV-101 + QF-1 ON GC-Q (60 cm x 1/8" S.S.)

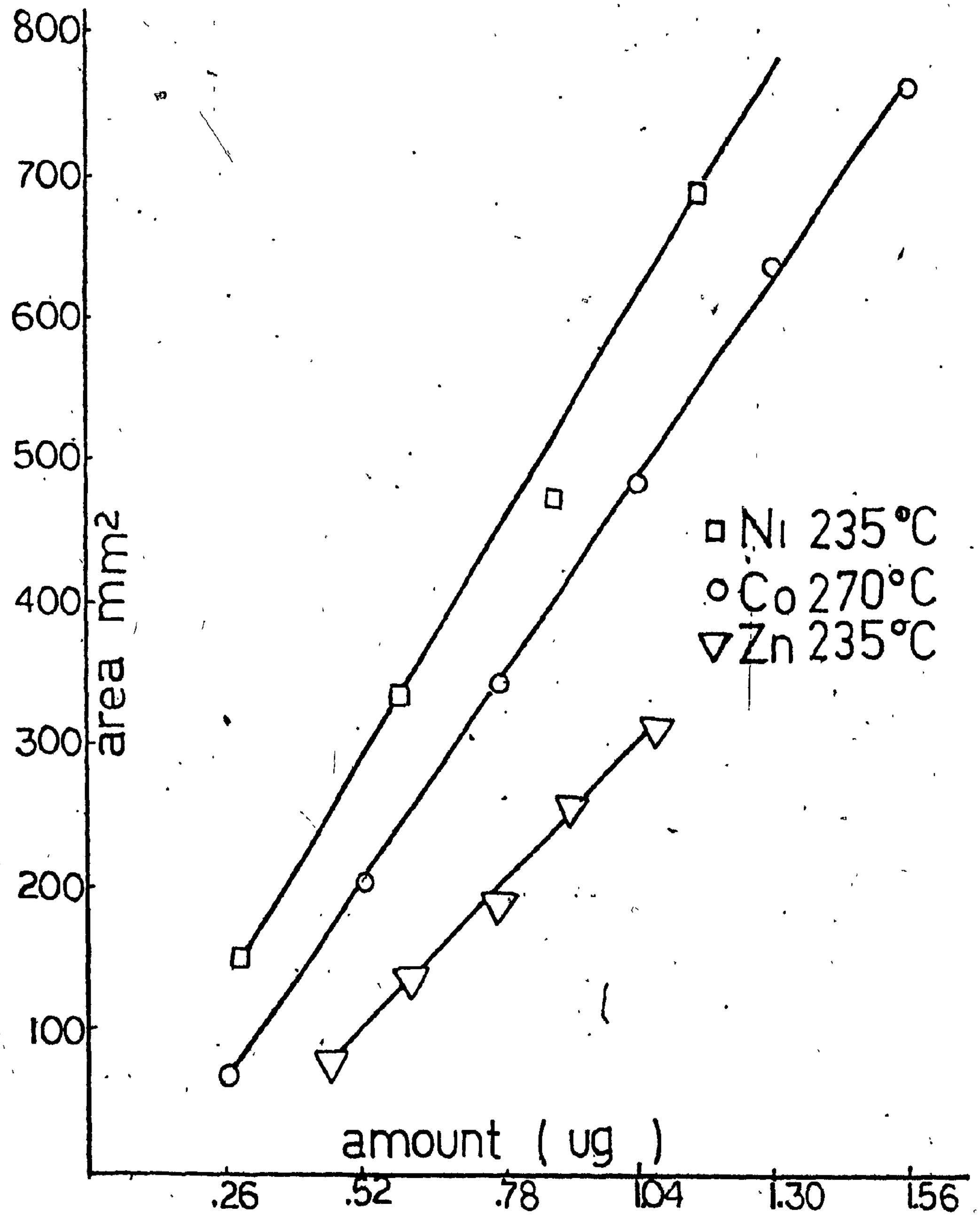


FIGURE G-VII

RESPONSE ON 5% OV-101 + QF-1

ON GC-Q (60 cm x 1/8" S.S.)

AT 235°C

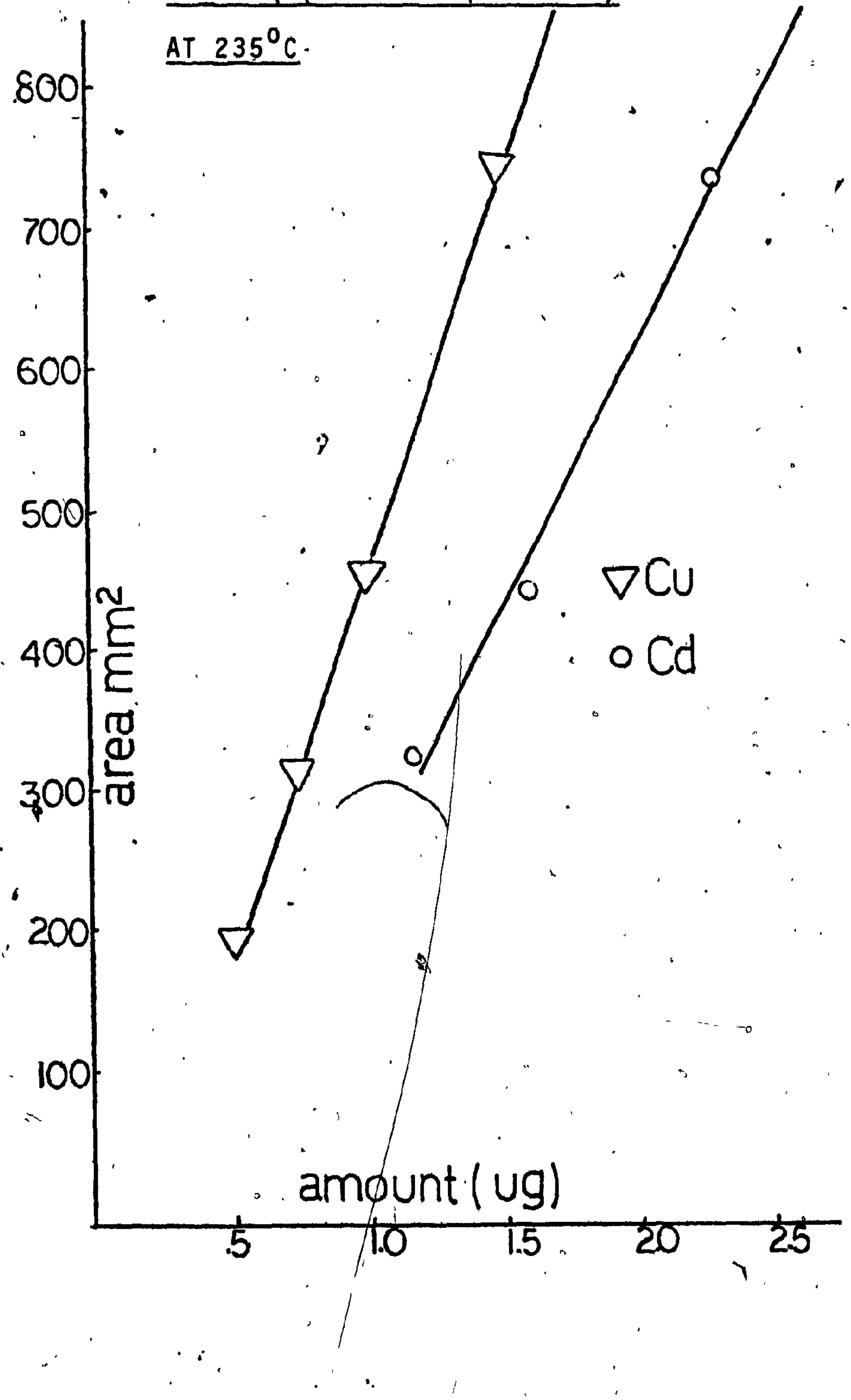


FIGURE G-VIII

RESPONSE ON 3% SE-30 ON CW-HP

(40 cm x 1/8" S.S.) AT 230°C

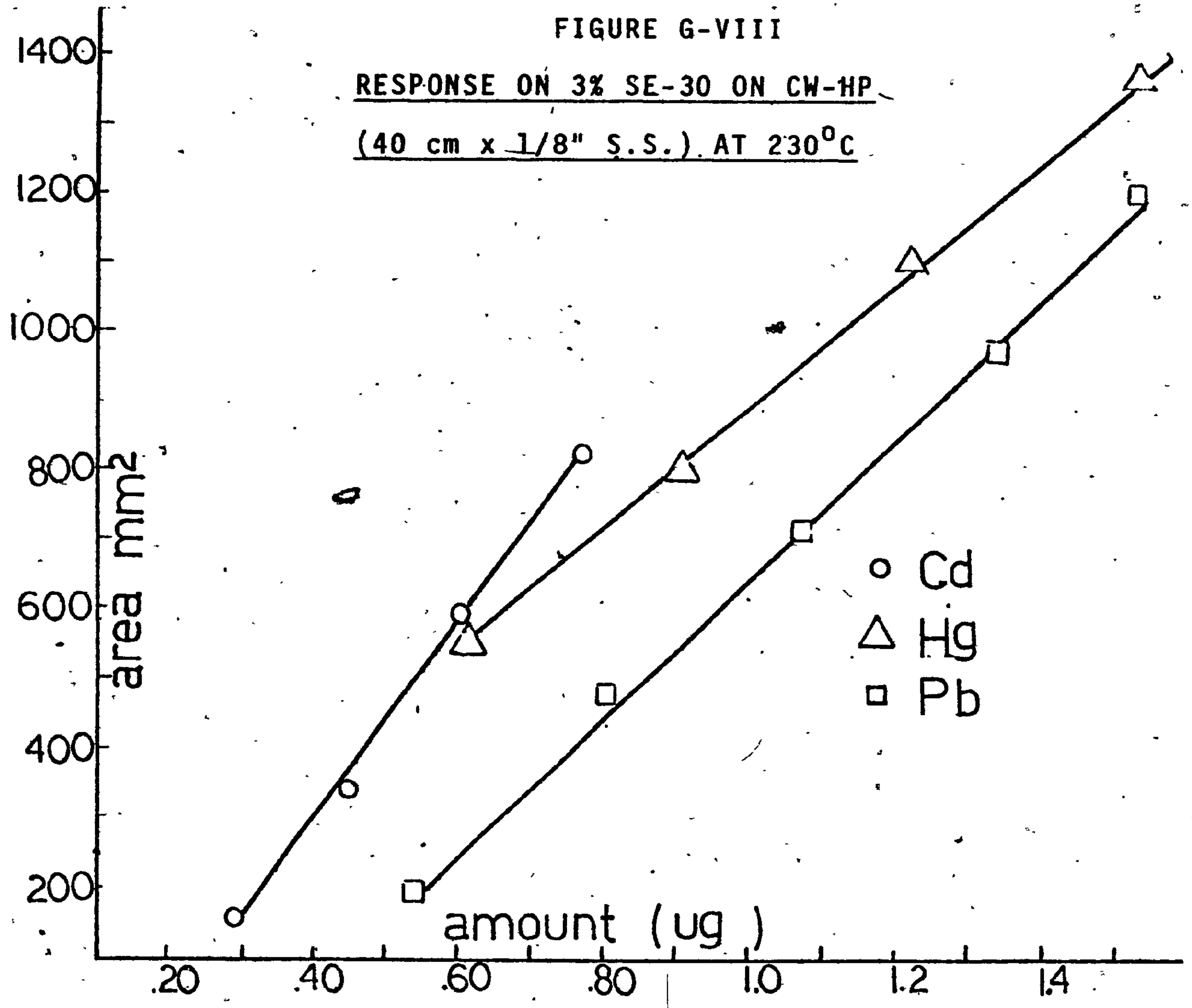


FIGURE G-IX

RESPONSE ON 3% SE-30 ON CW-HP

(40 cm x 1/8" S.S.) AT 250^{o}C

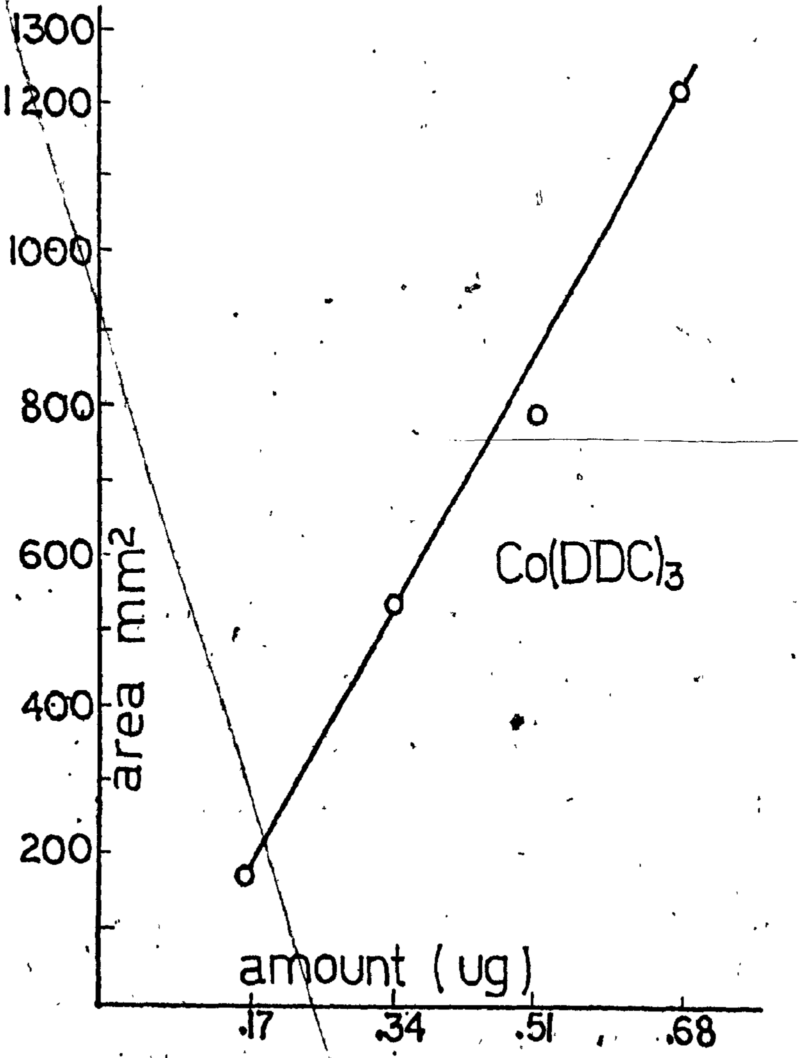


FIGURE G-X

RESPONSE ON 5% OV-101 ON CW-HP

(60 cm x 1/8")

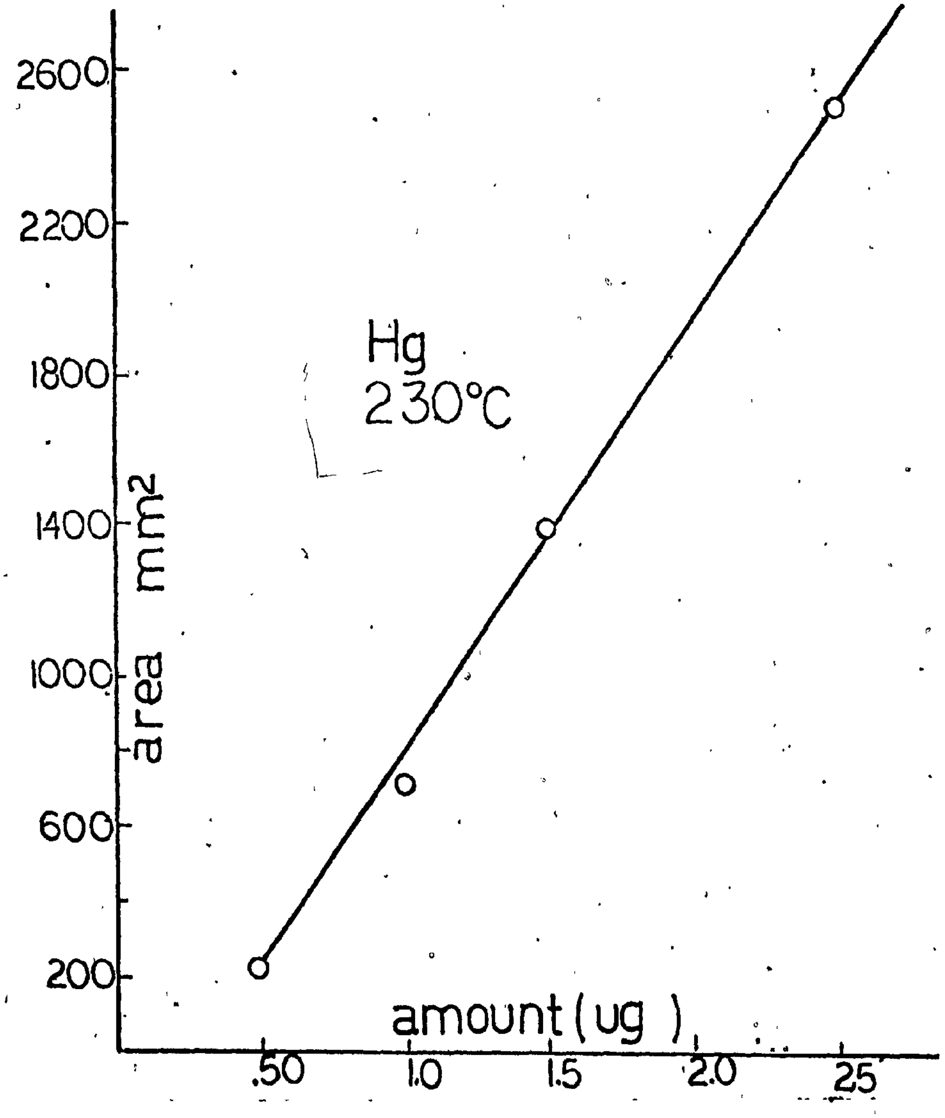


FIGURE G-XI

RESPONSE ON 5% OV-101 ON CW-HP

(60 cm x 1/8")

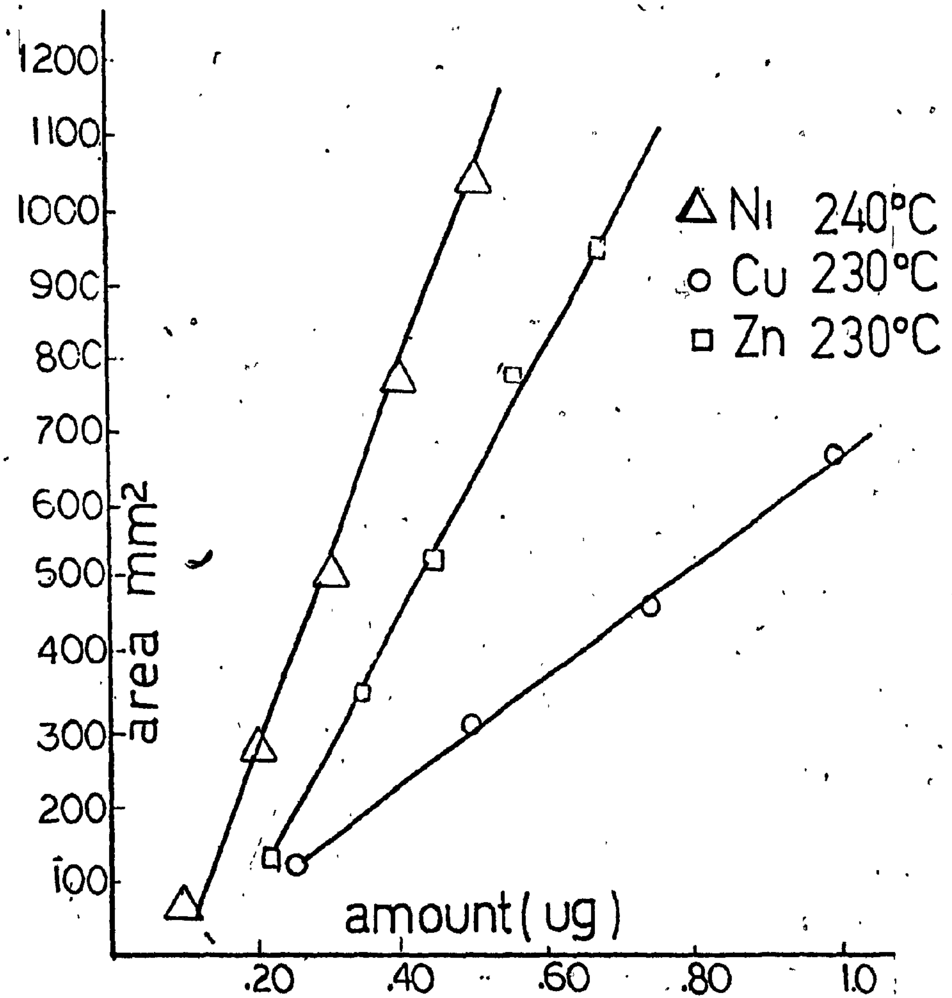


TABLE G-X

REGRESSION PARAMETERS OF DATA IN FIG. G-X AND FIG. G-XI

	$Ni(DDC)_2$	$Cu(DDC)_2$	$Zn(DDC)_2$	$Hg(DDC)_2$
Y Intercept (mm^2)	-211.2	-62.9	-307	-383
Slope (mm^2/ng)	2406	709	1849	1160
Corr. Coeff.	0.996	0.999	1.000	0.999
Column Temp.	240°C	230°C	230°C	230°C

FIGURE G-XII

RESPONSE ON 5% OV-101 ON CW-HP

(60 cm x 1/8" S.S.)

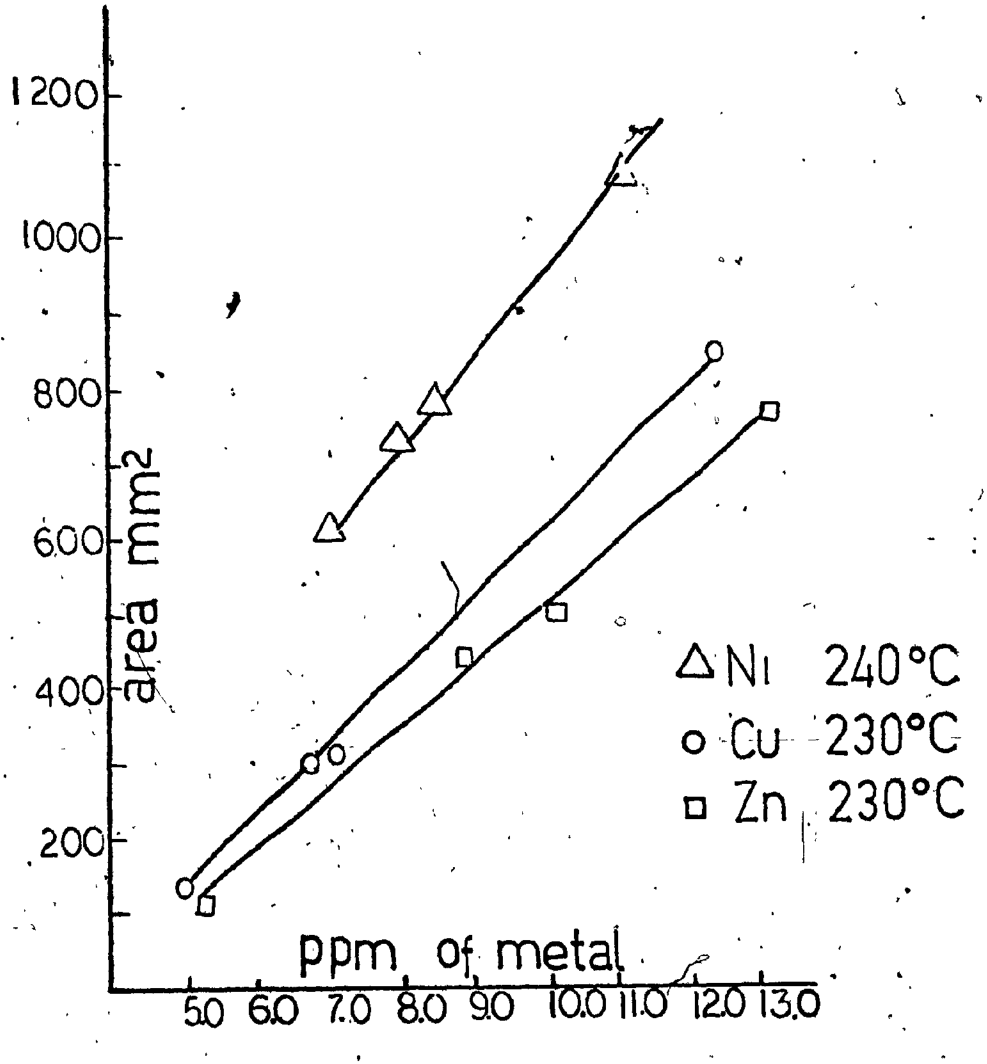


FIGURE G-XIII

RESPONSE ON 3% SE-30 ON CW-HP

(40 cm x 1/8" S.S.)

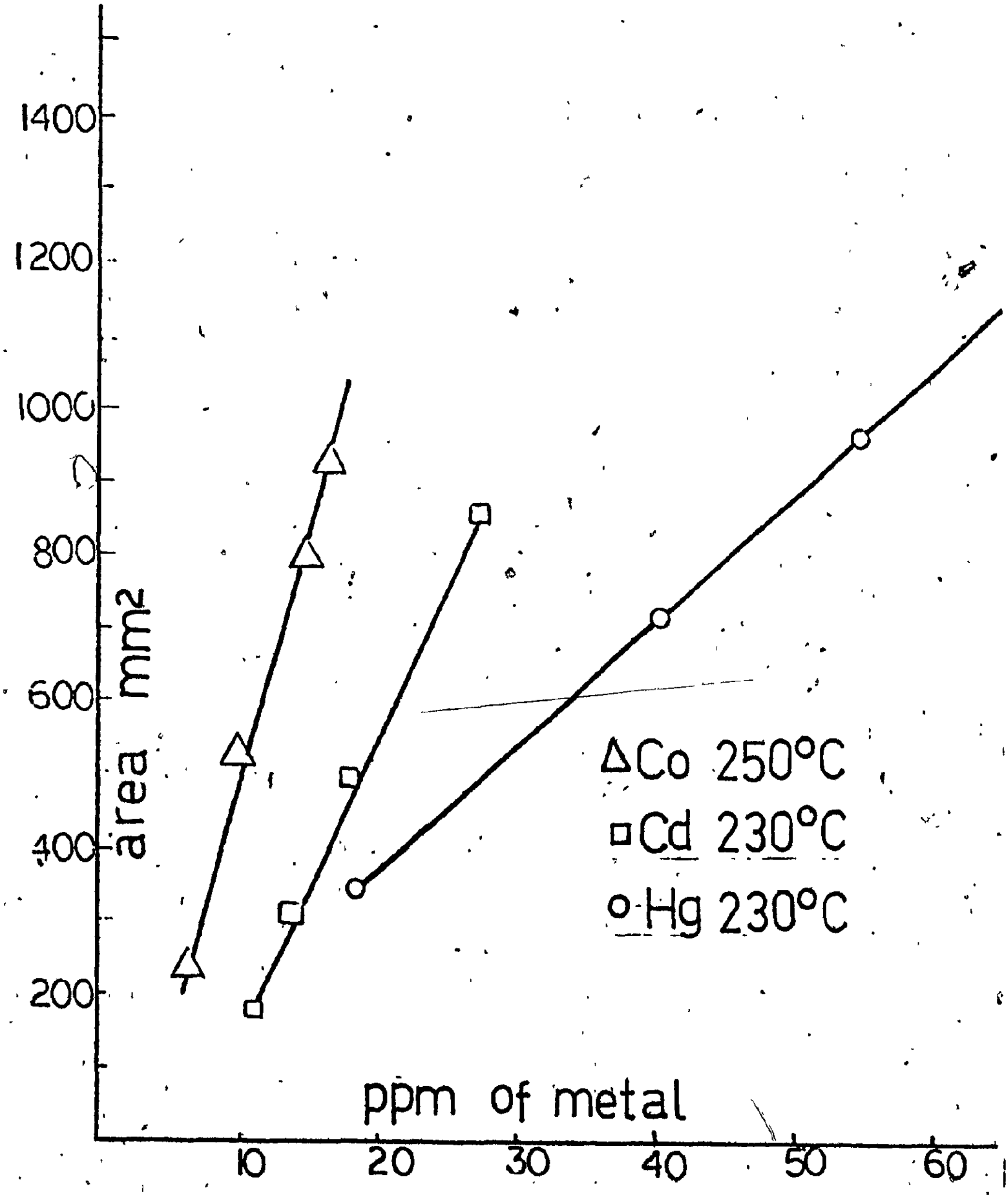


FIGURE G-XIV

RESPONSE ON 3% SE-30 ON CW-HP

(40 cm x 1/8" S.S.)

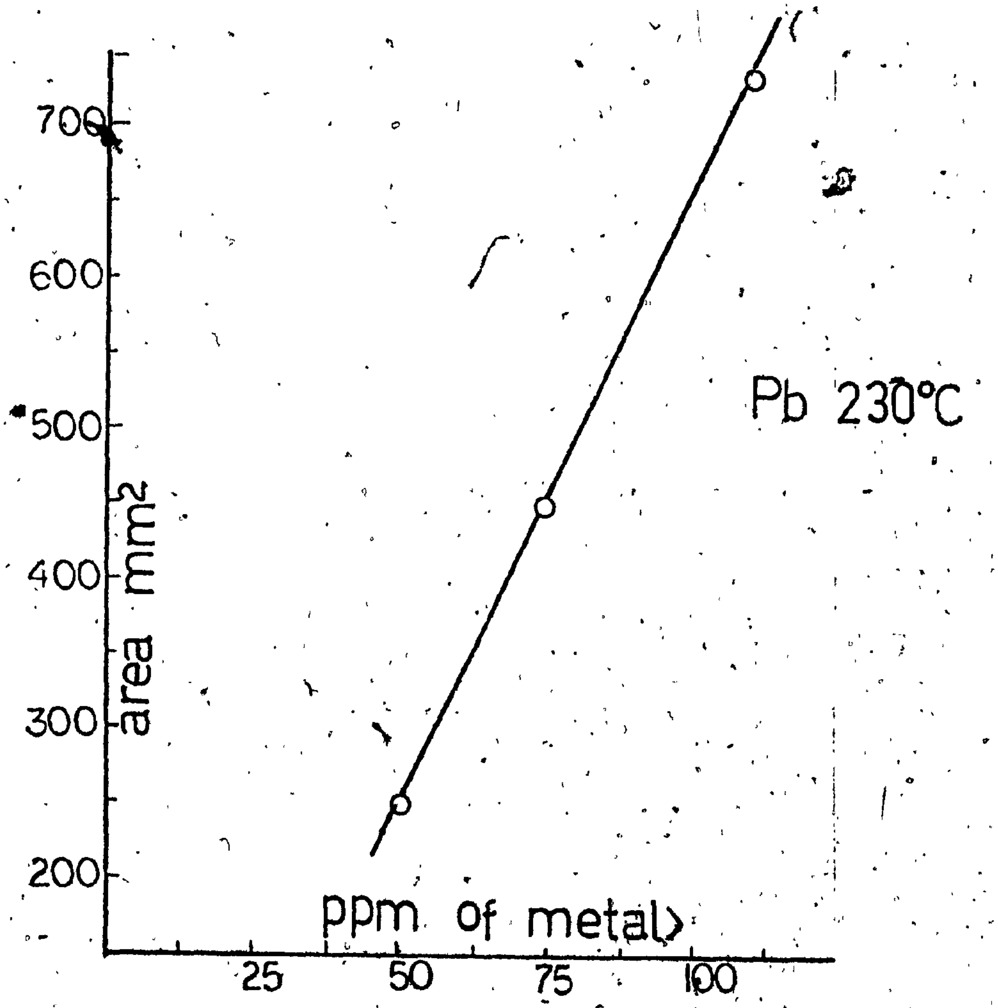


FIGURE G-XV

RESPONSE ON 5% OV-101 + 5% QF-1 ON GC-Q AT 240°C (60 cm x 1/8")

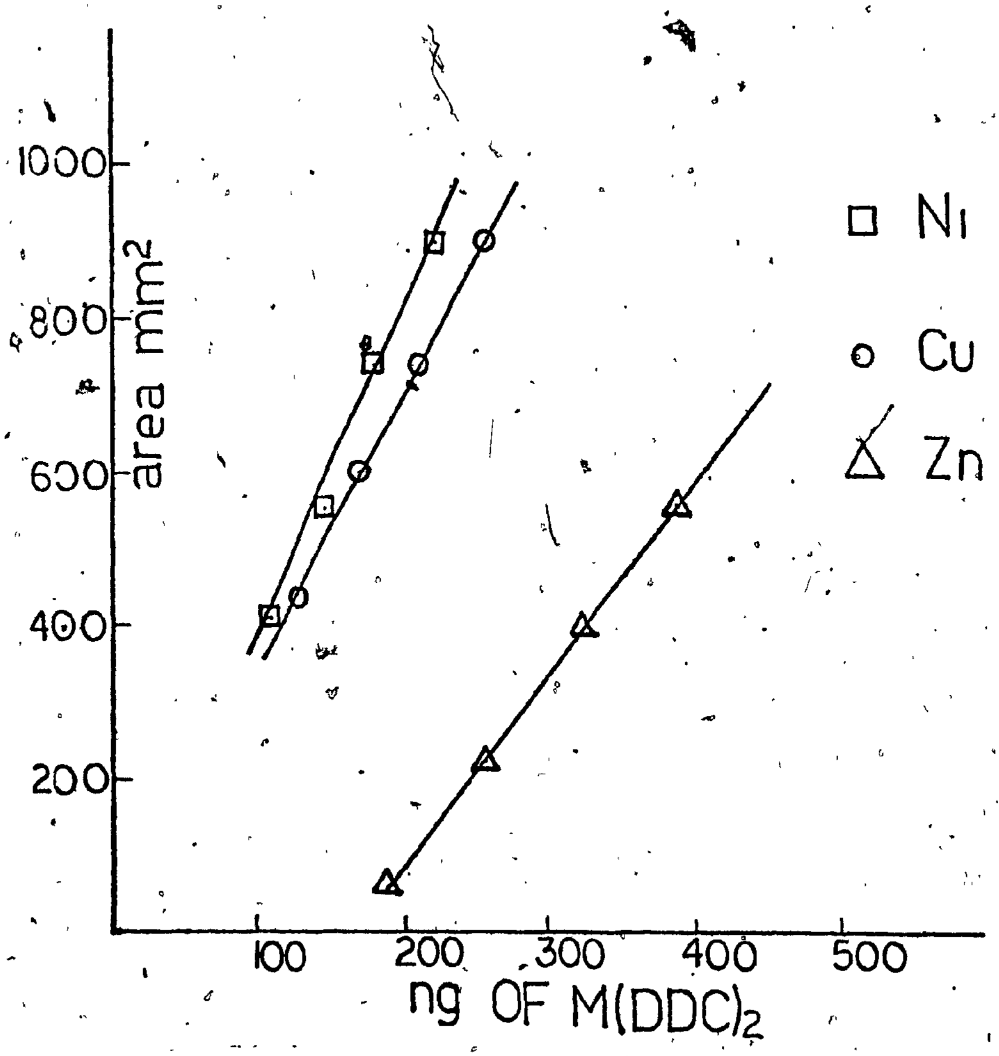


FIGURE G-XVI

RESPONSE ON 5% OV-101 + 5% QF-1 ON GC-Q AT 235°C (60 cm x 1/8")

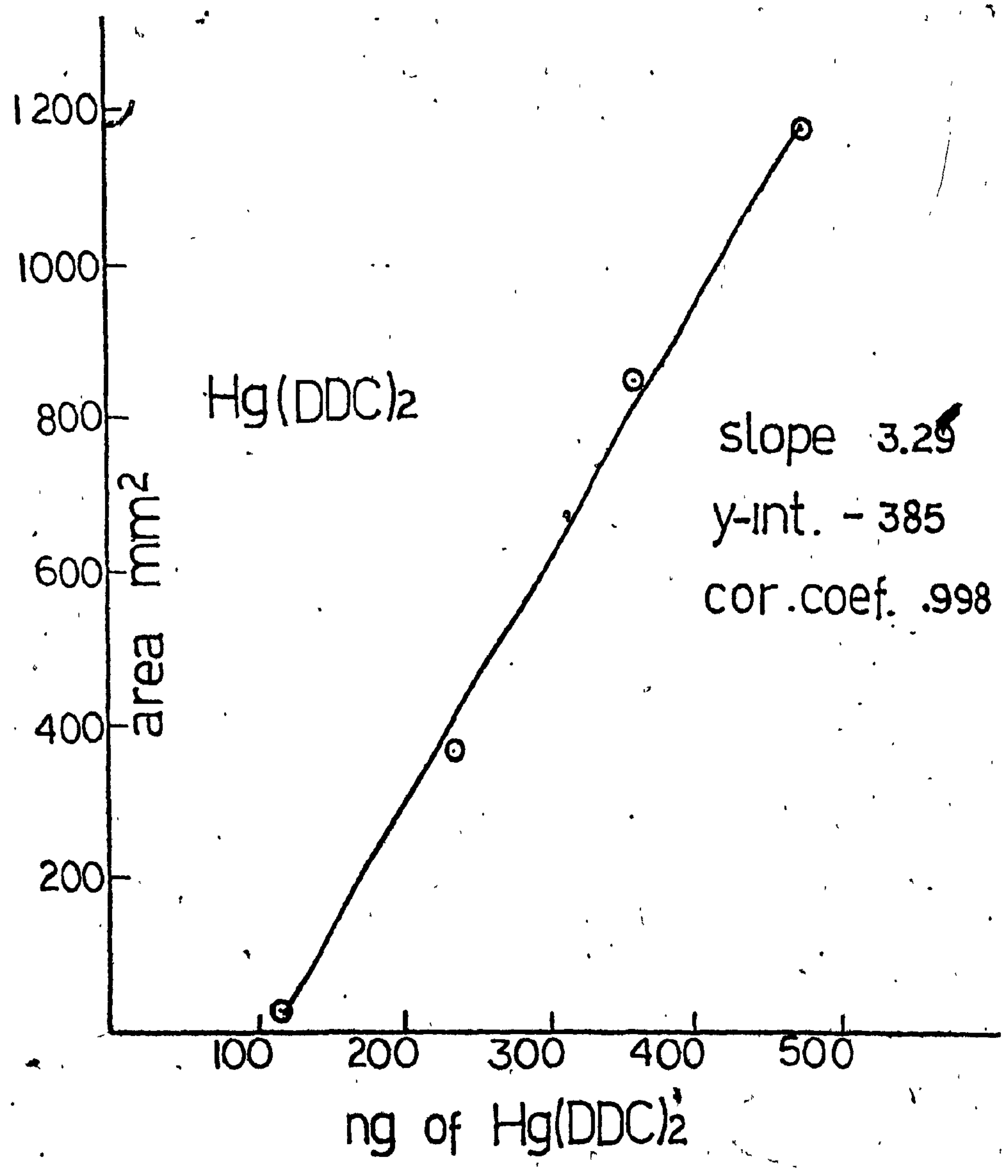


FIGURE G-XVII

RESPONSE ON 5% OV-101 + 5% QF-1
ON GC-Q AT 260°C (60 cm x 1/8")

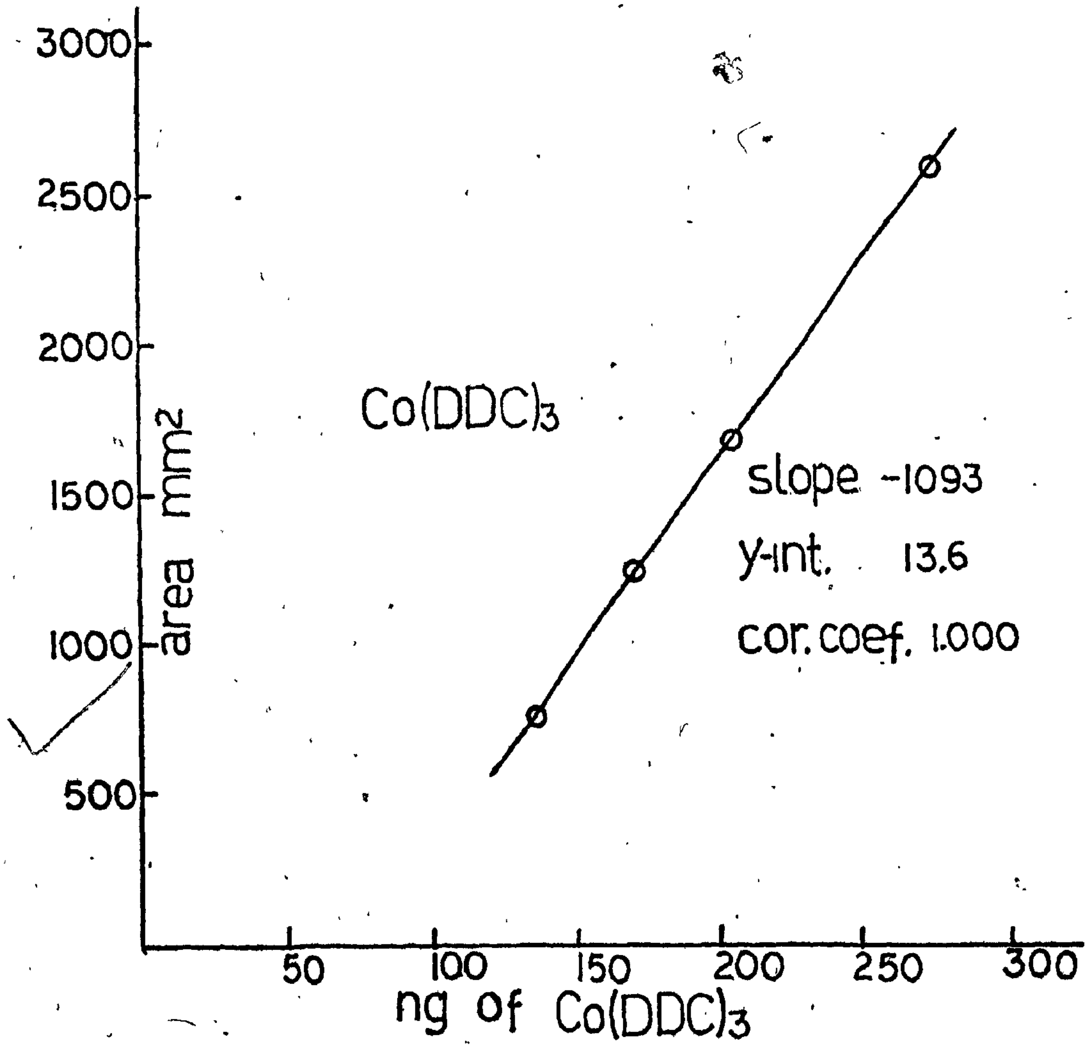


FIGURE G-XVIII

RESPONSE ON 5% OV-101 + 5% QF-1 ON CW-HP

(30 cm x 1/8" S.S.) AT 225°C

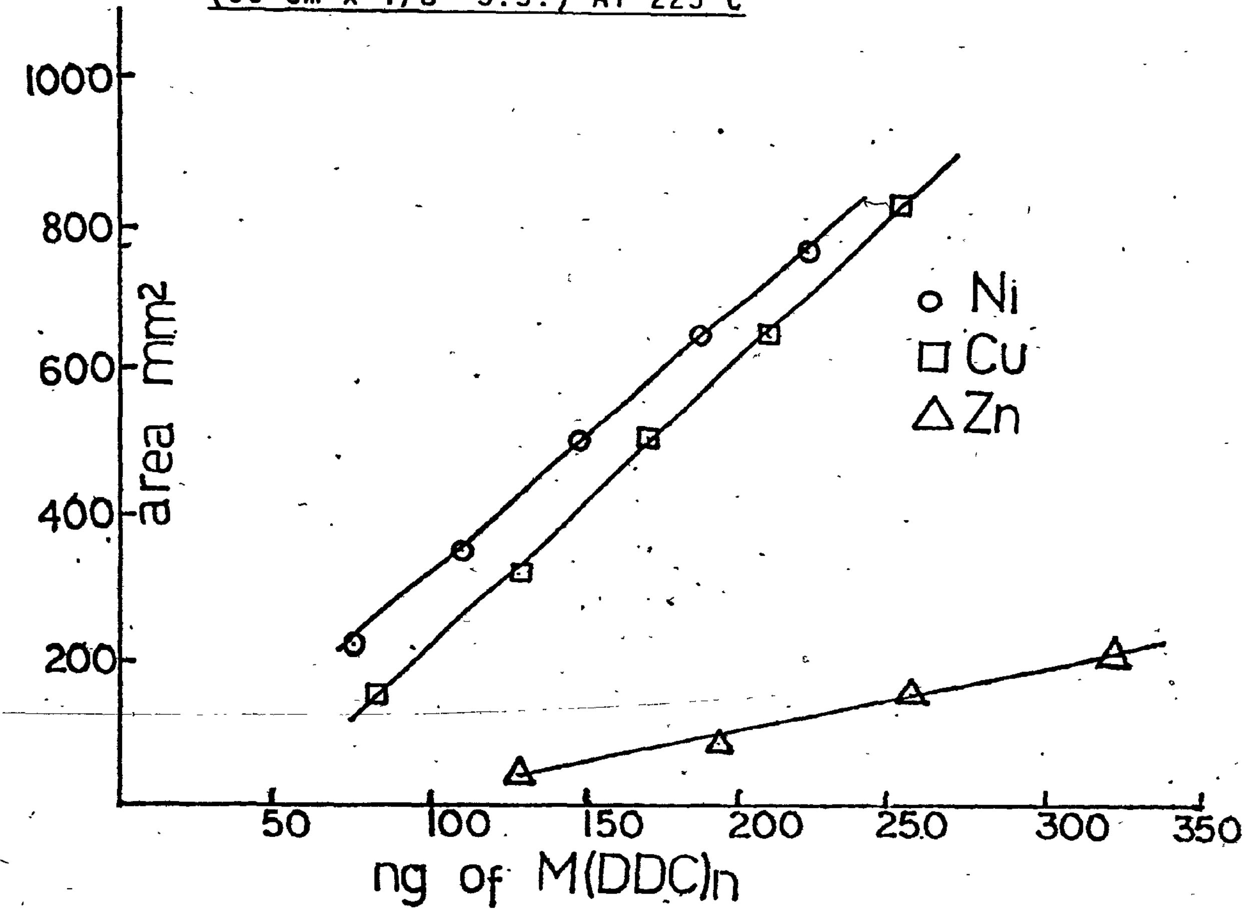
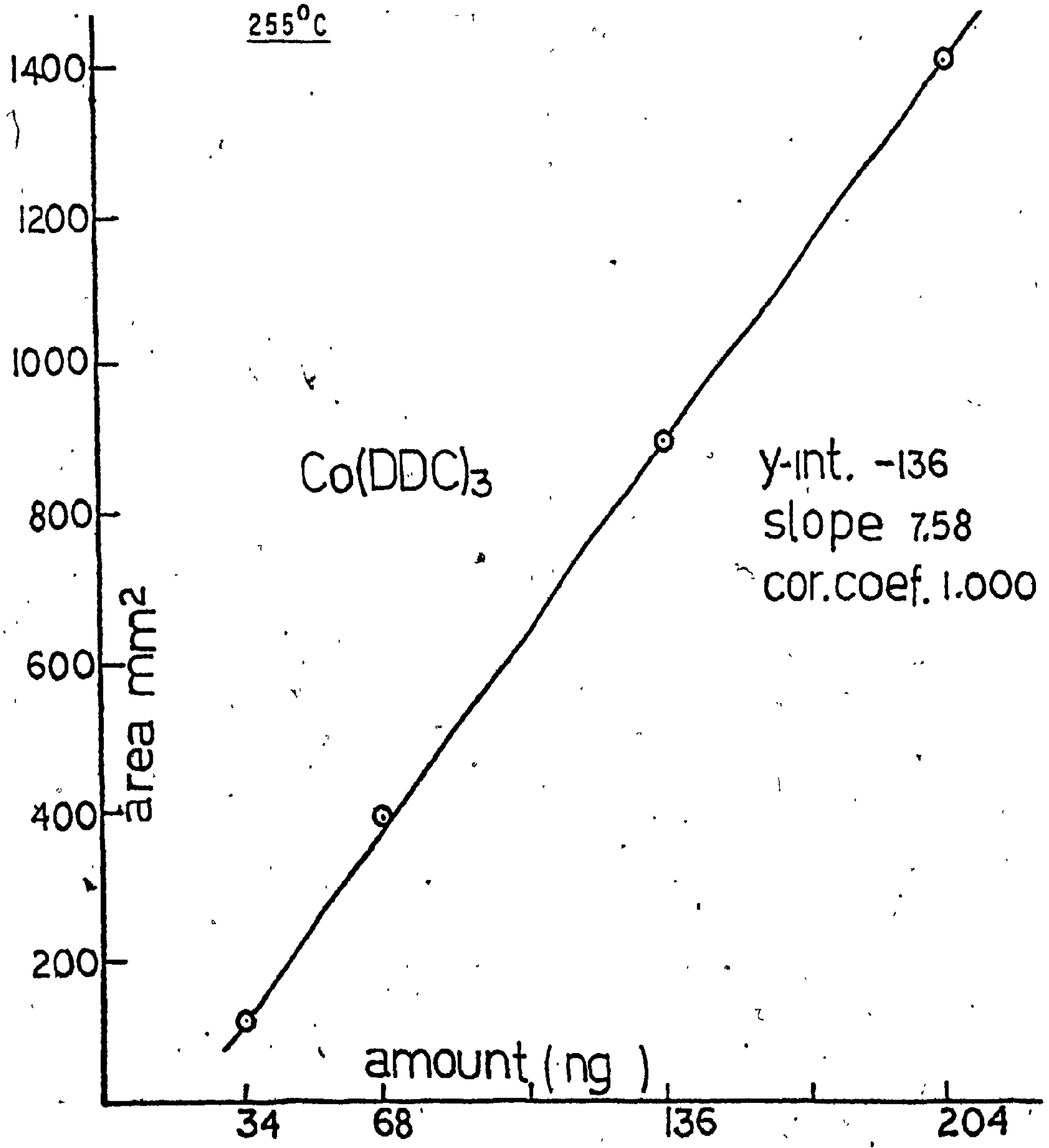


TABLE G-XVIII

LINEAR REGRESSION PARAMETERS FOR LINES ON FIG. G-XVIII

	$Zn(DDC)_2$ (64 ng/µl)	$Cu(DDC)_2$ (42 ng/µl)	$Ni(DDC)_2$ (37 ng/µl)
Y Intercept (mm^2)	-67.2	-174.6	-51.0
Slope (mm^2/ng)	0.827	3.93	3.69
Corr. Coeff.	0.997	0.999	0.999
Ret. Time	2.0 mins.	3.4 mins.	4.7 mins.

FIGURE G-XIX


RESPONSE ON 5% OV-101 + 5% QF-1
ON CW-HP (30 cm x 1/8" S.S.) AT
255°C
1400
1200
1000
800
600
400
200
area mm2
amount (ng)
34
68
136
204
Co(DDC)3
y-int. -136
slope 7.58
cor.coef. 1.000

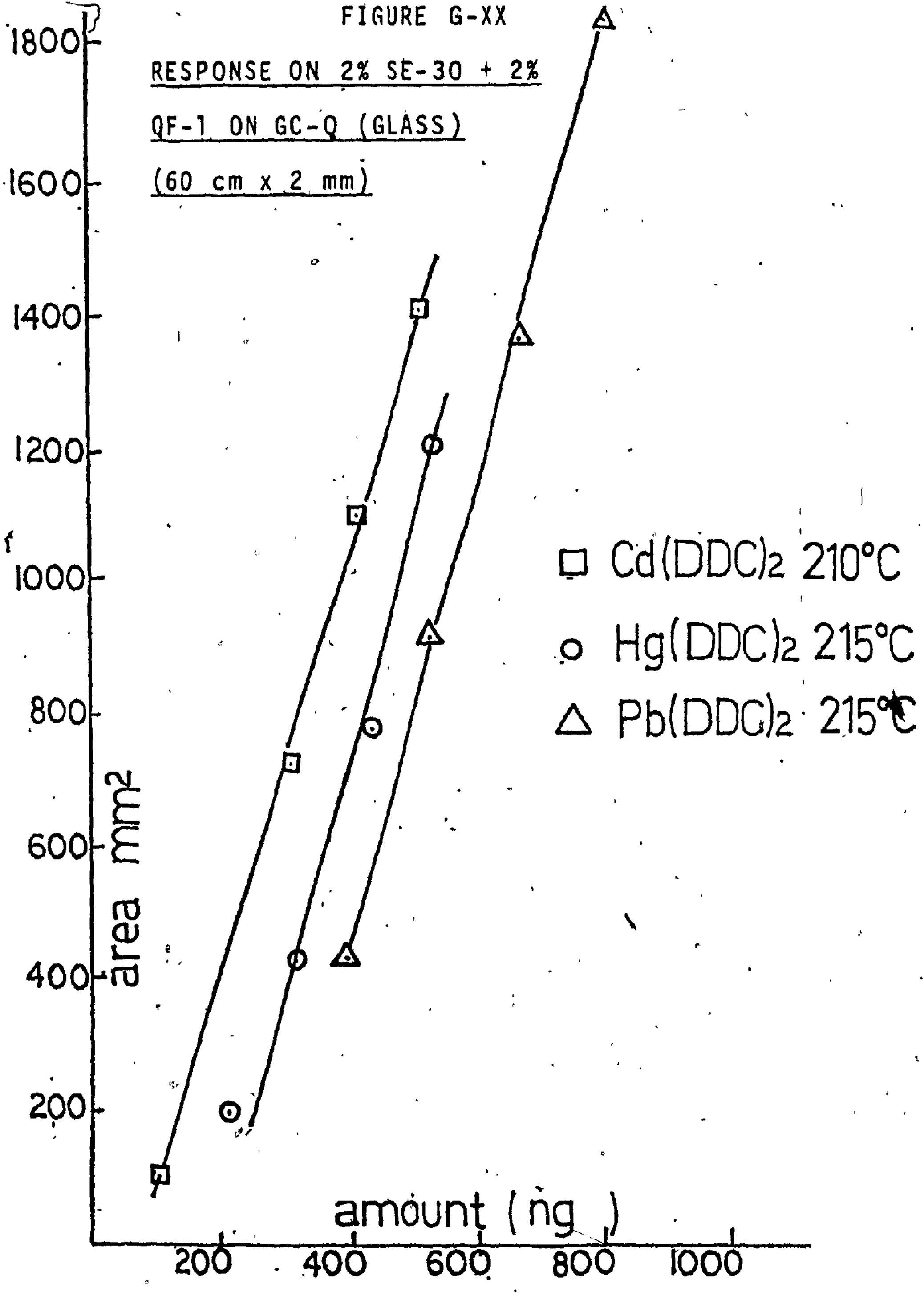


FIGURE G-XX

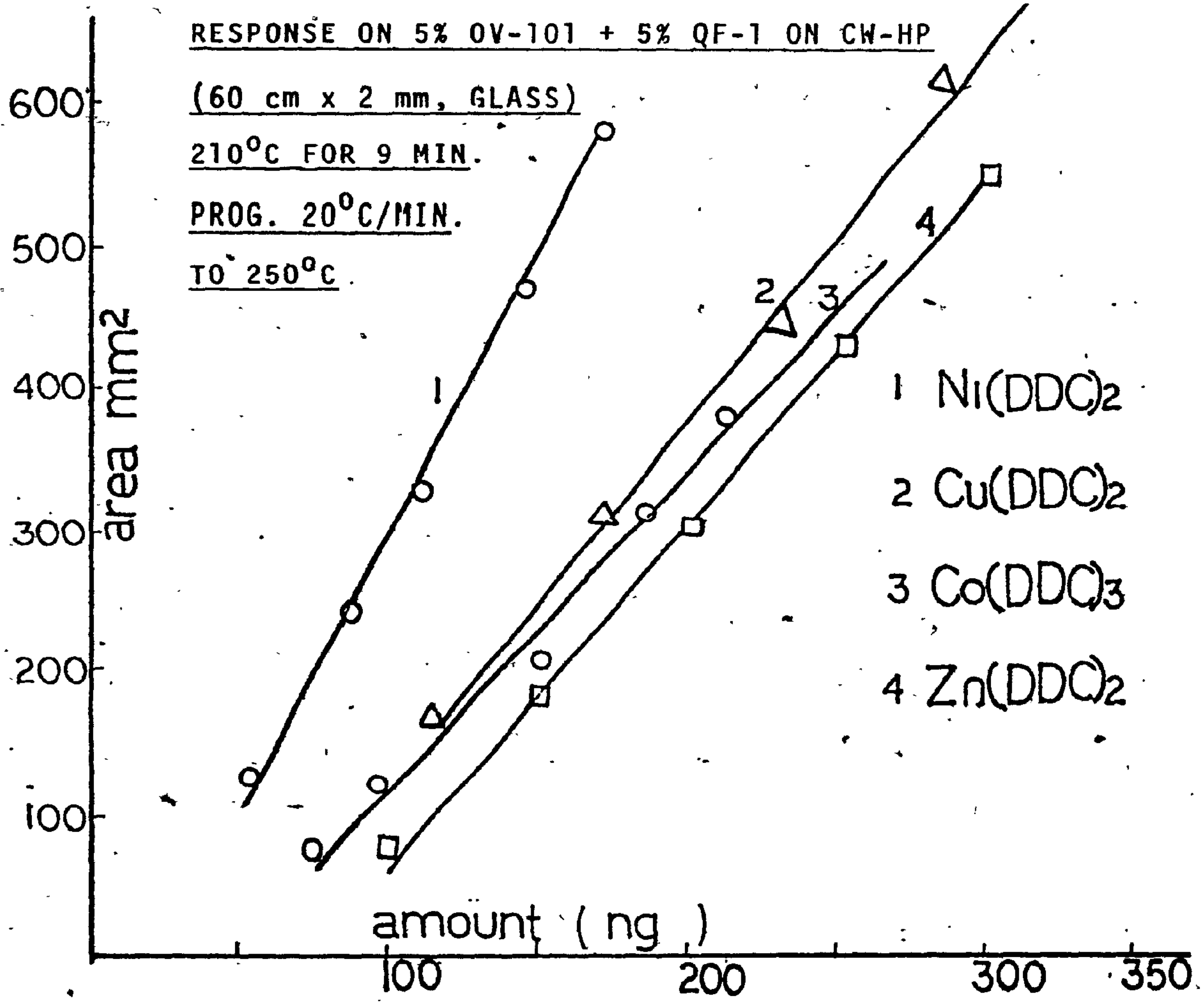
RESPONSE ON 2% SE-30 + 2% QF-1 ON GC-Q (GLASS) (60 cm x 2 mm)

TABLE G-XX

REGRESSION PARAMETERS OF CURVES IN FIG. G-XX

	$Hg(DDC)_2$	$Cd(DDC)_2$	$Pb(DDC)_2$
Slope (mm^2/ng)	3.7	3.20	3.53
Y Intercept (mm^2)	-532	-237	-969
Corr. Coeff.	0.991	0.999	1.000
Column Temp.	215°C	210°C	215°C
Ret. Time (mins.)	5.0	3.7	3.0

FIGURE G-XXI



RESPONSE ON 5% OV-101 + 5% QF-1 ON CW-HP

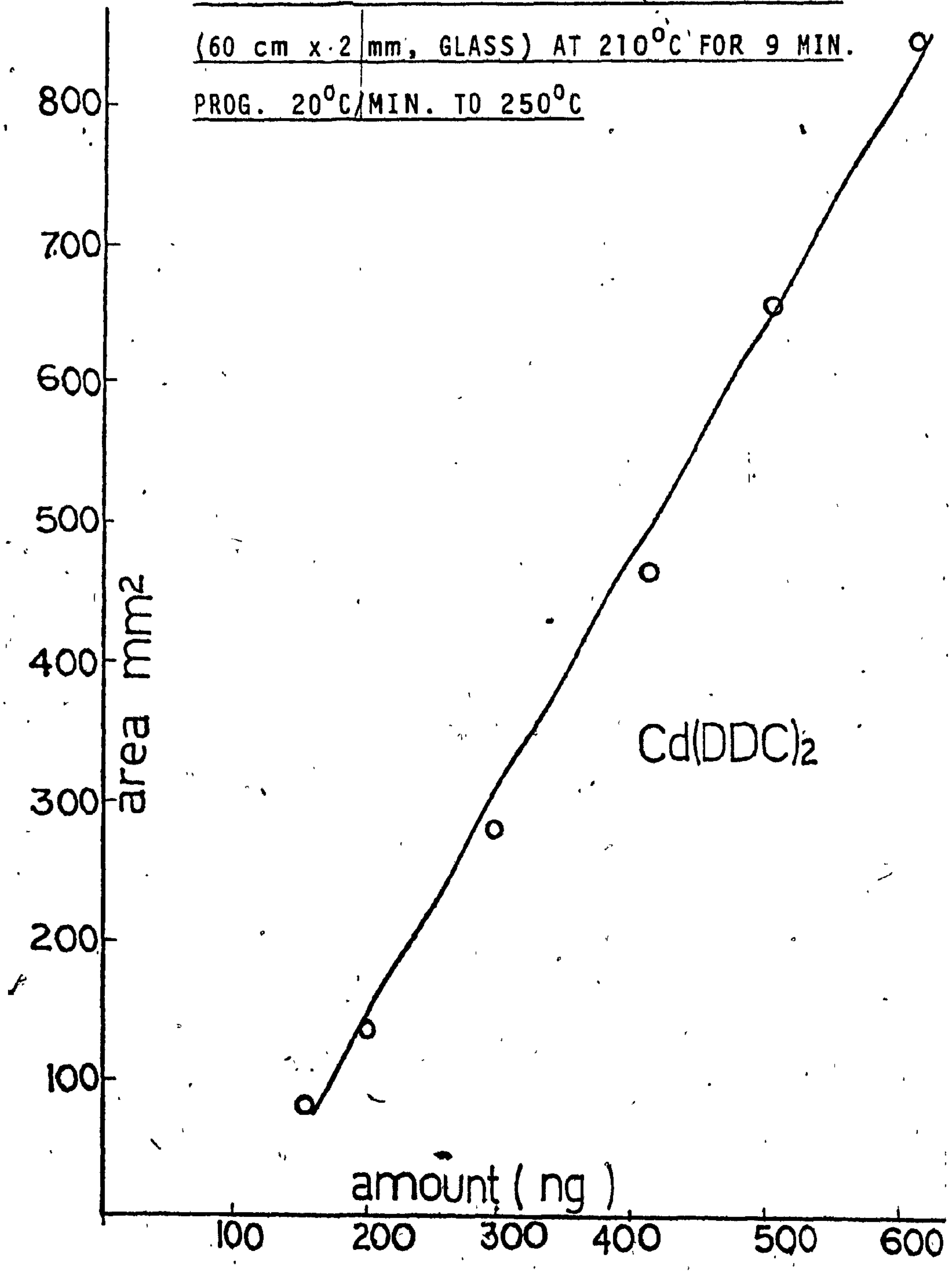
(60 cm x 2 mm, GLASS)

210°C FOR 9 MIN.

PROG. 20°C/MIN.

TO 250°C

FIGURE G-XXI A



RESPONSE ON 5% OV-101 + 5% QF-1 ON CW-HP (60 cm x 2 mm, GLASS) AT 210°C FOR 9 MIN. PROG. 20°C/MIN. TO 250°C

TABLE G-XXI

REGRESSION PARAMETERS FOR FIG. G-XXI AND FIG. G-XXI(A)

	$Zn(DDC)_2$	$Cd(DDC)_2$	$Cu(DDC)_2$	$Ni(DDC)_2$	$Co(DDC)_3$
Y Intercept (mm^2)	-166	-159	-128	-90.8	-103
Slope (mm^2/ng)	2.33	1.61	2.51	3.94	2.23
Corr. Coeff.	1.000	0.992	0.999	0.999	0.994
Ret. Time (mins.)	4.7	7.1	9.2	12.2	18.7

Column Temp. (210°C for 9 mins. then programmed at 20°C/min. to 250°C).

FIGURE G-XXII

RESPONSE ON 1.5% OV-101 + 1.5% QF-1 ON CW-HP (GLASS, 60 cm x 2 mm)

205°C FOR 8 MIN., PROG. 20°C/MIN. TO 245°C

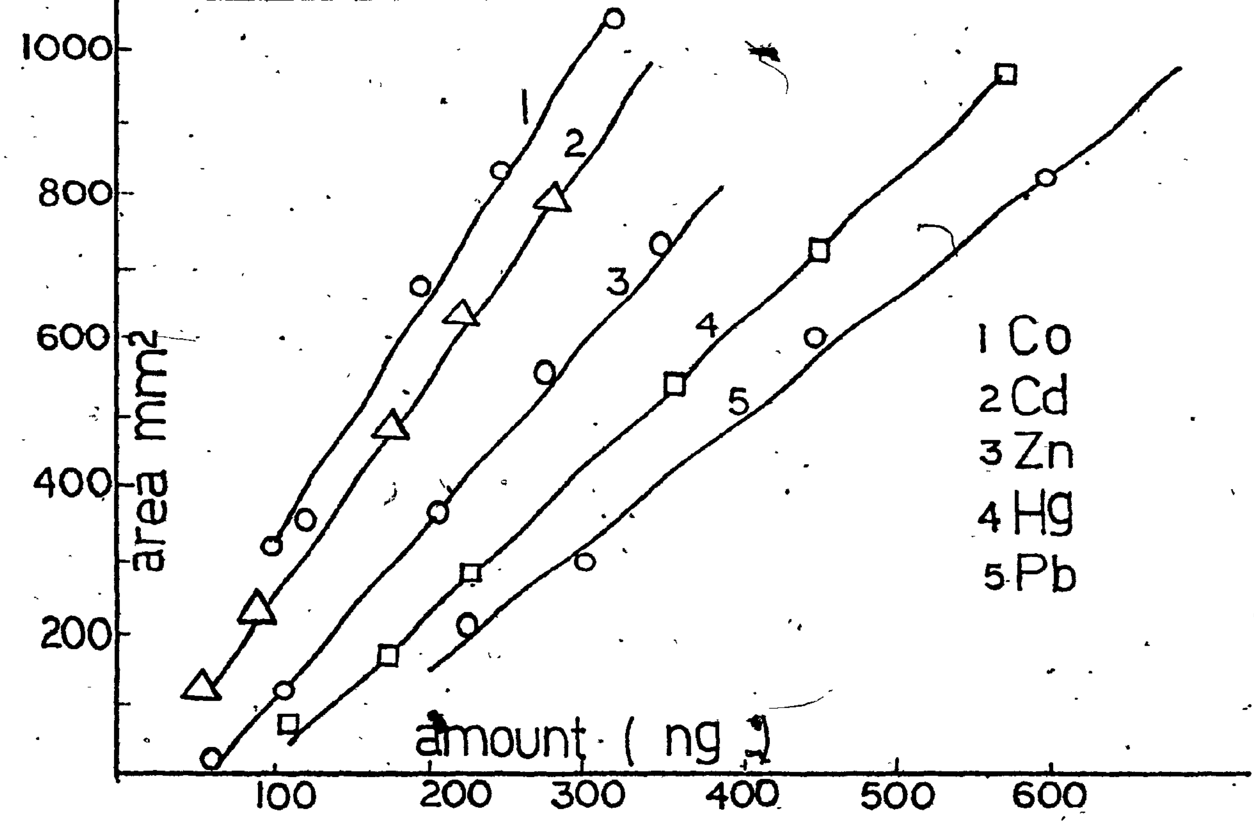


TABLE G-XXII

REGRESSION PARAMETERS FOR CALIBRATION LINES ON FIG. G-XXII

	$Zn(DDC)_2$	$Cd(DDC)_2$	$Pb(DDC)_2$	$Hg(DDC)_2$	$Co(DDC)_3$
Y Intercept (mm^2)	-150	-51.0	-201	-182	-51.0
Slope (mm^2/ng)	2.51	3.02	1.72	1.99	3.47
Corr. Coeff.	1.000	0.999	0.999	0.999	0.998
Ret. Time (mins.)	2.6	4.0	5.1	7.3	14.8

Column Temp. (205°C for 8 mins, then programmed at 20°C/min. to 245°C).

FIGURE G-XXIII

RESPONSE ON 1% QF-1 + 1% OV-101 ON GC-Q

(60 cm x 2 mm, GLASS)

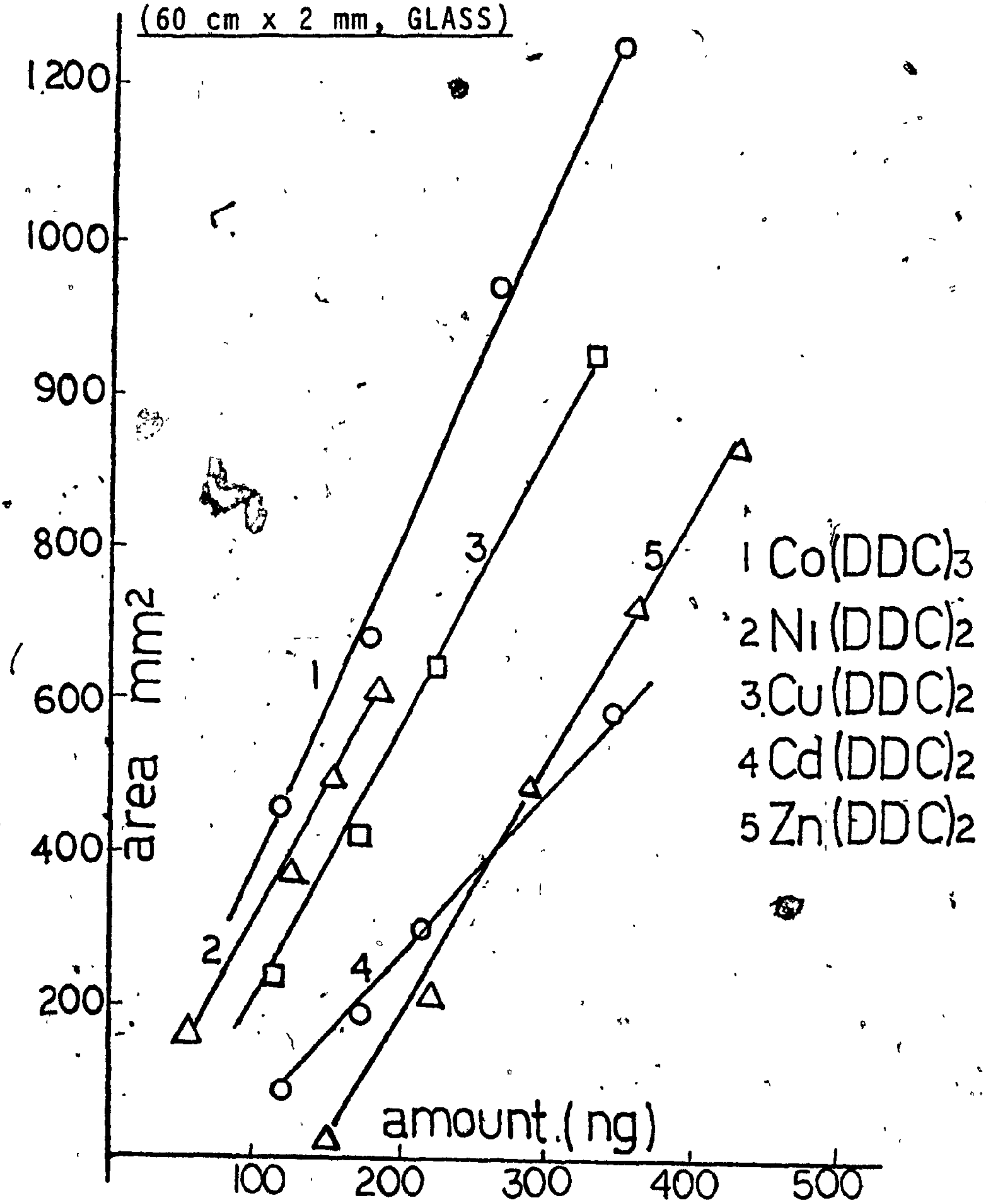


TABLE G-XXIII

REGRESSION PARAMETERS FOR CALIBRATION LINES IN FIG. G-XXIII

	$Zn(DDC)_2$	$Cd(DDC)_2$	$Cu(DDC)_2$	$Ni(DDC)_2$	$Co(DDC)_3$
Y Intercept (mm^2)	-455	-157	-184	-38.8	-66.0
Slope (mm^2/ng)	3.24	2.19	3.79	3.58	4.44
Corr. Coeff.	0.999	1.000	0.999	0.998	0.999
Ret. Time (mins.)	3.5	5.7	6.2	8.8	14.0

Temp. Col. 190°C for 7.0 mins., then programmed at 20°C/min. to 245°C.

APPENDIX II

In this study there were several findings that require theoretical interpretation. They include:

(i) The reason for the observed order of elution of each metal chelate on columns where separation was obtained.

(ii) The cause of decomposition of some chelates on stainless steel columns using GC.

(iii) The explanation for the improvement in resolution obtained when glass columns were used as opposed to metal columns.

(iv) The reason for the order of elution of compounds observed in HPLC using silica type adsorbents (LC-6, 10um, silica 106-310).

In gas chromatography the order of elution of compounds in a mixture depends mostly on the volatility of the components and on their affinity for the stationary liquid phase. Of these two factors, volatility seems to be the more dominant one for a $M(DDC)_n$ mixture. The order of elution did not change in going from nonpolar liquid phases such as OV-101 or SE-30, to a relatively polar liquid phase such as QF-1. The volatility of a compound depends on a number of complex factors, some of which are considered below.

In this study of $M(DDC)_n$, for the series $Zn(DDC)_2$, $Cd(DDC)_2$ and $Hg(DDC)_2$, the order of elution was:

$Zn(DDC)_2$, $Cd(DDC)_2$ and then $Hg(DDC)_2$.

Cardwell and Desarro (32) found, for the series $Ni(DDC)_2$, $Pb(DDC)_2$ and $Pt(DDC)_2$, that the elution order was:

$Ni(DDC)_2$, $Pd(DDC)_2$ and then $Pt(DDC)_2$.

This order can be explained on the following basis. Charged or highly polar species in which intermolecular forces are high are generally nonvolatile, but as has been pointed out by Sievers and Sadlowski (92), in a metal chelate the ligand shields the metal ion from the intermolecular forces that would normally render it nonvolatile by surrounding it with an organic shell. This accounts for whatever volatility the $M(DDC)_n$ chelates exhibit. Clearly, one should expect the ligand to shield the smaller metal ion from intermolecular forces more effectively than larger metal ions. Hence, Zn(II) chelates should be eluted before Cd(II) chelates and Hg(II) chelates, since the atomic radii increases from 74 pm to 110 pm in this series.

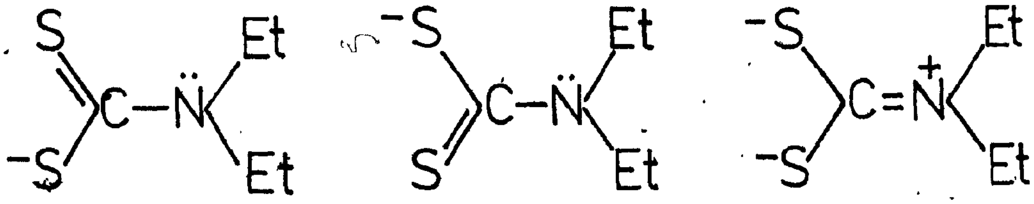
When transition metal chelates in general are considered, however, other factors must be involved besides ionic size since the ionic radii of transition metal ions do not change very much in going from Co(III) to Zn(II).

It has been proposed by Patsalides and coworkers (93) that for the series Zn(II), Cd(II) and Hg(II), the metal becomes softer (or more polarizable) from left to right so that the respective metal chelates will also be more polarizable. Therefore, volatility will decrease going from Zn to Hg in this series. This is also consistent with the results reported by Cardwell and Desarro (32).

The following order of elution was found in this study: ZnDDC)$_2$, Cu(DDC)$_2$, Ni(DDC)$_2$ and then Co(DDC)$_3$. In order to explain this order, the bonding of the metals to the sulphur of the ligand must be considered carefully. In fact, the particular metal ion in its particular oxidation state must be considered.

It has been well documented that in the case of Ni(DDC)$_2$, dπ - dπ bonding is involved (21,94). This being the case, donation of electrons from the metal to the ligand will increase the electron density on the π-cloud of the chelate rings. This will increase the polarizability of the chelate molecule and lower the volatility of the Ni(DDC)$_2$ chelate compared to the Cu(DDC)$_2$ and Zn(DDC)$_2$ chelates. Back-π donation has also been observed to a lesser extent in the case of Cu (21). Further evidence of dπ-dπ bonding has been given by Otavec et al. (95). They found that the average interatomic distance of the M-S bonds increased from 220.1 pm for Ni-S to 246.5 pm for Zn-S. This is consistent with results found in this study.

No existence of π-bonding has been reported for Co(DDC)$_3$ so that other factors must be contributing to its low volatility and consequently long retention time. The most important factor seems to be that Co(III) is a hard acid due to its large charge and small size. This means that although the Co(III) bonding electrons are not readily available, it still has high polarizing power because of its highly concentrated charge and will make the electrons of the ligand more available for bonding. This will increase the electron density in the π-cloud because of electron donation from the nitrogen atom, and structure (c) below will become important.



(a) (b) (c)

This fact alone would not account for the lower volatility of $Co(DDC)_3$, compared to other metal chelates. What does is that there is a third ligand surrounding the metal ion. This makes the $Co(DDC)_3$ into a highly polarizable molecule and therefore reduces its volatility. The same explanation applies to $Cr(DDC)_3$ which is even less volatile than $Co(DDC)_3$.

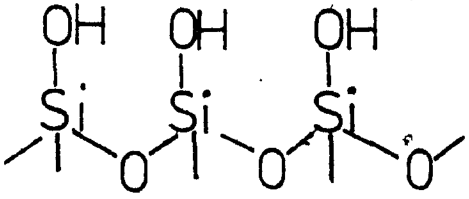
It appears from the results of this study that electronic effects due to bonding are more important than ionic radii in establishing elution order of $M(DDC)_n$ in GC. For example, $Cu(DDC)_2$ is eluted after $Cd(DDC)_2$ and $Zn(DDC)_2$ even though its ionic radius is smaller than that of Cd or Zn. $Hg(DDC)_2$ though eluted after $Cu(DDC)_2$ as predicted from ionic radii data, has about the same volatility as $Ni(DDC)_2$, a smaller ionic radius metal ion. This can be explained if one considers that Hg(II) is a very soft acid and soft acids are usually involved in $d\pi$-$d\pi$ bonding (93,96).

It was found in this study that $Pb(DDC)_2$, $Cd(DDC)_2$ and $Hg(DDC)_2$ frequently decomposed when chromatographed using stainless steel tubing columns. Considering the size of these metal ions, it can be seen that they are soft metals (low charge, large size) (97). When soft acids react with a soft base such as DDC^-, the effect should be to render the soft acid even softer (98). Soft acids and soft bases are known to interact with metal surfaces (where the metal is usually in the zerovalent state) and are absorbed. This is especially true for gaseous phase processes (99). The above argument is at least part of the explanation for the poor behaviour of Pb, Cd and Hg chelates on stainless steel tubing. In addition, S is a good nucleophile and may initiate pyrolytic decomposition in these soft acid compounds. Also, sulphur forms extraordinarily stable sulphides with soft acids (metals) which may be formed when the chelates are heated to high temperature (93).

The fact that soft acids are more readily adsorbed on a metal surface may explain the poor resolution observed on stainless steel columns for mixtures containing such soft acid metal chelates. In fact, the best separation with stainless steel columns was for Co(DDC)$_3$, Ni(DDC)$_2$, Cu(DDC)$_2$ and Zn(DDC)$_2$, which are either borderline or hard acid metals, according to the hard-soft-acid-base criteria (97).

In HPLC the following order of elution was found: Hg(DDC)$_2$, Cu(DDC)$_2$, Ni(DDC)$_2$ and then Co(DDC)$_3$.

This meant that Cu(DDC)$_2$, Ni(DDC)$_2$ and Co(DDC)$_3$ were eluted in the same order as by GC. Hg(DDC)$_2$, however, was eluted more quickly than had been the case in GC. In order to explain the latter discrepancy it is necessary to examine the column used in HPLC. A silica type adsorbent which has a hard base on its surface was used:



Since hard bases form more stable complexes with hard acids and less stable complexes with soft acids, it is to be expected that Hg(DDC)$_2$ would form the least stable complex on the support surface and, therefore, it would elute most quickly. On this same basis, Co(DDC)$_3$, being the hardest acid in the group, should be eluted last and this in fact was what occurred.

More evidence to support this hypothesis is provided in reports by G. Schweds (42,42A) in reversed phase HPLC studies where the order of elution obtained for a mixture of these same metal chelates was reversed. This is to be expected since the mobile phase was a hard base (ethanol/water) and the stationary phase, LiChrosorb RP-8, contained octylsilyl groups on the surface (a soft base).