SYNTHESIS AND CHARACTERISATION OF DOUBLE METAL CYANIDES

A
REPORT ON
Laboratory Project submitted for the
partial fulfilment of the degree
of
MASTER OF PHILOSOPHY
in
CHEMISTRY
(Industrial Methods of Chemical Analysis)

By

MINAKSHI VERMA

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROORKEE
ROORKEE-247 667 (INDIA)

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled, "**SYNTHESIS AND CHARATERISATION OF DOUBLE METAL CYANIDES**" in partial fulfilment of the requirement for the award of the **Degree of Master of Philosophy** submitted in the Department of Chemistry of the University is an authentic record of my own work carried out during a period from January **1998 to July 1998** under the supervision of **Prof. Kamaluddin**.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

Minakshi Verma.

(MINAKSHI VERMA)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

(DR KAMALUDDIN)

Date : 31st July '98

31/7/98

(Dr. KAMALUDDIN)
Professor
Department of Chemistry
University of Roorkee
Roorkee - 247 667

C.L. Sharma

(Dr. C.L. SHARMA)
Professor & Head
Department of Chemistry
University of Roorkee
Roorkee - 247 667

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MINAKSHI VERMA

CONTENTS

ABSTRACT

Double metal cyanides are the special class of compounds having importance in scientific and biological fields. The present work describes the synthesis of potassium hexacyanomanganate (III) and potassium hexa-cyanochromate(III) which were then used to prepare a series of complexes by replacing outer cation with zinc, copper and cobalt, respectively. In order to characterise these complexes different techniques were used. I.R. spectra revealed peaks corresponding to C N, metal - cyanide stretching, metal-cyanide bending, OH-stretching and OH-bending in almost all the complexes. Thermogravimetric analysis indicated the presence of water of crystallisation associated with the synthesized complexes. Magnetic studies showed paramagnetic behaviour for all the complexes with different number of unpaired electrons. Percentage of different transition metals in different complexes were calculated using AAS which were found to resemble with the proposed molecular formula. X-ray diffraction analysis showed all the complexes to be crystalline except cobalt hexacyanochromate(III) which was found amorphous in nature.

INTRODUCTION

GENERAL INTRODUCTION

I. 1 INTRODUCTION AND LITERATURE SURVEY

Double metal cyanide is a special class of compounds in inorganic chemistry. This group of compounds has attracted the attention on account of their importance in various fields. A general formula of double metal cyanides may be written as $M'_n [M''_m (CN)_6]$, where M' and M'' are two different ttransition metal elements and n & m are natural numbers depending upon the oxidation states of M' & M''. Many such complexes of Cr, Mn, Fe, Co, Ni, Cu, W, Zn group have been synthesized and characterised earlier [1-13]. Kourim *et al.* have made extensive investigation on various metal ferrocyanides [14-16]. Among these Cr (III), Mn (III), Fe (III) metals combine quite easily with cyanide ligand to form stable complexes with respect to decomposition by moisture and atmospheric oxygen.

Cyanide ligand is a powerful co-ordinating agent which is capable of stabilising a wide range of stereochemical configuration on account of their behaviour to complex with number of oxidation states of transition metals. The most common oxidation states to which cyanide ligand complexes is 2 and 3. It does form complexes with metals in low oxidation states though the compounds formed are chemically less stable.

The molecular orbital configuration of cyanide ion is :

KK $\left|(\sigma 2s)^2(\sigma 2s)^2(\sigma 2p)^2(\pi 2p)^4(\pi 2p)^0\right|$,

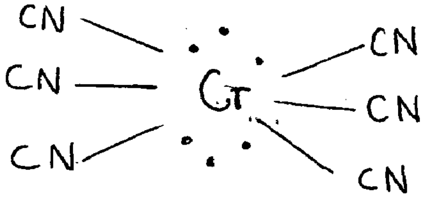
Which allows the two lone pairs ,one on the carbon and other on the nitrogen (lying on the carbon-nitrogen axis) to undergo co-ordination through overlap with the metal d-orbital. Literature survey (17-19), however, reveals that bonding of the cyanide ion occurs usually through carbon except when cyanide acts as a bridge. In that case, the bonding takes place through both the carbon and nitrogen ends.

The cyanide ion may behave both as a σ bonding ligand as well as a π bonding ligand. Structural evidence for π bonding in cyanide complexes is available from $K_{M\text{-}C}$ and $K_{C\text{-}N}$ (force constants for metal-carbon and carbon-nitrogen bonds, respectively) values reported in the literature. It is reported that d^{10} cyanide complexes have lower K_{M-C} and higher K_{C-N} values than those with fewer d-electrons, presumably because there is little π bonding in d^{10} system [20].

The reason why transition metals form stable complexes lies in the fact that they may use their d-orbitals for $d\pi$-$p\pi$ backbonding in addition to the original σ co-ordinate bond $M \leftarrow (CN^{-})$. The bonding involves the overlap of (σ^{*} 2s) orbital with $nd\sigma$, $(n+1)s$ and $(n+1)p$ metal orbitals which constitutes the normal ligand- metal σ co-ordinate bond followed by the backdonation of electrons from the filled d-orbitals of metal atom to the vacant (π^{*} 2p) orbital of ligand. This type of backdonation of electrons avoids the accumulation of excess negative charge on the metal atoms which thereby strengthens the metal-carbon bond and weakens the metal-nitrogen bond.

From the structural point of view these complexes both as a solid and as a solution are of octahedral symmetry and those that are not are usually treated as distorted octahedral.

The structure of $[(Cr\ (CN)_6]^{3-}$ ion in $K_3\ [Cr(CN)_6]$ was proved by Kalandiya [21] and was represented as given below :



A highly interesting feature of chemistry of Cr (III) complexes is photoaquation reaction that they undergo. Photodecomposition is another property which has previously been claimed by various workers [22-23] on irradiation by light of wavelength 254nm. The quantum yield for photoaquation are found generally high. These reactions are wavelength and temperature independent except in the photoexchange of $[Cr(H_2O)_6]^{3+}$ with water and extent of reaction enhances with ligand strength except in the aquation of $[Cr(CN)_6\ ]^{3-}$ [24].

$$[Cr(CN)_6]^{3-} \xrightarrow[H_2O]{h\nu} [Cr(CN_5)\ (H_2O)]^{3-}$$

On the other hand, quantum yield of non-octahedral complexes is found to be low, ranging from unity to 10^{-4} and their reactions are also temperature and wavelength dependent. Sokol *et al.* have made extensive studies on the aqueous decomposition of pentacyano cobaltate(II) [25] which are found to be temperature dependent. Photoaquation reaction of other nonoctahedral complex, aquo-heptacyanotungstate(IV) also shows the reaction to be temperature and pH dependent [13].

Various instrumental techniques such as X-ray diffraction, thermogravimetry, atomic absorption, magnetic studies, UV, IR spectroscopy etc. are taken in to account in the structural elucidation of the complexes.

Infrared spectrum is an important record which gives sufficient information regarding the structure of compounds. For a species to absorb infrared radiation there must be some change in its dipole moment, as absorption in this region occurs due to the changes in the vibrational and rotational levels. Each functional group absorbs at definite frequency e.g., the hydroxyl group in a compound absorbs at 3600 - 3200 cm^{-1} where as $-C\equiv N$ group absorption ranges from 2080-2200 cm^{-1}. The shift in the absorption position helps in predicting the factors which cause shift. There has been a number of metal substituted ferro and ferricyanides of Cu, Ni, Co and Mn for which infrared studies have been made earlier [26-27]. Infrared spectroscopic detection of bridging cyanide group has been investigated earlier by Dows and coworkers [28]. Their studies reveal that linear M-C-N-M bridge system have C-N stretches about 70 cm^{-1} higher than the corresponding C-N terminal stretches and this has been used as a diagnostic test for such bridges. Shriver [29] and ford-smith [30] also have reported this type of shift in absorption frequency in cyanide containing complexes. Cullough *et al.*. [31] have investigated infrared and visible bsorption studies of pentacyanonickelate(II) ion in aqueous solution earlier and found single new absorption peak characteristic of pentacyanonickelate (II) ion. There has been many other evidences [32-33] which show a sharp and intense $-C{\equiv}N$ stretching frequency at 2100 cm^{-1} and for bridging cyanide at 2200 - 2280 cm^{-1} in many other metal-cyano complexes.

Magnetic susceptibility helps in knowing the magnetic behaviour of the complexes. The presence or absence of the moment and its magnitude gives support to the prediction regarding the filling of orbitals in the metal atom. It also helps in elucidating the paramagnetic or diamagnetic behaviour of the metal complexes.

As to ascertain the special arrangement of the structural units of a substance in the crystalline state, X-ray diffraction studies are taken into consideration. X-ray diffraction provides a convenient and practical means for the qualitative identification of crystalline compounds. It is quite easier to identify structure with the help of powdered diffraction pattern which is based upon the position of lines (in terms of θ or 2θ) and their relative intensities. A comprehensive index based on the Hanawalt system is published in card form by the American Society for testing and materials (ASTM) which provides d-spacing and relative line intensities for pure compounds.

Another analytical instrumental technique is atomic absorption spectroscopy which is widely used in the characterisation of metal complexes. This technique involves the study of the absorption of radiation by neutral atoms in the gaseous state. The sample is first converted into atomic vapours and then their absorption is measured at a selected wavelength which is characteristic of each individual element. This technique helps in knowing the % of different transition metals in the complex.

Thermogravimetric analysis plays an important role in sorting out correct molecular formula of the complexes. This technique involves change in weight of a system under examination with increase in temperature at a predetermined and preferably at a linear rate. It involves the principle that water is evolved at the begining of heating. Usually water of crystallisation is evaporated at 80-120°C. Further loss in weight up to 250-270° C may be caused due to the evaporation of H-bonded or complexed water molecules. If temperature is raised further higher, generally loss of carbon and nitrogen containing species in the form of CO_2 and N_2 occur and ultimately metal oxides are formed as the residue.

The Double metal cyanide complexes have extensive use as ion exchanger and as a adsorbent. They have been found selective in radiochemical technology for concentrating and isolating $^{137}Cs^+$ from fission waste [34] and oceanic fall outs [35]. Ion exchange adsorption of Cs^+ by potassium hexacyanocobaltate(II)ferrate(II) have been studied previously by Prout *et al.* [36]. They prepared the granular form of the above compound and found it to be highly selective adsorbent for Cs^-. This material is suitable for the use in the large scale ion exchange column and offers the possibility of isolation and removal of radioactive material. Ion exchange of Cs and Rb on tungsten ferrocyanide has been investigated earlier by J. Krit [37]. Further chemical composition and crystallographic structure of new inorganic ion exchanger ferrocyanide molybdate have been reported by Baetsle and coworkers [38]. Certain other evidences [39-40] are also available in the literature indicating the ion exchange properties of these metal cyanide complexes. Copper, zinc, molybdenum and chromium ferrocyanides have been found to possess strong affinities towards several phenols [41-42].

Metal cyanide complexes have been found their use in colorimetric estimation of various metal ions. Potassium hexacyanoferrate(II) was used as colorimetric reagent for the determination of Cr(III) for the first time by Malik and coworkers

[43]. Besides this, potassium hexacyanochromate(III) was also used for quantitative estimation of Be(II), Sn(II), Hg(II), Cr(III), and Mo (VI) metal ions by Malik and coworkers [44] and it was found that the sensitivity of the method doubled in presence of organic base chromicyanide [45]. Metal cyano complexes have been thought to have some catalytic role in chemical evolution also. Beck [46] considered that CN^- might have formed stable complexes with transition metals present in the primeval seas. Orgel [47] supported the possibility of formation of cyano complexes and thought them to play important role in chemical evolution. Kamaluddin and coworkers have prepared a number of metal ferrocyanides and studied their interaction in detail with organic molecules such as nucleotides [48] and amino acids [49].

The influence of metal cyano complexes in biological field has also been recognised. In general, complexed cyanides do not appear to have markedly poisonous properties until and unless one or more cyanide groups are removed from the co-ordination sphere. In living beings free CN^- imparts high toxicity by complexing with haemoglobin, thus preventing the normal metabolism. The replacement of easily removable cyanide groups by amino acid and the formation of mixed ligand cyanides may also be of great biological importance.

The proteins are life sustaining materials and are known to react with metal complexes [46]. Their reactions are met with in some biological processes [50]. In view of the importance of complexes as a means of activating physiological and biological reactions, their studies have become of great importance.

I.2 STATEMENT OF THE PROBLEM

Existing literature shows that Double metal cyanides form an important class of compound. They have been proved to work as a good ion exchanger especially in the extraction of radio active cations. Double metal cyanides could have also existed on the primitive earth and might have acted as a prebiotic catalyst. These compounds have also been used in the qualitative analysis of several organic compound as they show specific colour reactions. In view of the above it has been proposed to make a detailed study on the synthesis and characterisation of Double metal cyanide of manganese and chromium.

EXPERIMENTAL

CHAPTER - II

EXPERIMENTAL

II.1 MATERIALS REQUIRED:

In order to synthesize various Double metal cyanides, following materials were used. Required materials with their makes and grades are given in the following table.

S. No.	Name	Molecular Weight	Make	Grade
1.	Manganese chloride ($MnCl_2.4H_2O$)	197.94	E. Merck	A.R.
2.	Zinc chloride ($ZnCl_2$)	136.28	E. Merck	A.R.
3.	Copper chloride ($CuCl_2$)	170.0	Central Drug House	A.R.
4.	Cobalt sulphate ($CoSO_4.7H_2O$)	281.10	E.Merck	A.R.
5.	Potassium dichromate ($K_2Cr_2O_7$)	294.18	E.Merck	A.R.
6.	Potassium cyanide (KCN)	65.12	Sisco, India	A.R.

7.	Ethyl alcohol (C_2H_5OH)	46.07	Riedel-deHäen, Germany	L.R.
8.	Ammonium hydroxide (NH_4OH))	35.05	Sudha Chemicals	L.R.
9.	Copper sulphate ($CuSO_4.5H_2O$)	249.60	E. Merck	A.R.
10.	Zinc sulphate ($ZnSO_4.7H_2O$)	287.43	Qualigens	A.R.
11.	Manganese sulphate ($MnSO_4$)	151.06	B.D.H.	A.R.
12.	Cobalt chloride ($CoCl_2.6H_2O$)	237.83	B.D.H.	A.R.

II.2 EQUIPMENTSUSED:

During the course of characterisation of the synthesized Double metal cyanide complexes, following equipments were used :

1. FTIR Spectrophotometer of Perkin-Elmer 1600 series was used to record IR spectra of mixed metal cyanide complexes.

2. Magnetic moment measurements were carried out with the help of Vibrating sample magnetometer, Model-155, Parc, Princeton (New Jersey).

3. X-ray Diffractometer system PW 1410/20, Philips (Holland) was used in carrying out X-ray diffraction studies of various complexes.

4. Stanton Redcroft, Model STA-780 Series (UK) thermal gravimetric analyser was used to record thermal gravimetric plots (TGA).

5. To calculate % of various transition metals in the Double metal cyanide complexes, atomic absorption analysis were carried out on Atomic absorption spectrophotometer (AAS) Model- 3100, Perkin Elmer (U.S.A.).

Note: Magnetic measurements, X-ray studies and thermogravimetric behaviour of complexes were studied at University science instrumentation centre (USIC), University of Roorkee, Roorkee.

II.3 METHOD USED/PROCEDURAL DETAILS:

II.3.A Synthesis of Potassium Hexacyanomanganate(III):

Synthesis of Potassium hexacyanomanganate(III) was performed according to the procedure reported earlier [51-52]. The synthesis was accomplished in two steps :

(i) Preparation of Manganese (III) orthophosphate :

To the warm solution of 34.2g of manganese(II) chloride in 50 ml of water was added 30g of sirupy phosphoric acid and 10g of conc. nitric acid. The solution was then concentrated near to dryness during which the colour changes from amethyst to green-grey precipitates. Stirring was continued throughout as precipitates tend to stick to the bottom of the beaker. To the precipitates 50 ml distilled water was added. The solution so formed was filtered through buckner funnel using whatman filter paper number -1. Residue was collected and washed several times with water and dried finally.

(ii) Preparation of Potassium hexacyanomanganate (III) :

This step involved the slow addition of manganese (II) orthophosphate to the warm solution containing 30g of KCN in 80 ml of water with continuous stirring. Above mixing had resulted in the formation of deep red coloured solution. Completion of reaction was indicated by the complete dissolution of phosphate. The solution was then cooled. Enough water (5-10 ml) was added to dissolve the crust if any, leaving the red crystalline needles of Potassium hexacyanomanganate(III). These needles were collected on a buckner funnel and sucked dry. For purification, recrystallisation was done several times from water.

Probable chemical reaction that leads to the synthesis of Potassium hexacyanomanganate(III) is as under :

$$3MnCl_2 + HNO_3 + 3H_3PO_4 + H_2O \rightarrow \underset{\text{(Manganese ortho phosphate)}}{3MnPO_4.H_2O} + NO + 6\,HCl$$

$$6KCN + MnPO_4.H_2O \rightarrow K_3\,[Mn(CN)_6] + K_3PO_4 + H_2O$$

II.3.B Synthesis of copper, zinc, cobalt derivatives of potassium hexacyanomanganate (III):

The synthesis of copper derivative of Potassium hexacyanomanganate(III) was performed by the slow addition of 0.1M $CuCl_2$ solution to the 50 ml of 0.1M solution of $K_3 [Mn(CN)_6]$. Slight excess of $CuCl_2$ was added in order to achieve completion of reaction, which was indicated by the formation of dirty green mass of precipitates. This solution was kept standing on water bath at 50-60°C for 2-3 hrs. to make the green mass settled. These precipitates were then collected and washed thoroughly with water. Zinc and cobalt derivatives of potassium hexacyanomanganate(III) were prepared through a similar procedure mentioned above. Equimolar solutions of cobalt sulphate and zinc chloride were used to get brown powdered precipitates of cobalt hexacyanomanganate(III) and black coloured zinc hexacyanomanganate(III).

II.3.C Synthesis of Potassium hexacyanochromate (III) :

Synthesis was done according to the procedure recommended earlier by Christensen [51,53]. In the procedure, initial step involved was the reduction of solution containing 25g of potassium dichromate in 500 ml of H_2O by sulphur dioxide. The solution was then boiled off to remove excess of SO_2. To the boiling solution was added conc. NH_4OH solution with constant stirring. The precipitated chromium(III) hydroxide was suction filtered on a large buchner funnel and washed thoroughly with boiling water to remove excess of NH_3. It was then dissolved in 100 ml of glacial acetic acid and the solution was evaporated almost to dryness over a very small flame. The tacky paste of chromium(III) acetate was then dissolved in 180 ml of water. This solution was poured into a flask containing 75g of potassium cyanide dissolved in about 300 ml of water. 2g of activated charcoal was added to the solution and after stirring the hot mixture for several minutes, it was filtered and evaporated to 300 ml in an evaporating dish. The hot solution was again treated with charcoal and filtered while hot On cooling in ice, the product crystallised out as pale yellow needles. The material was suction filtered and pressed well. The mother liquor was further evaporated to obtain 2 or 3 more crops of product. All the crystals so formed were thoroughly washed with 95% alcohol and dried in a dessicator away from the light. To have pure product this material was further recrystallised with water 2-3 times. Probable chemical reaction for the formation of Pot. hexacyanochromate(III) is as under :

$$Cr_2O_7 + 3SO_2 + 2H^+ \longrightarrow 2Cr^{+++} + 3SO_4 + H_2O$$

$$Cr^{+++} + 3OH \longrightarrow Cr(OH)_3$$

$$Cr(OH)_3 + 3CH_3COOH \rightarrow Cr(CH_3COO)_3 + 3H_2O$$

$$Cr(CH_3COO)_3 + 6KCN \rightarrow K_3[Cr(CN)_6] + 3CH_3COOK$$

II.3.D Synthesis of copper, zinc and cobalt derivatives of potassium hexacyanochromate(III) :

Synthesis of metal chromicyanide derivatives have been carried out exactly in the similar way as done in case of potassium hexacyanochromate (III) derivatives.

Firstly 250 ml, 0.1M solution of potassium hexacyanochromate was prepared. 50 ml of this solution was taken in 3 separate beakers. To each beaker was added equimolar solution of copper chloride, zinc chloride and cobalt sulphate separately with continuous stirring. Each, of the solution was kept on water bath at 50-60°C for 2-3 hrs. Constant heating for a longer time resulted in the formation of green crystalline precipitates of copper hexacyanochromate(III), dirty white powdered precipitate of zinc hexacyanochromate(III) and brick red coloured cobalt hexacyanochromate(III). All the precipitates were filtered and collected. For further purification, recrystallisation was done with water.

II.4 I.R. SPECTRAL STUDIES :

Infrared spectral studies of different Double metal cyanides were conducted in KBr disc. A thin film of KBr containing a little amount of complex sample was prepared and subjected to FTIR spectrophotometer. Absorption frequencies corresponding to metal-cyanide bonds and other functional groups have been collected in Table -1 and recorded spectra have been arranged in Figures : 1-8.

II.5 ATOMIC ABSORPTION STUDIES :

Atomic absorption studies were conducted to calculate % transition metals in various synthesized Double metal cyanide complexes. To carry out absorption analysis solutions for all the complexes were prepared. For this, 1mg of each sample was dissolved in 5 ml of conc. HCl. If turbidity appears, few drops of conc. HNO_3 were further added with slow heating. These solutions were then madeup to 100 ml with distilled water.

Absorption of different metals viz. manganese, chromium, copper, zinc and cobalt were studied using lamp of corresponding metal at particular wavelength in spectrophotometer. Sensitivity check standards were used to calibrate the instrument for different metal ions. After calibration, standards having concentration less than sensitivity check were subjected to instrument and the respective values of absorbance were noted. The calibration curves were drawn with the help of concentration versus absorbance data of the standards. From these plots, concentration of metals (ppm) was determined. Different calibration curves have been given in Figures: 9-13.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Synthesis of Double metal cyanides of $K_3[Mn(CN)_6]$ and $K_3[Cr(CN)_6]$ were carried out by replacing outer cation (K^+) by different transition metal atoms. On the basis of valency balance, a possible molecular formula of the Double metal cyanides thus formed may be written as follows:

Complex	Expected Molecular Formula
Zinc hexacyanomanganate (III)	$Zn_3 [Mn(CN)_6]_2$
Copper hexacyanomanganate (III)	$Cu_3[Mn(CN)_6]_2$
Cobalt hexacyanomanganate (III)	$Co_3 [Mn(CN)_6]_2$
Zinc hexacyanochromate (III)	$Zn_3 [Cr(CN)_6]_2$
Copper hexacyanochromate (III)	$Cu_3[Cr(CN)_6]_2$
Cobalt hexacyanochromate (III)	$Co_3[Cr(CN)_6]_2$

In order to study the properties and structure of Double metal cyanides various instrumental techniques were used. Results of different studies which were made for the characterisation are as under:

III.1 INFRARED STUDIES :

Infrared studies are perhaps most relevant for the structural elucidation of compounds. The region of electromagnetic spectrum for infrared radiations ranges from 4000-400 cm^{-1}. Higher frequency portion (4000-1300 cm^{-1}) is called functional group region. I.R.Spectrum of Double metal cyanides are shown through Figures : 1-8. Prominent frequencies corresponding to different groups are depicted in Table- 1. Results shown in table clearly indicates three prominent peaks in almost all the spectra. Among them one characteristic peak is for $C \equiv N$ group which ranges between 2080-2190 cm^{-1} and the other two corresponds to metal-carbon stretching (ν_{M-C}) and metal-carbon banding (δ_{M-CN}) having range of 630-760 cm^{-1} and

450-550 cm^{-1}, respectively. Sharp peaks corresponding to OH-stretching and OH-bending are also seen in almost all the complexes which implies the presence of water molecules in respective complexes. However, I.R. spectra is not sufficient to investigate type of water molecule, i.e. whether the water is in complexed form or present as water of crystallisation. This aspect can be made elaborated by thermogravimetric analysis.

III.2 THERMOGRAVIMETRIC ANALYSIS :

Thermogravimetric analysis were conducted to calculate the probable molecular formula of the complexes by knowing the number of water molecules present in their latttice. T.G. analysis were conducted under following conditions :

Sample weight = 10 mg
Heating rate = 10°C/min
Chart speed = 20 cm/hr
Atmosphere = Static air

Reference = Al_2O_3

Holder = Al_2O_3

Recorded thermograms of all complexes have been shown in Figures : 14-21. Detailed studies of thermograms reveal that there is no significant water loss in potassium hexacyanomanganate (III), zinc hexacyanomanganate(III) and potassium hexacyanochromate(III) complexes. Slight loss in weight with temperature indicates the traces of moisture which might be added through the atmosphere as an impurity. In rest of the complexes viz. zinc hexacyanomanganate(III), cobalt hexacyanomanganate(III), zinc hexacyano chromate (III), copper hexacyanochromate (III) and cobalt hexacyanochromate(III), significant loss of water is evident. In these complexes 1, 6, 5, 1 and 5 molecules of water of crystallisation are expected, respectively. Loss of water of crystallisation takes place up to 120°C. Beyond this temperature loss of CN^- also begins. An important feature of most of the thermograms is that before the formation of final residue a hump is observed which indicates that during the course of heating some highly stable adduct is formed with the static air. Thermograms also show that observed % loss of CN^- in the complexes is found very low which indicate that all the cyanide groups were not detached during the decomposition and final residue formed still have some cyanide groups attached to the central metal atom. This assumption is further confirmed by the fact that observed % residue is much higher compare to theoretical values, if we consider the formation of mixed metal oxides as the end product.

III.3 ATOMIC ABSORPTION ANALYSIS :

Percentage of different transition metals in Double metal cyanides were calculated with help of standard curves (Figures: 9-13). Percentage of metal determined experimentally are nearly same to the theoretically calculated values obtained from the proposed molecular formula. The comparison between observed % and calculated

% have been given in Table -2. Close resemblance between the two data suggests that the proposed molecular formulae of the synthesized Double metal cyanides are correct.

III.4 MAGNETIC MEASUREMENTS :

Magnetic susceptibility measurements have proved to be extremely useful in the characterisation of materials at micro and macro levels. Magnetic susceptibility observations were made through magnetic moments of the complexes which help to evaluate number of unpaired electrons in the complexes to know whether the complex is diamagnetic or paramagnetic.

Magnetic moment of any complex can be given as under :

$$\mu_{obs} = 2.84 \sqrt{\frac{\mu MT}{B \times W}}$$

$$\mu_{cal.} = n\sqrt{n+2}$$

$$\mu = M \chi B$$

μ' = Magnetic moment of complex in B.M.

M = Molecular weight of the complex

T = Temperature in kelvin

B = Magnetic field applied (5000 gauss)

W′ = Weight of complex used for analysis

n = Number of unpaired electrons in transition metal

χ = Magnetic susceptibility

Data of μ', μ_{cal} and μ_{obs} for all the complexes have been given in Table - 3. Data presented show that all the complexes possess significant magnetic moment which implies presence of unpaired electrons in them. Due to the presence of unpaired electrons, the complexes are supposed to show paramagnetic character and are expected to be attracted strongly in the magnetic field. Greater the magnetic moment, greater would be paramagnetic character. Thus cobalt hexacyanochromate(III) is expected to be highly paramagnetic in nature with of 10 unpaired electrons. The number of unpaired electrons present in various synthesized complexes are as under :

Complex	Unpaired electrons
Potassium hexacyanomanganate(III)	3
Zinc hexacyanomanganate(III)	4
Copper hexacyanomanganate(III)	1
Cobalt hexacyanomanganate(III)	7
Potassium hexacyanochromate (III)	3
Zinc hexacyanochromate (III)	3
Copper hexacyanochromate (III)	3
Cobalt hexacyanochromate (III)	10

Table- 3 again shows that μ_{obs} values are little higher in magnitude than $\mu_{cal.}$. The difference between the two is attributed to the orbital contribution to the magnetic moment.

III.5 X-RAY DIFFRACTION STUDIES :

In order to investigate crystal structure, X-Ray diffraction patterns were recorded under following conditions :

Target - Copper ($\lambda = 1.5418$ A°)
Filter - Nickel
Scanning angle - 3° - 90°
Chart speed - 1cm/min
G.M. speed - 1°/min
Current - 20mA
Voltage - 35 KV
Range - 2Kc/s

The X-ray spectra so obtained consisted of large number of peaks with varying intensities. For some prominent peaks θ values were calculated which were then used to calculate d - values of corresponding peak with the help of bragg's equation.

Bragg's equation :

$$d = \frac{\lambda}{2\sin\theta}$$

d = Inter planar spacing

λ = Wave length of X-ray used (1.5418 A°)

θ = Angle between X-ray beams

Peak heights were used to calculate relative intensities of the different peaks. Data of relative intensities and d-values have been given in Table: 4-10. The X-ray diffractogram for different metal cyanides have been shown in Figures: 22-29.

Data in Table: 4-10 show that all the complexes except cobalt hexacyanochromate(III) are crystalline where as this complex is amorphous in nature as its X-ray diffractogram shows no significant measurable peak. d-values and relative intensities of different synthesized metal cyano complexes are not available in A.S.T.M. data file. Therefore, it is not possible to compare calculated values with the standard values. Crystal structure elucidation of different compounds are still to be done.

TABLES & FIGURES

Table - 1

Infrared spectral data of synthesized Double metal cyanides

S.No	Complex	ν_{M-CN} (cm^{-1})	δ_{M-C} (cm^{-1})	$\nu_{C\equiv N}$ (cm^{-1})	ν_{OH} (cm^{-1})	δ_{OH} (cm^{-1})
1.	$K_3[Mn(CN)_6]$	-	482	2114	3339 3443 3584	1642
2.	$Zn_3[Mn(CN)_6]_2$	633	-	2180	3458 3584	1632
3.	$Cu_3[Mn(CN)_6]_2$	664	518	2136	3210 3329 3507	1627
4.	$Co_3[Mn(CN)_6]_2$	-	511	2177	3372 3502	1599 1720
5.	$K_3[Cr(CN)_6]$	621	-	2125	3286 3423 3491	1645
6.	$Zn_3[Cr(CN)_6]_2$	760	525	2098 2225	3330 3472 3495	1625
7.	$Cu_3[Cr(CN)_6]_2$	682	514	2116	3399 3541	1618
8.	$Co_3[Cr(CN)_6]_2$	683	550	2161	3294 3371	1614

Table - 2

Data for % transition metals in synthesized Double metal cyanide complexes

S.No.	Complex	Molecular formula	Mol. wt.	Obs. value of transition metal (%)	Cal. value of transition metal (%)
1.	Potassium hexacyano manganate (III)	$K_3[Mn(CN)_6$	328.0	Mn=16.77	Mn=15.86
2	Zinc hexacyano manganate (III)	$Zn_3[Mn(CN)_6]_2.H_2O$	636.2	Mn=17.29 Zn=30.84	Mn=15.48 Zn=31.80
3.	Copper hexacyano manganate (III)	$Cu_3[Mn(CN)_6]_2$	612.6	Mn=17.96 Cu=31.10	Mn=14.42 Cu=33.00
4.	Cobalt hexacyano manganate (III)	$Co_3[Mn(CN)_6]_2.6H_2O$	707.0	Mn=15.56 Co=25.04	Mn=14.65 Co=26.10
5.	Potassium hexacyano chromate (III)	$K_3[Cr(CN)_6]$	325.0	Cr=16.00	Cr=16.62
6.	Zinc hexacyano chromate (III)	$Zn_3[Cr(CN)_6]_2 .5H_2O$	702.2	Cr=14.82 Zn=27.94	Cr=15.60 Zn=25.82
7.	Copper hexacyano chromate (III)	$Cu_3[Cr(CN)_6]_2. H_2O$	624.6	Cr=16.65 Cu=30.50	Cr=16.10 Cu=34.82
8.	Cobalt hexacyano chromate (III)	$Co_3[Cr(CN)_6]_2. 5H_2O$	683.0	Cr=15.22 Co=25.92	Cr=14.86 Co=27.34

Table - 3

Magnetic susceptibility measurements of synthesized Double metal cyanides

Experimental conditions :

Temperature = 301K

Applied magnetic field = 5000 oersteds

S.No.	Complex	$\mu' = \mu - \mu_o$ (B.M.)	$W' = W - W_o$ (g)	$\mu_{cal.}$ (B.M.)	$\mu_{obs.}$ (B.M.)
1.	$K_3[Mn(CN)_6]$	0.400×10^{-2}	0.03576	3.87	4.23
2.	$Zn_3[Mn(CN)_6]_2$	0.352×10^{-2}	0.03232	4.90	5.80
3.	$Cu_3[Mn(CN)_6]_2$	0.006×10^{-2}	0.00360	1.73	2.23
4.	$Co_3[Mn(CN)_6]_2$	0.190×10^{-2}	0.00874	7.94	8.64
5.	$K_3[Cr(CN)_6]$	0.334×10^{-2}	0.03113	3.87	4.12
6.	$Zn_3[Cr(CN)_6]_2$	0.714×10^{-2}	0.11359	3.87	4.63
7.	$Cu_3[Cr(CN)_6]_2$	0.353×10^{-2}	0.07056	3.87	3.90
8.	$Co_3[Cr(CN)_6]_2$	1.555×10^{-2}	0.04064	10.95	11.26

Table - 4

X-Ray diffraction data for $K_3[Mn(CN)_6]$

S.No.	2θ	Sinθ	d = λ/2sinθ	I/I_0x100%
1.	21.4	0.1857	4.152	100.00
2.	30.4	0.2622	2.941	55.00
3.	34.0	0.2924	2.637	70.00
4.	43.6	0.3714	2.076	65.00
5.	54.2	0.4555	1.693	75.00

Table - 5

X-Ray diffraction data for $Zn_3[Mn(CN)_6]_2$

S.No.	2θ	Sinθ	d = λ/2sinθ	I/I_0x100%
1.	21.7	0.1882	4.096	100.00
2.	26.4	0.2284	3.376	16.99
3.	37.5	0.3214	2.399	32.52
4.	43.5	0.3706	2.080	19.42
5.	58.6	0.4894	1.575	15.05

Table - 6

X-Ray diffraction data for $Cu_3[Mn(CN)_6]_2$

S.No.	2θ	$\sin\theta$	$d = \lambda/2\sin\theta$	$I/I_0 \times 100\%$
1.	25.3	0.2190	3.521	24.14
2.	27.6	0.2385	3.233	12.07
3.	29.8	0.2571	3.000	100.00
4.	41.4	0.3535	2.181	9.48
5.	52.8	0.4446	1.734	6.90

Table - 7

X-Ray diffraction data for $Co_3[Mn(CN)_6]_2$

S.No.	2θ	$\sin\theta$	$d = \lambda/2\sin\theta$	$I/I_0 \times 100\%$
1.	11.9	0.1037	7.435	44.44
2.	17.6	0.1530	5.039	100.00
3.	25.0	0.2164	3.563	48.15
4.	35.5	0.3049	2.529	51.85
5.	40.0	0.3420	2.254	48.15

Table - 8

X-Ray diffraction data for $K_3[Cr(CN)_6]$

S.No.	2θ	Sinθ	d = λ/2sinθ	I/I_ox100%
1.	10.5	0.0915	8.426	19.15
2.	11.6	0.1011	7.626	36.17
3.	15.8	0.1374	5.611	48.94
4.	18.1	0.1573	4.901	89.36
5.	20.2	0.1754	4.397	25.53
6.	21.3	0.1848	4.172	100.00
7.	23.5	0.2036	3.787	42.55
8.	31.8	0.2740	2.814	21.28

Table - 9

X-Ray diffraction data for $Zn_3[Cr(CN)_6]_2$

S.No.	2θ	Sinθ	d = λ/2sinθ	$I/I_0 \times 100\%$
1.	21.7	0.1882	4.097	100.00
2.	26.4	0.2284	3.376	18.05
3.	37.6	0.3223	2.392	24.81
4.	43.6	0.3714	2.076	13.53
5.	58.7	0.4901	1.573	9.77

Table - 10

X-Ray diffraction data for $Cu_3[Cr(CN)_6]_2$

S.No.	2θ	Sinθ	d = λ/2sinθ	$I/I_0 \times 100\%$
1.	23.9	0.2071	3.723	15.38
2.	25.4	0.2200	3.504	38.46
3.	29.8	0.2571	2.999	100.00
4.	47.2	0.4003	1.926	23.08
5.	55.0	0.4617	1.670	35.38

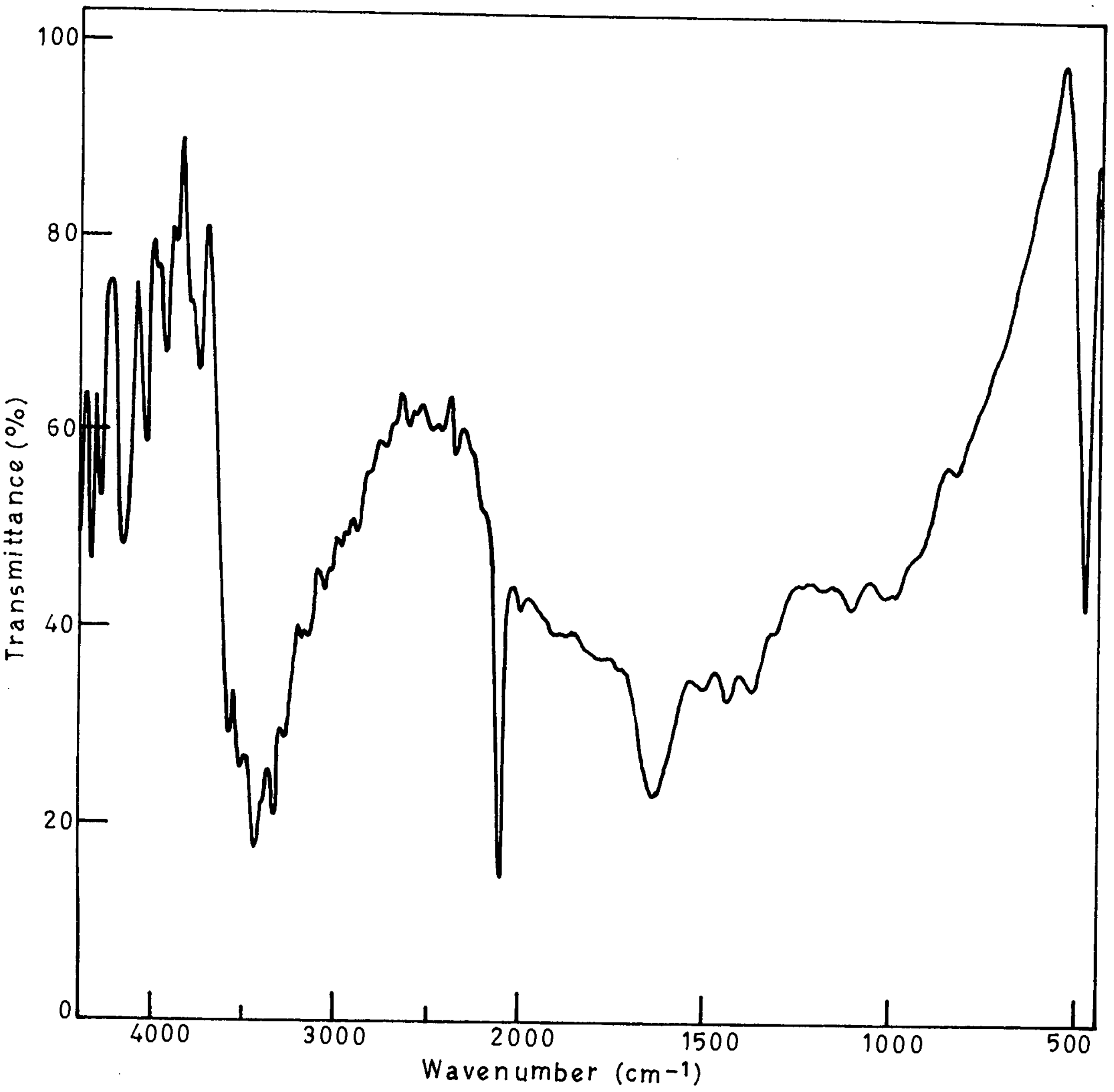


FIG.1 I.R. SPECTRUM OF POTASSIUM HEXACYANOMANGANATE(III)

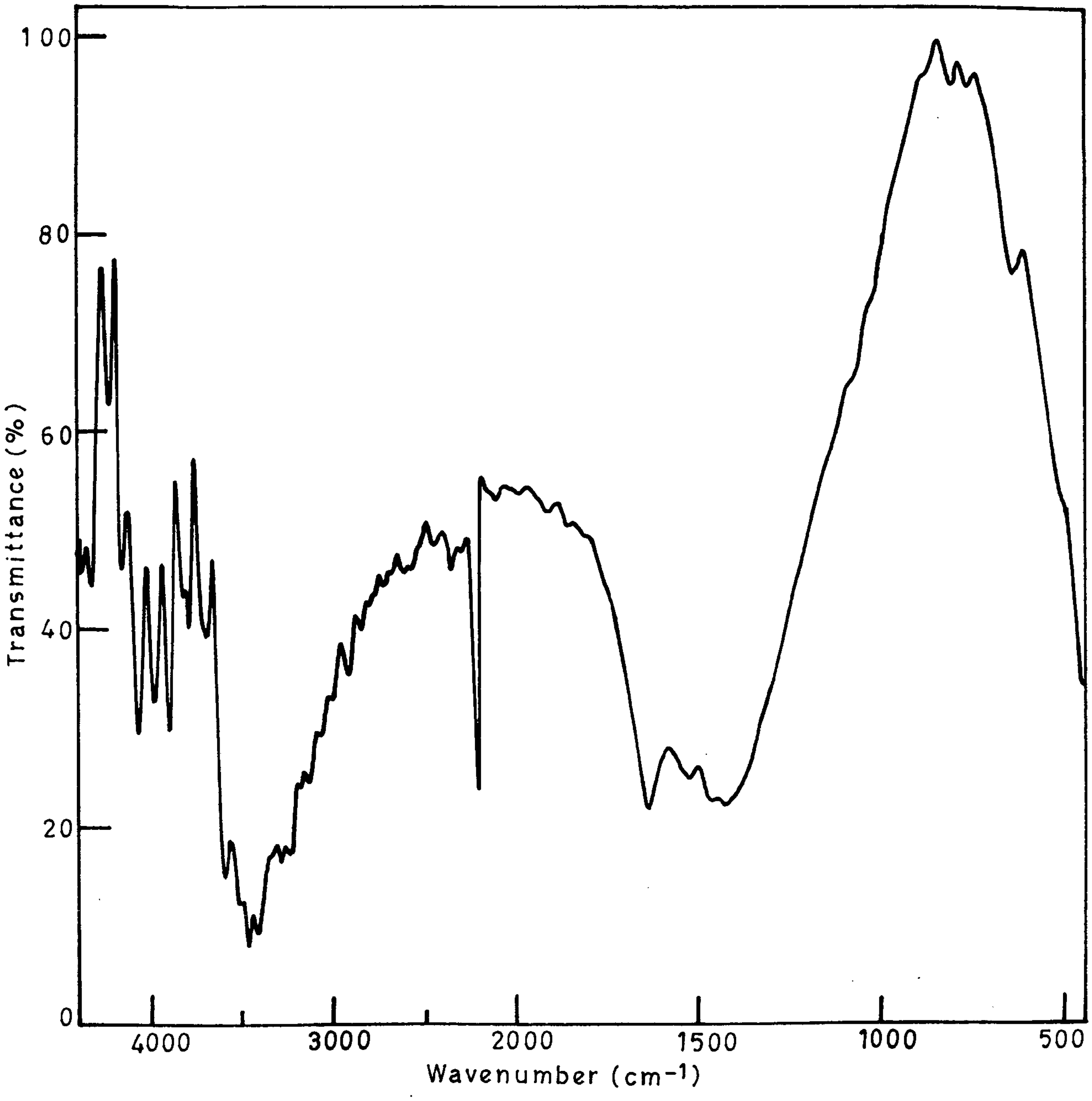


FIG.2 I.R. SPECTRUM OF ZINC HEXACYANOMANGANATE(III)

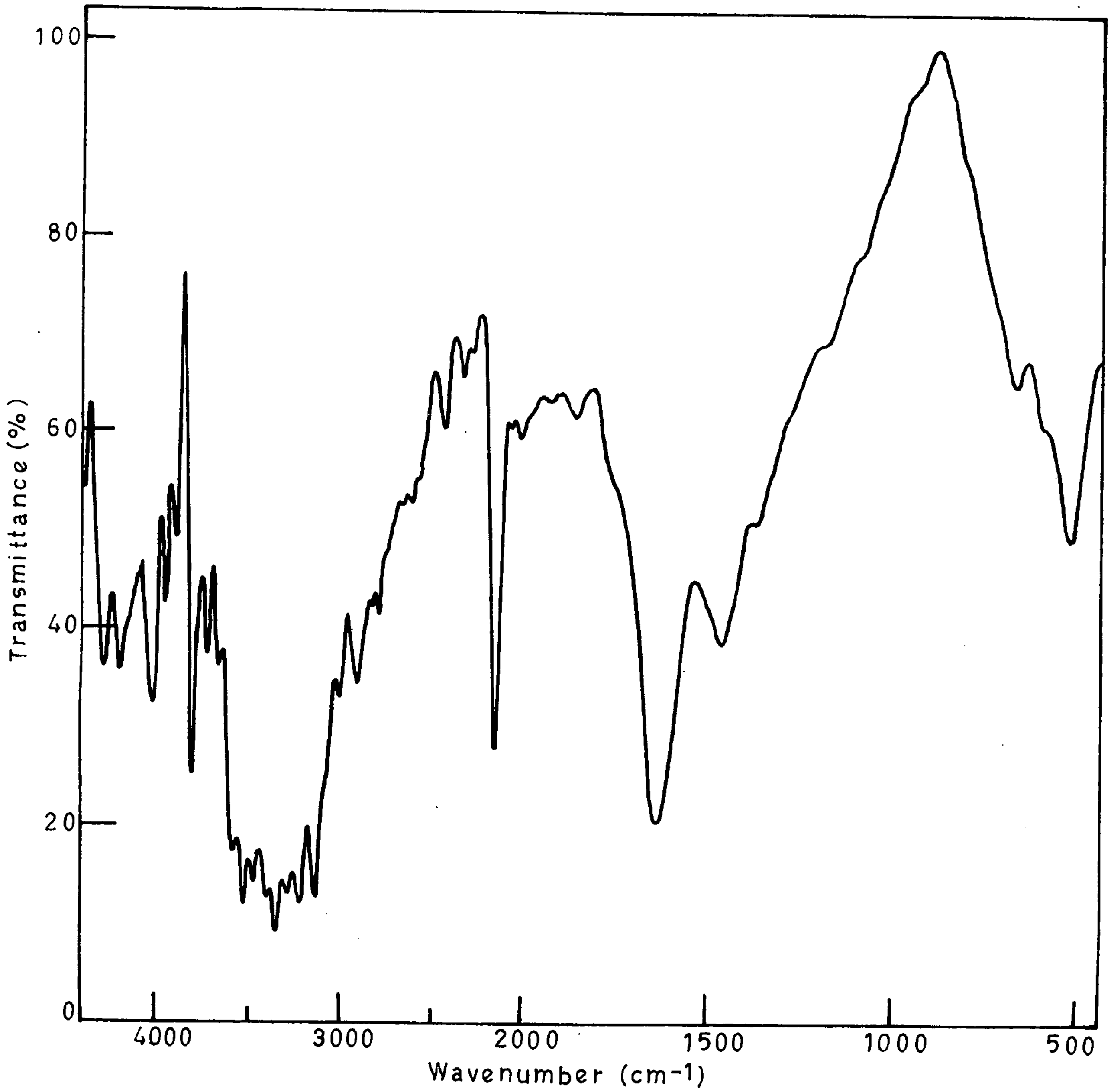


FIG.3 I.R. SPECTRUM OF COPPER HEXACYANOMANGANATE(III)

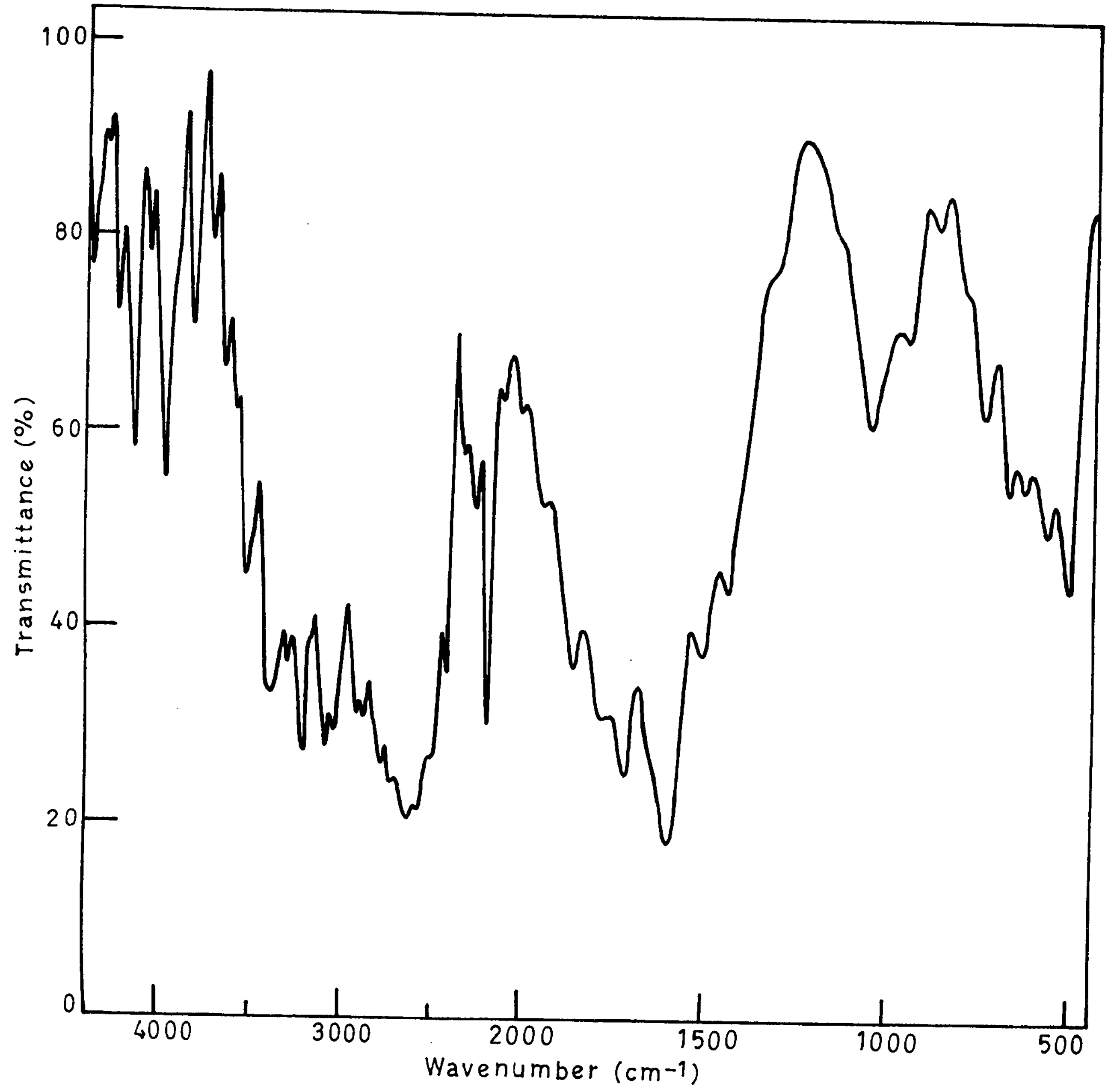


FIG.4 I.R. SPECTRUM OF COBALT HEXACYANOMANGANATE(III)

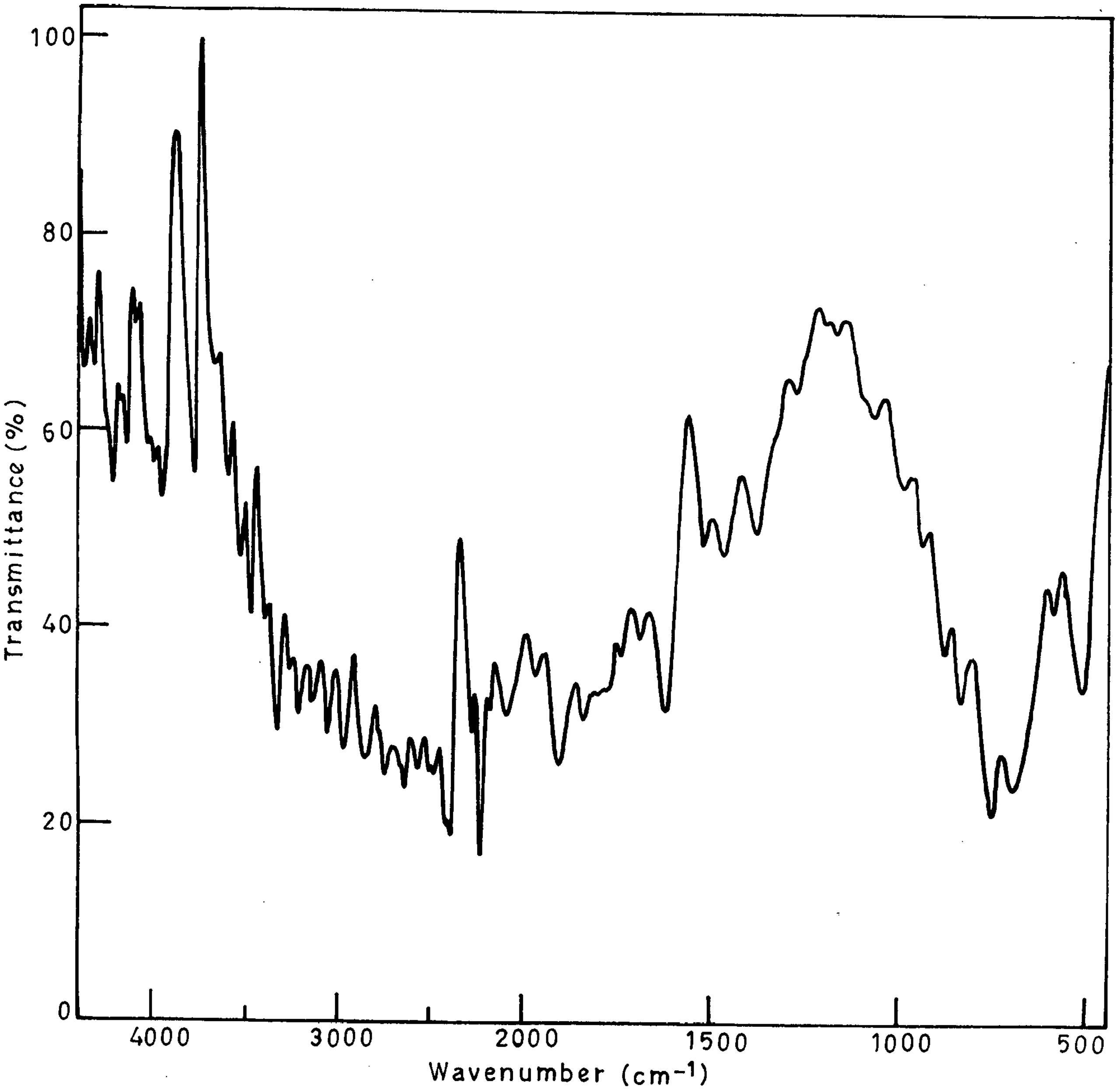


FIG.6 I.R. SPECTRUM OF ZINC HEXACYANOCHROMATE(III)

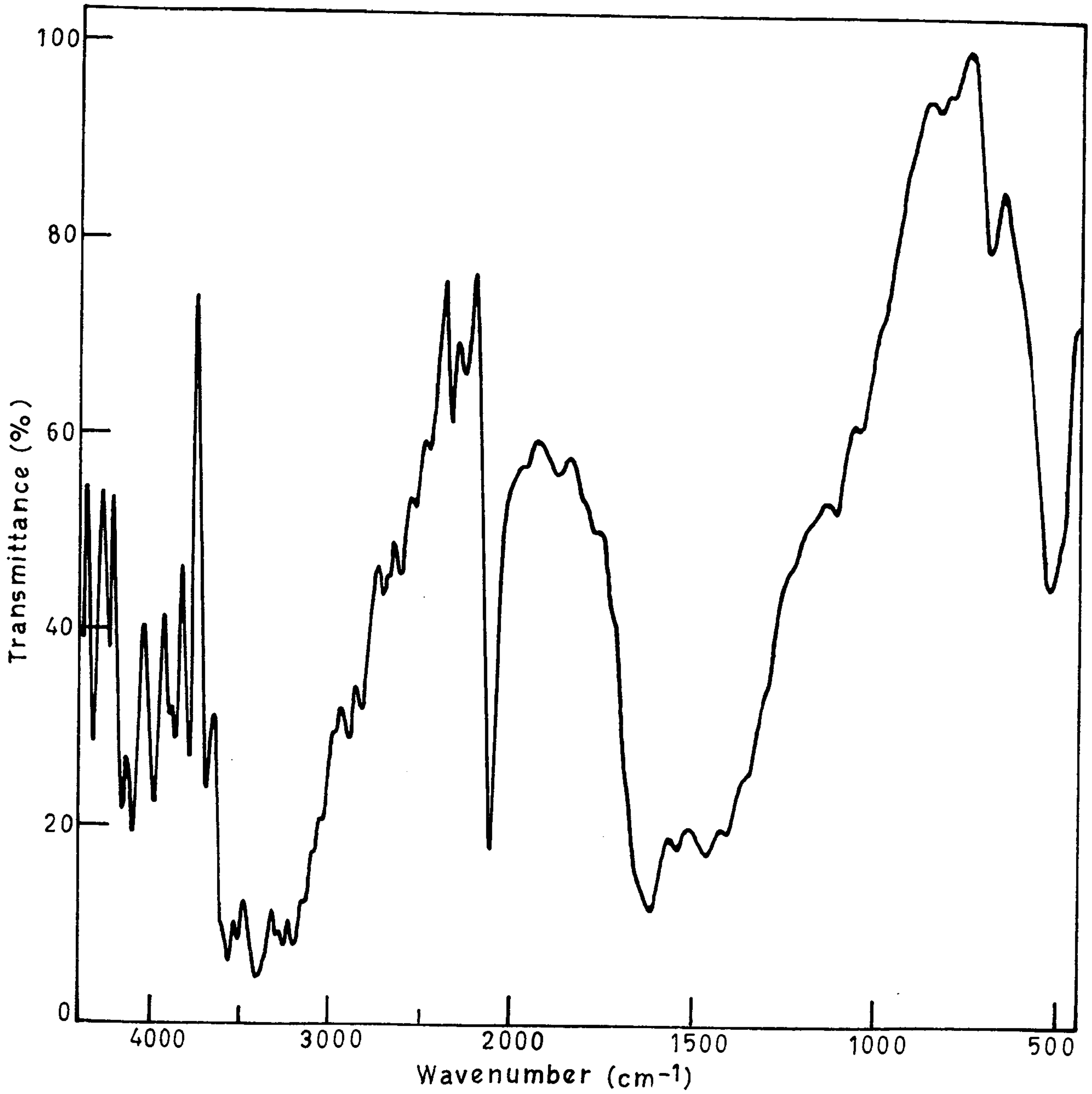


FIG.7 I.R. SPECTRUM OF COPPER HEXACYANOCHROMATE(III)

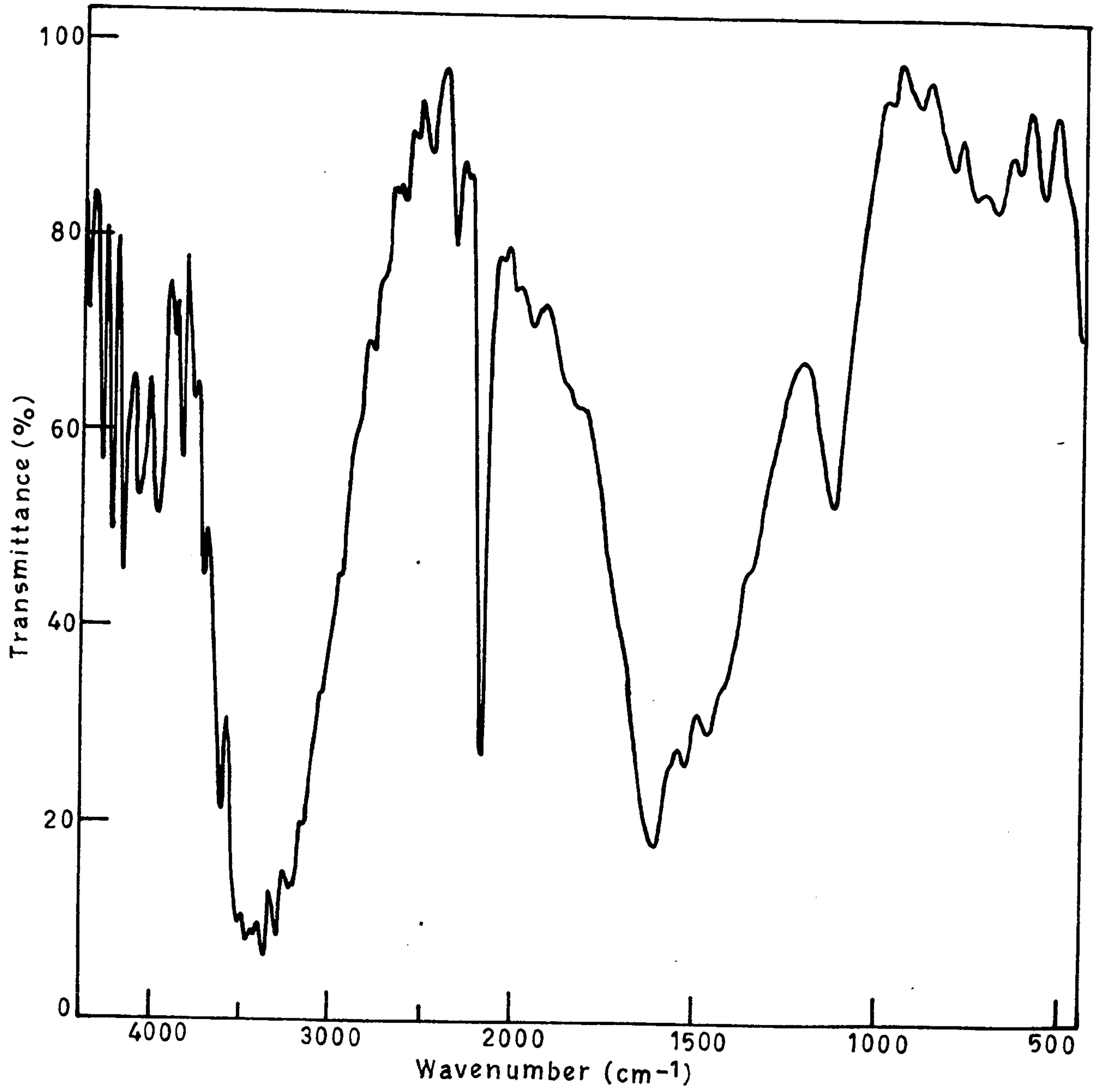


FIG.8 I.R. SPECTRUM OF COBALT HEXACYANOCHROMATE(III)

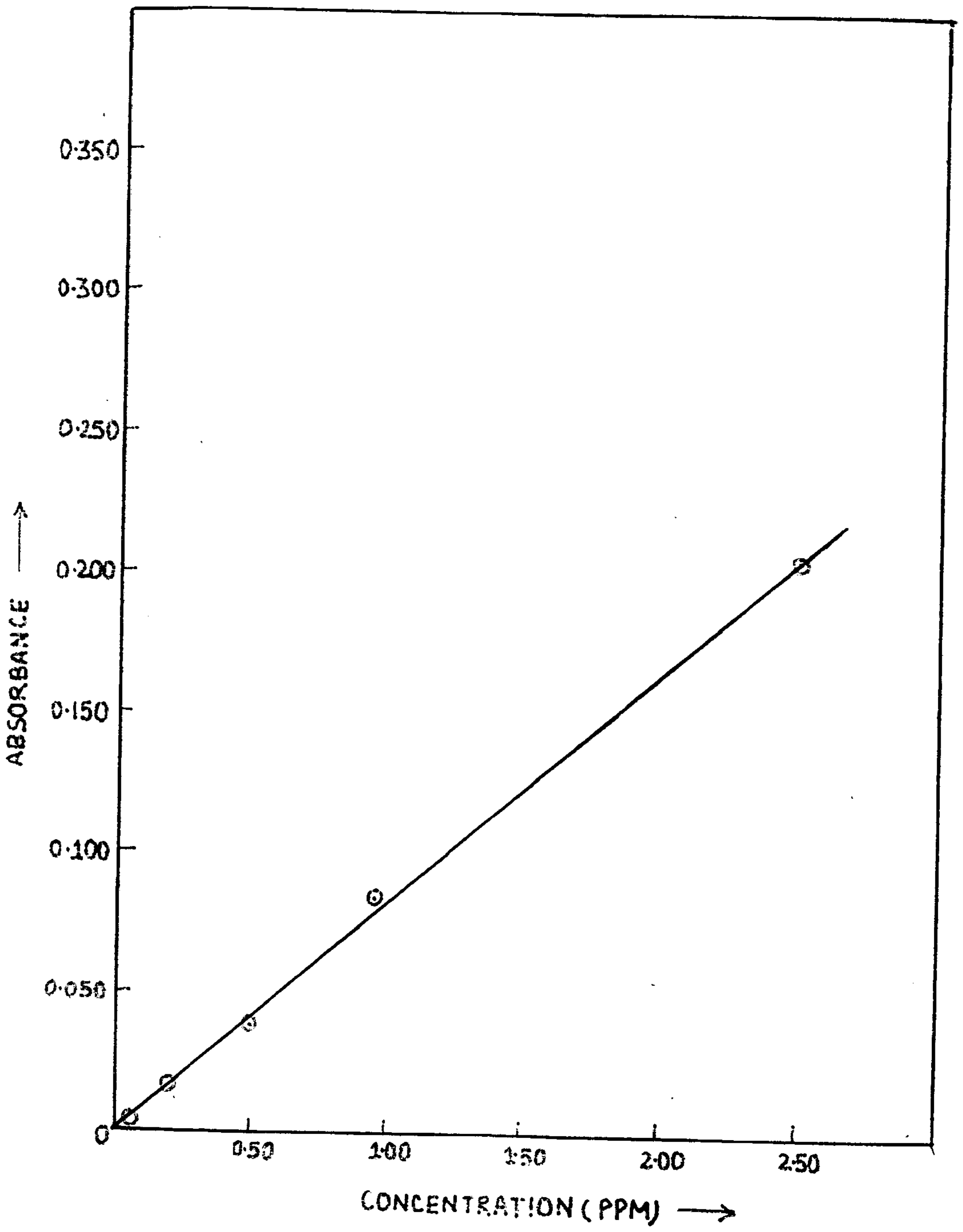


FIG.9 CALIBRATION CURVE FOR MANGANESE

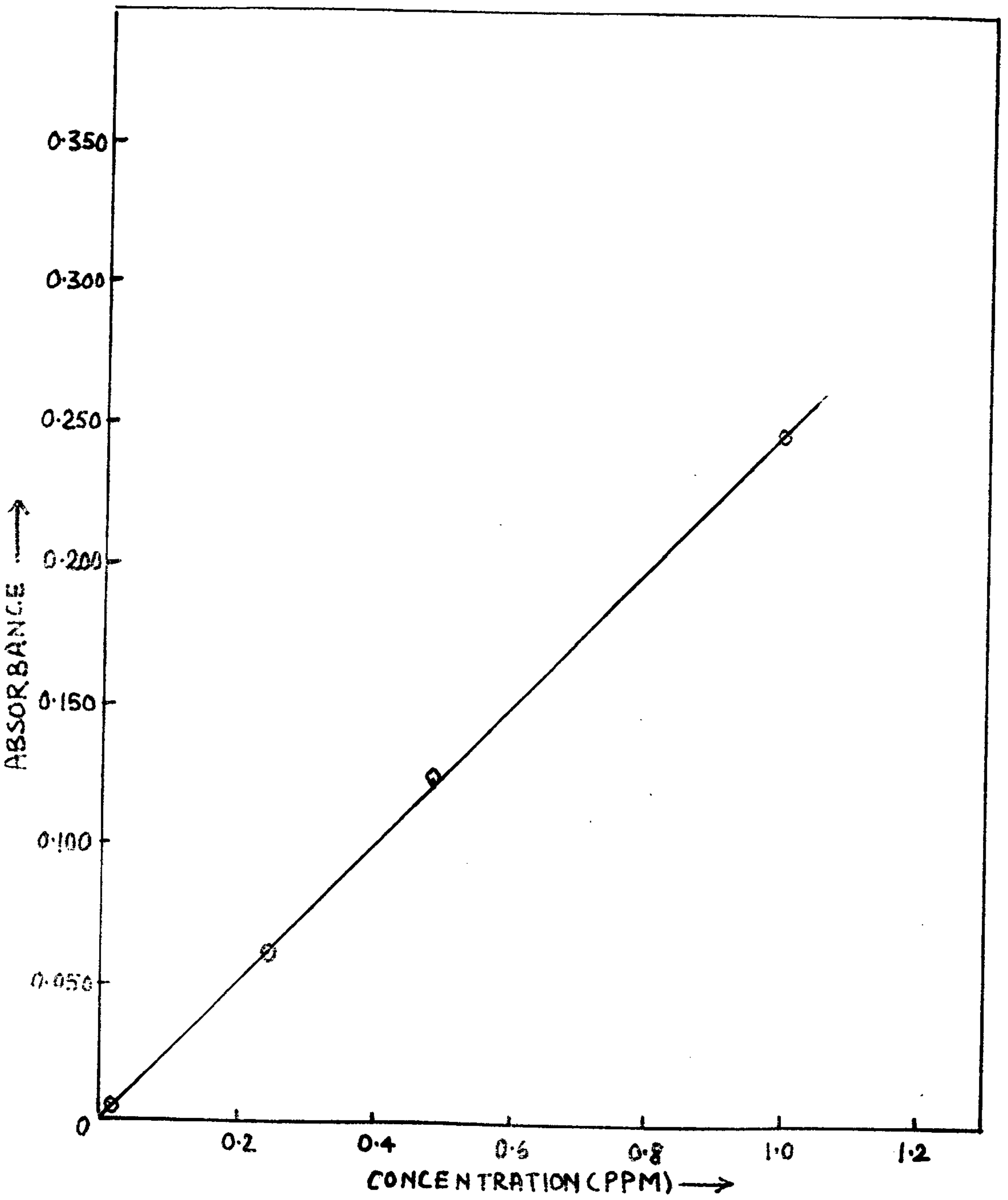


FIG.10 CALIBRATION CURVE FOR ZINC

247990

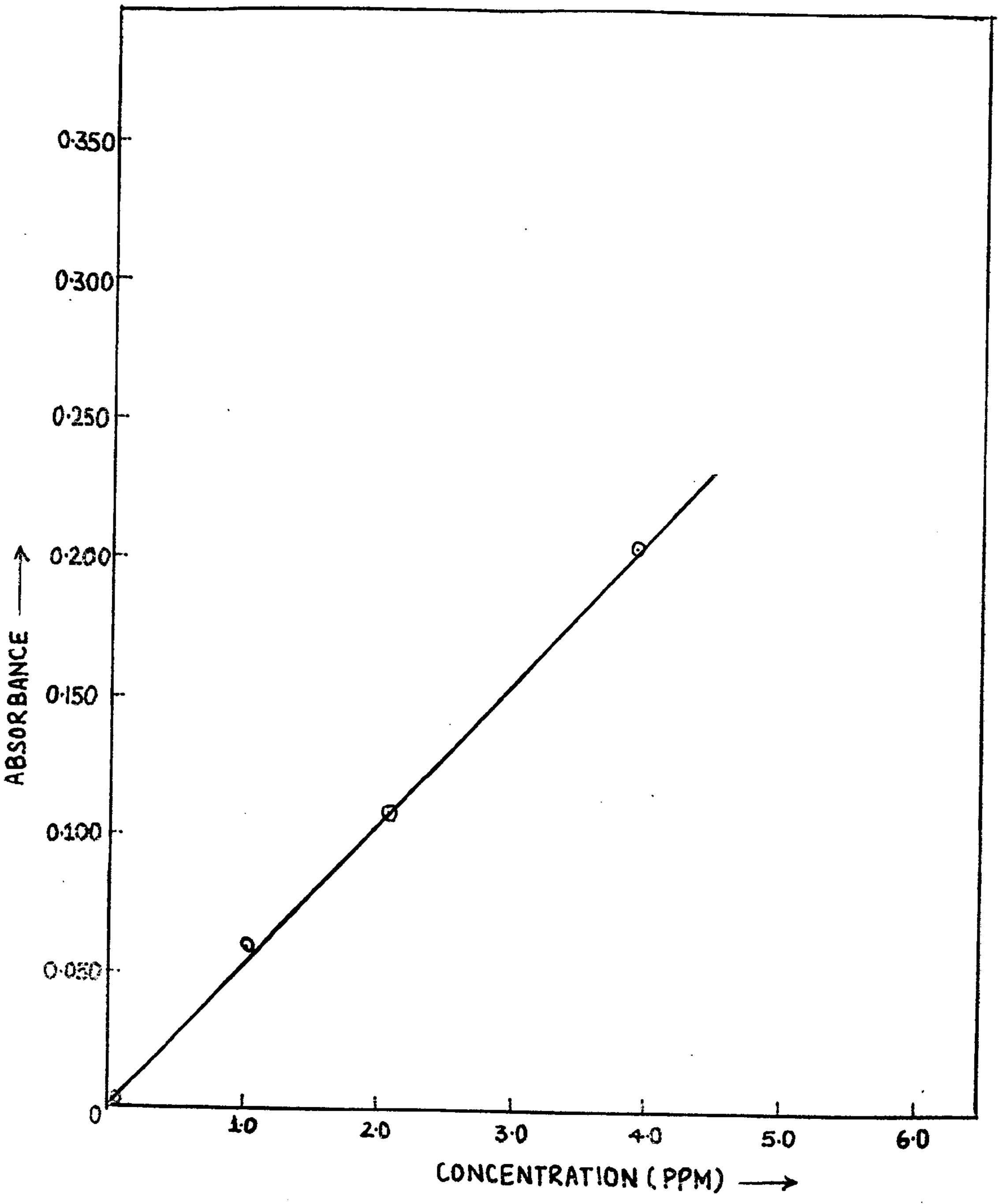


FIG.11 CALIBRATION CURVE FOR COPPER

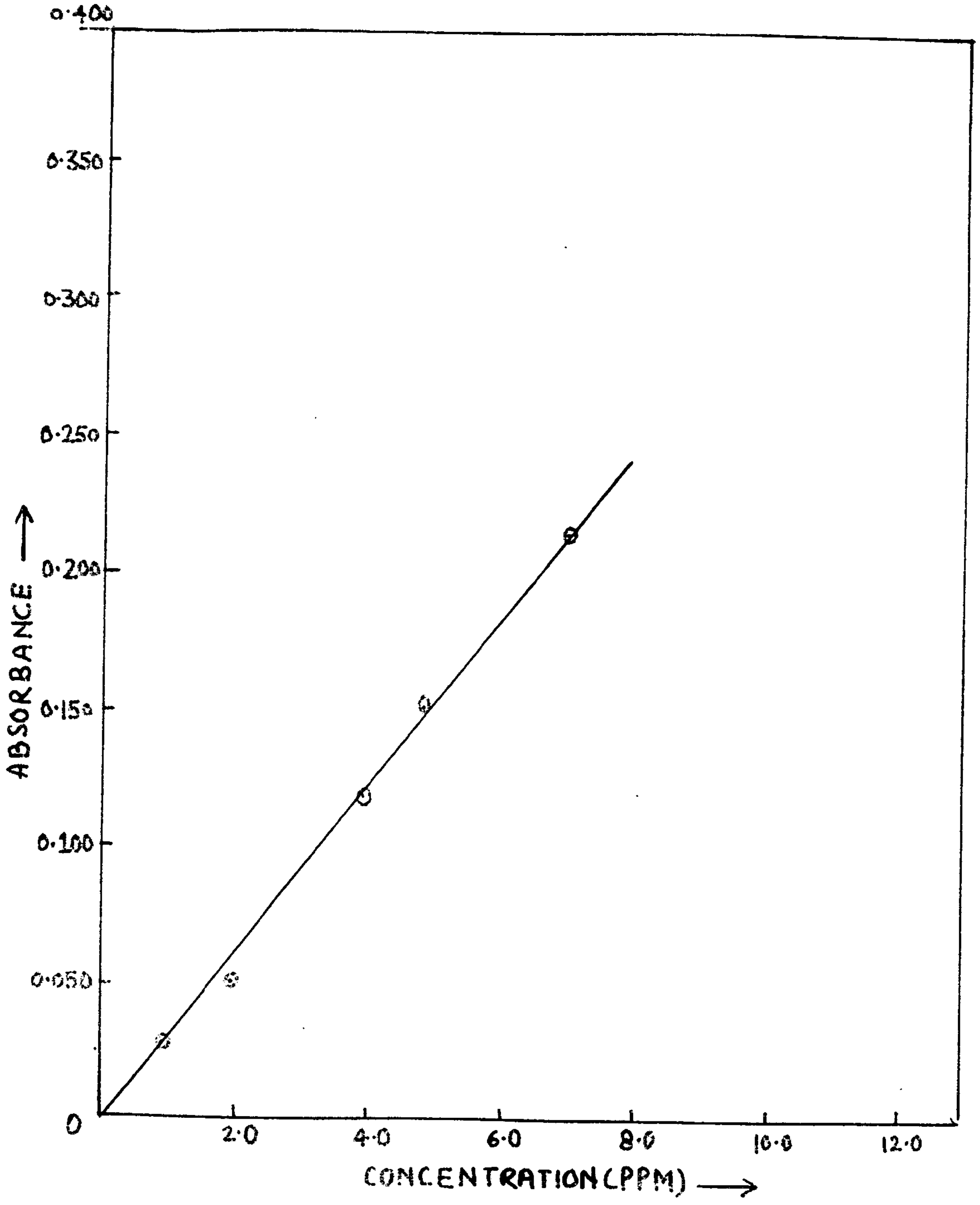


FIG.12 CALIBRATION CURVE FOR COBALT

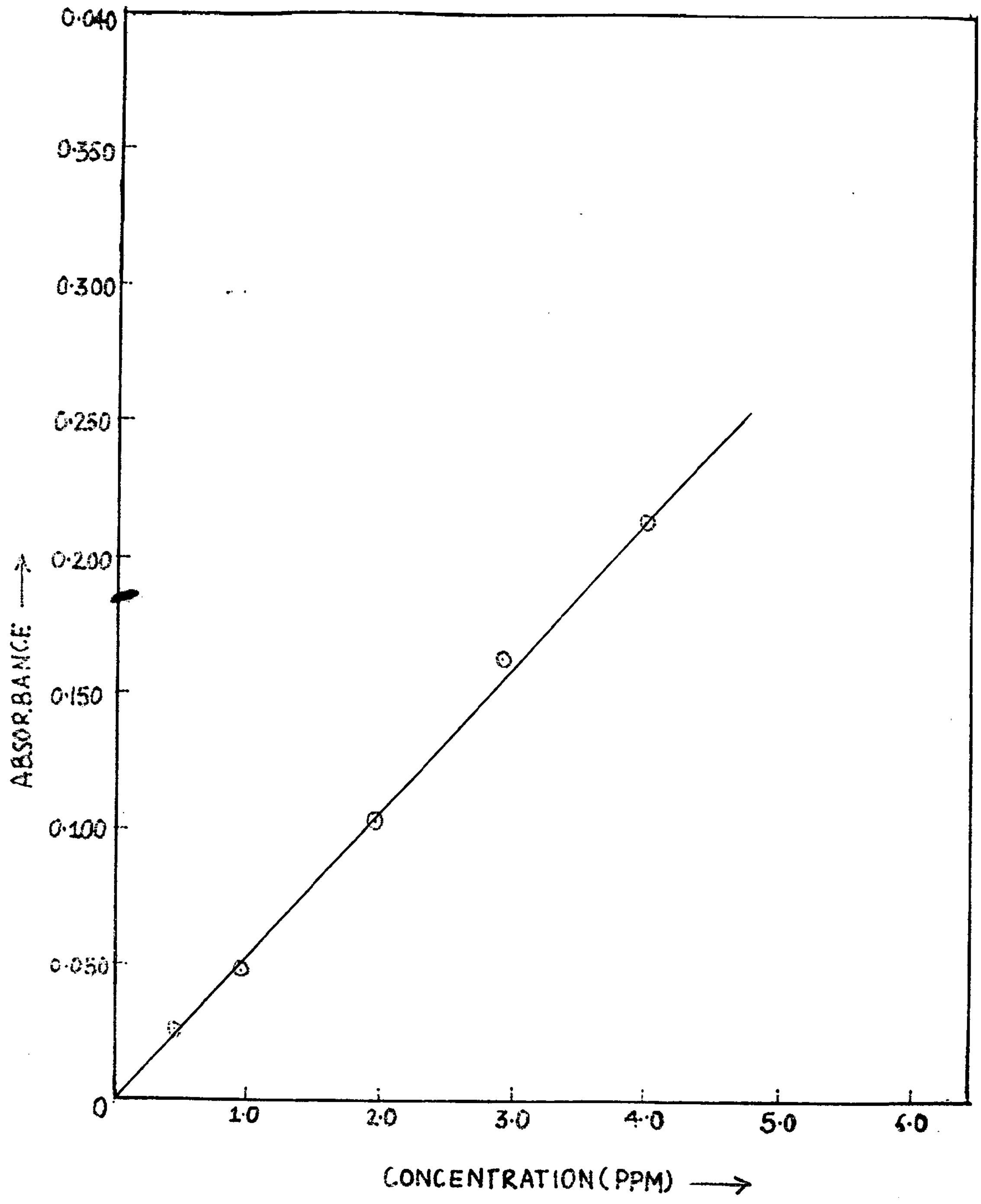
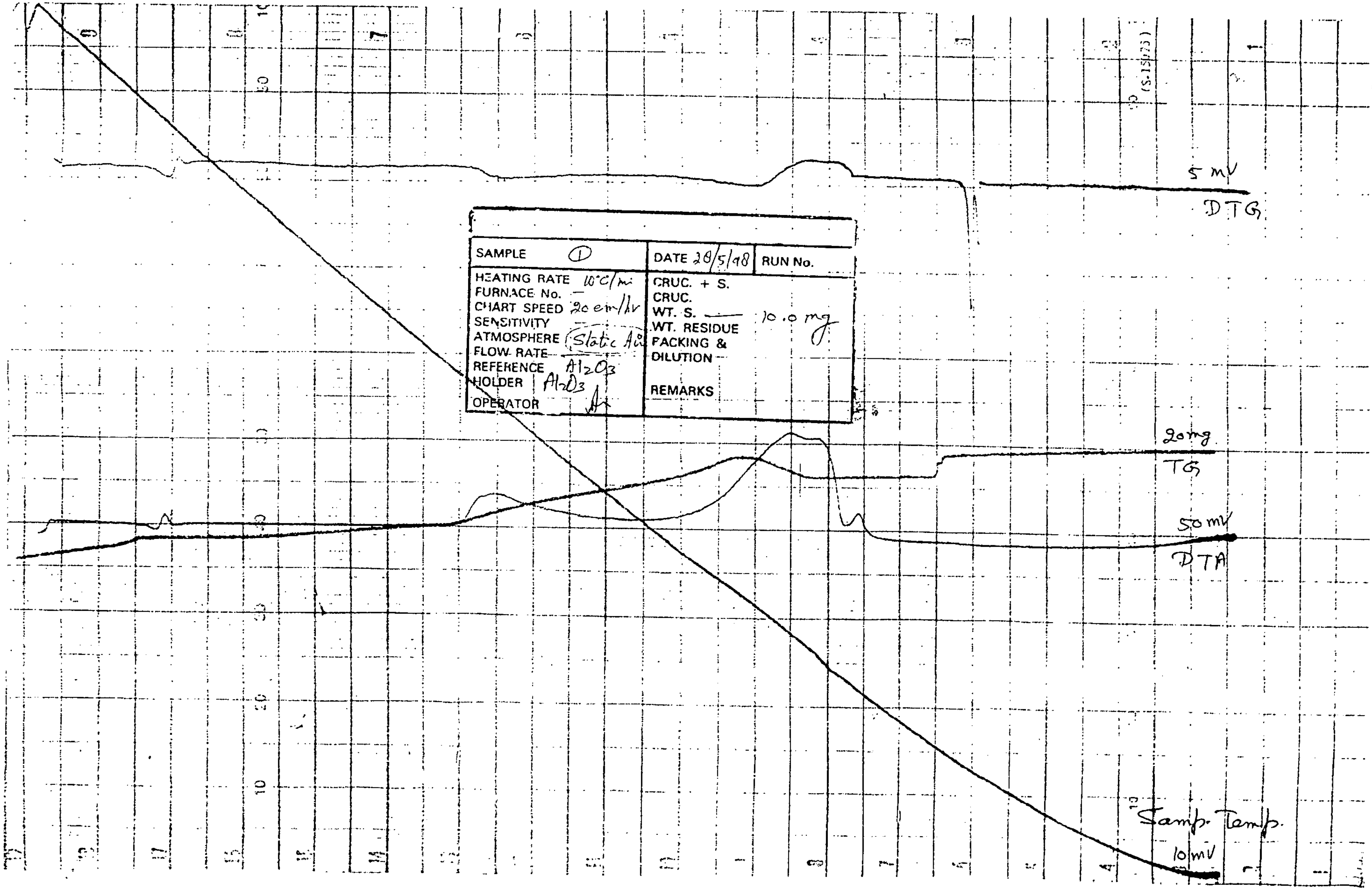
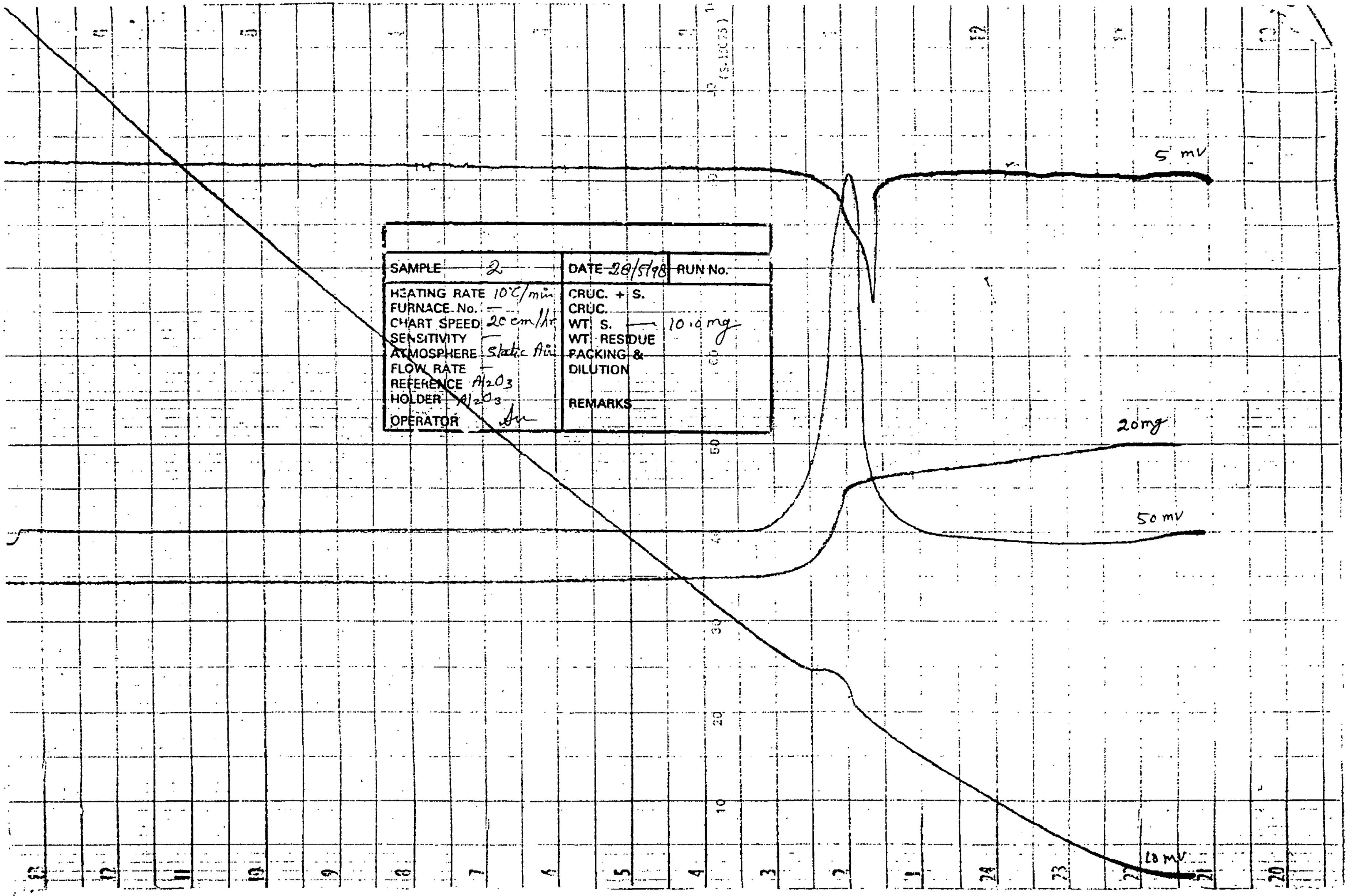


FIG. 13 CALIBRATION CURVE FOR CHROMIUM



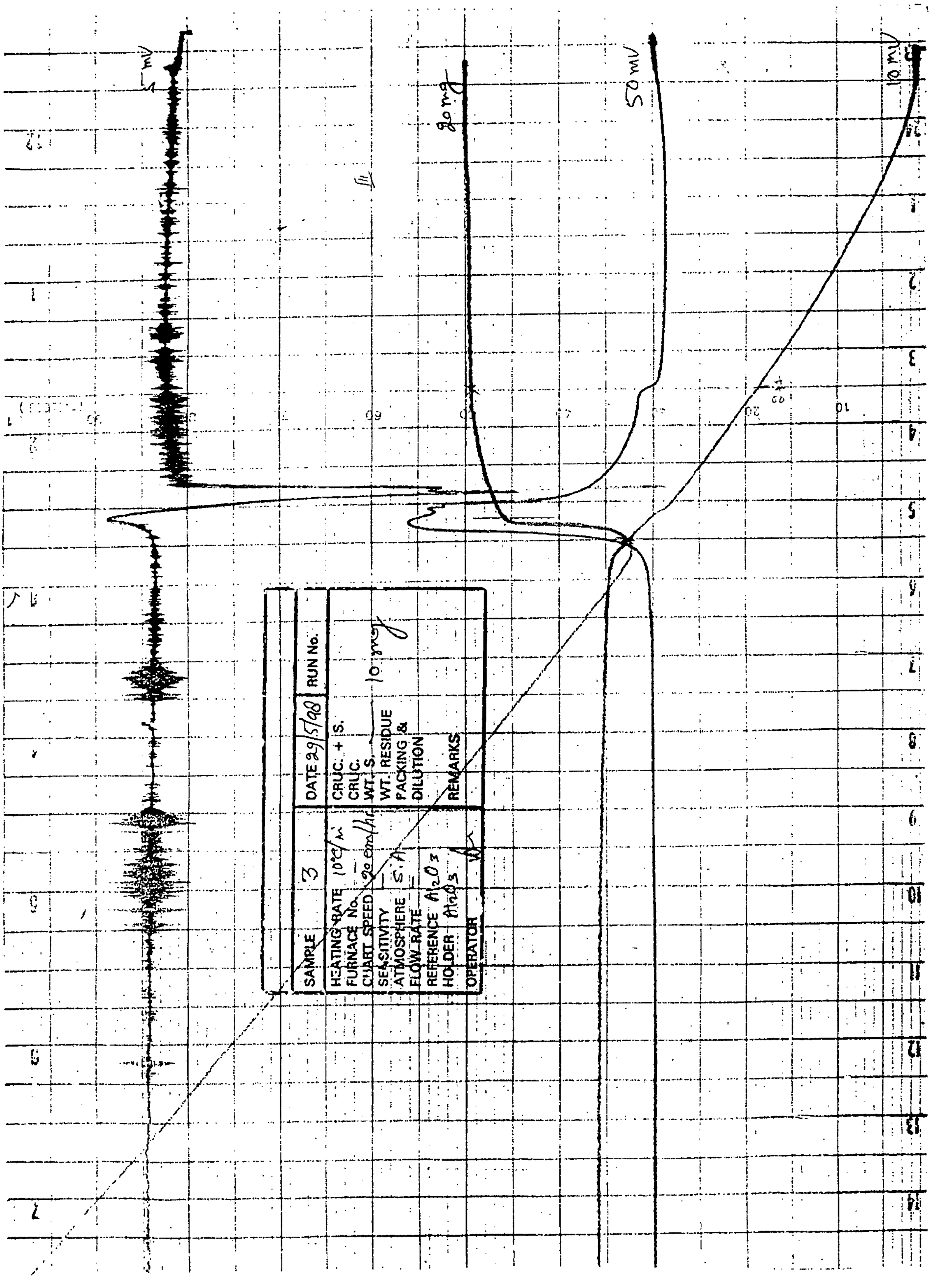
SAMPLE	①	DATE 28/5/98	RUN No.
HEATING RATE	10°C/mi	CRUC. + S.	
FURNACE No.	—	CRUC.	
CHART SPEED	20 cm/hr	WT. S. —	10.0 mg
SENSITIVITY	—	WT. RESIDUE	
ATMOSPHERE	Static Air	PACKING & DILUTION —	
FLOW RATE	—		
REFERENCE	Al_2O_3		
HOLDER	Al_2O_3	REMARKS	
OPERATOR			

FIG.14 THERMOGRAVIMETRIC PLOT FOR POTASSIUM HEXACYANOMANGANATE(III)



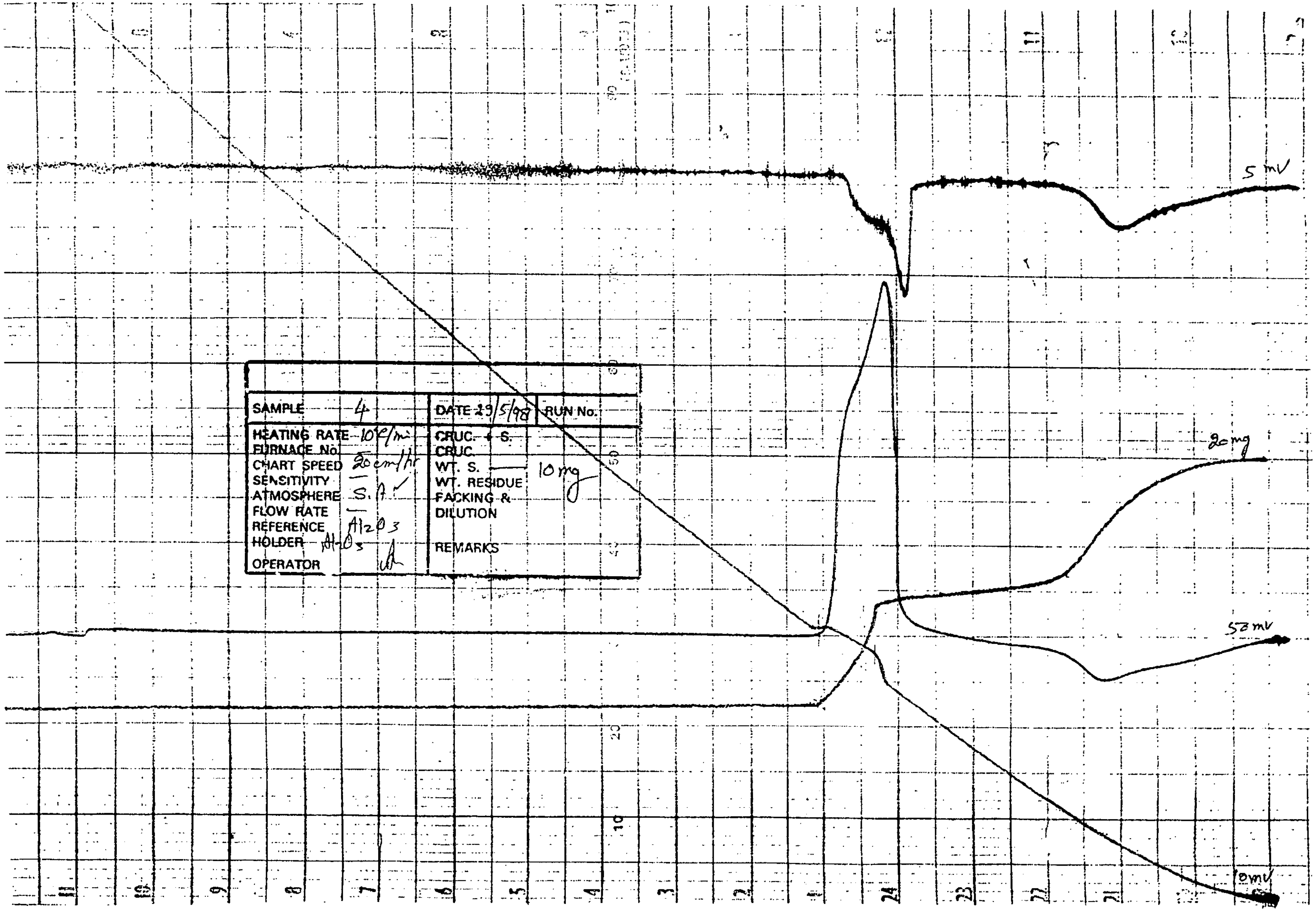
SAMPLE 2	DATE 20/5/98 RUN No.
HEATING RATE 10°C/min FURNACE. No. — CHART SPEED 20 cm/hr SENSITIVITY — ATMOSPHERE Static Air FLOW RATE — REFERENCE Al2O3 HOLDER Al2O3 OPERATOR	CRUC. + S. CRUC. WT. S. — 10.0 mg WT. RESIDUE PACKING & DILUTION REMARKS

FIG.15 THERMOGRAVIMETRIC PLOT FOR ZINC HEXACYANOMANGANATE(III)



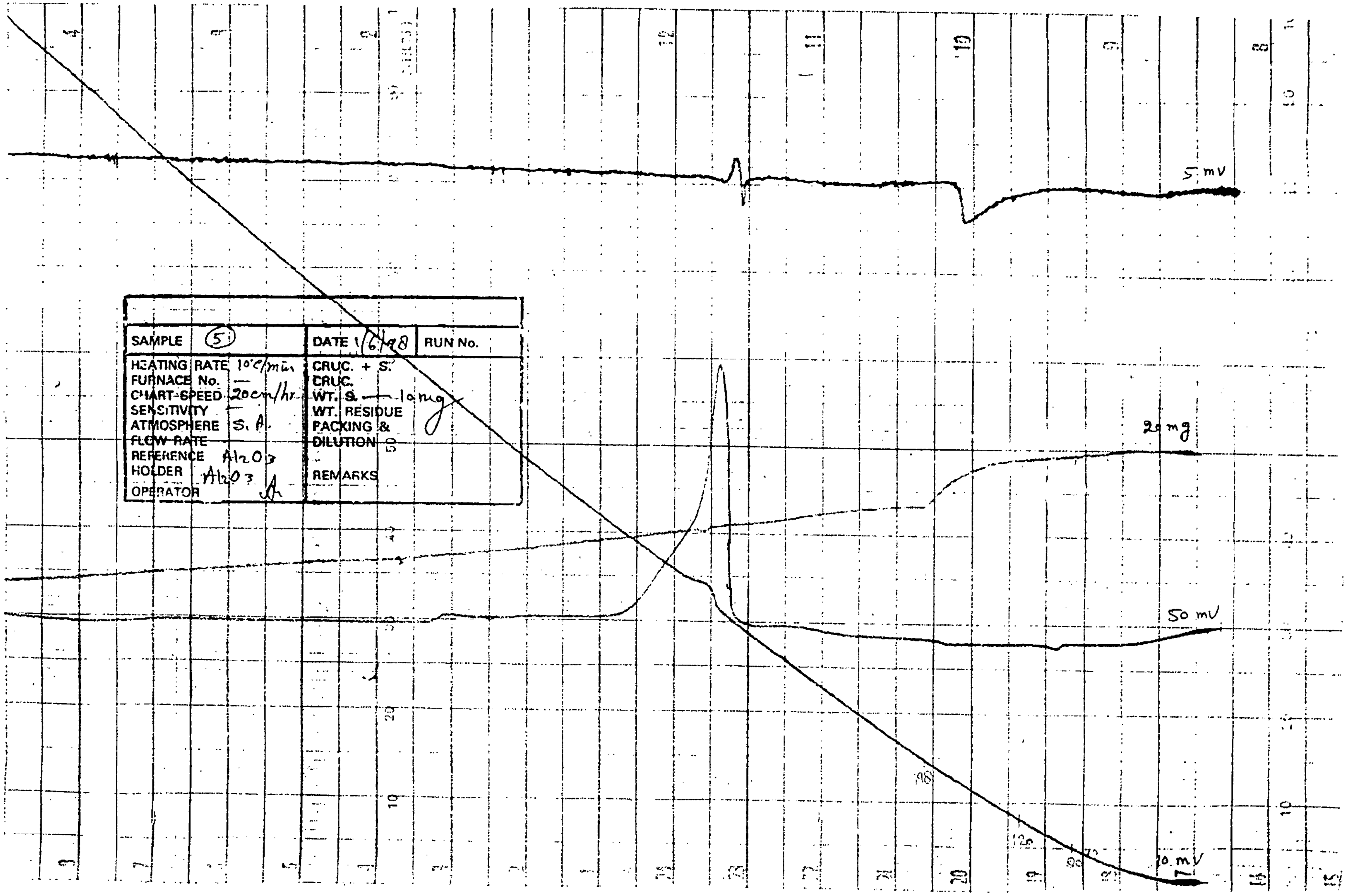
SAMPLE 3
DATE 29/5/98
RUN No.
HEATING RATE 10°C/mi
FURNACE No. —
CHART SPEED 20 cm/hr
SENSITIVITY —
ATMOSPHERE S.A
FLOW RATE —
REFERENCE Al_2O_3
HOLDER Al_2O_3
OPERATOR
CRUC. + S.
CRUC.
WT. S. 10 mg
WT. RESIDUE
PACKING & DILUTION
REMARKS

FIG.16 THERMOGRAVIMETRIC PLOT FOR COPPER HEXACYANOMANGANATE(III)



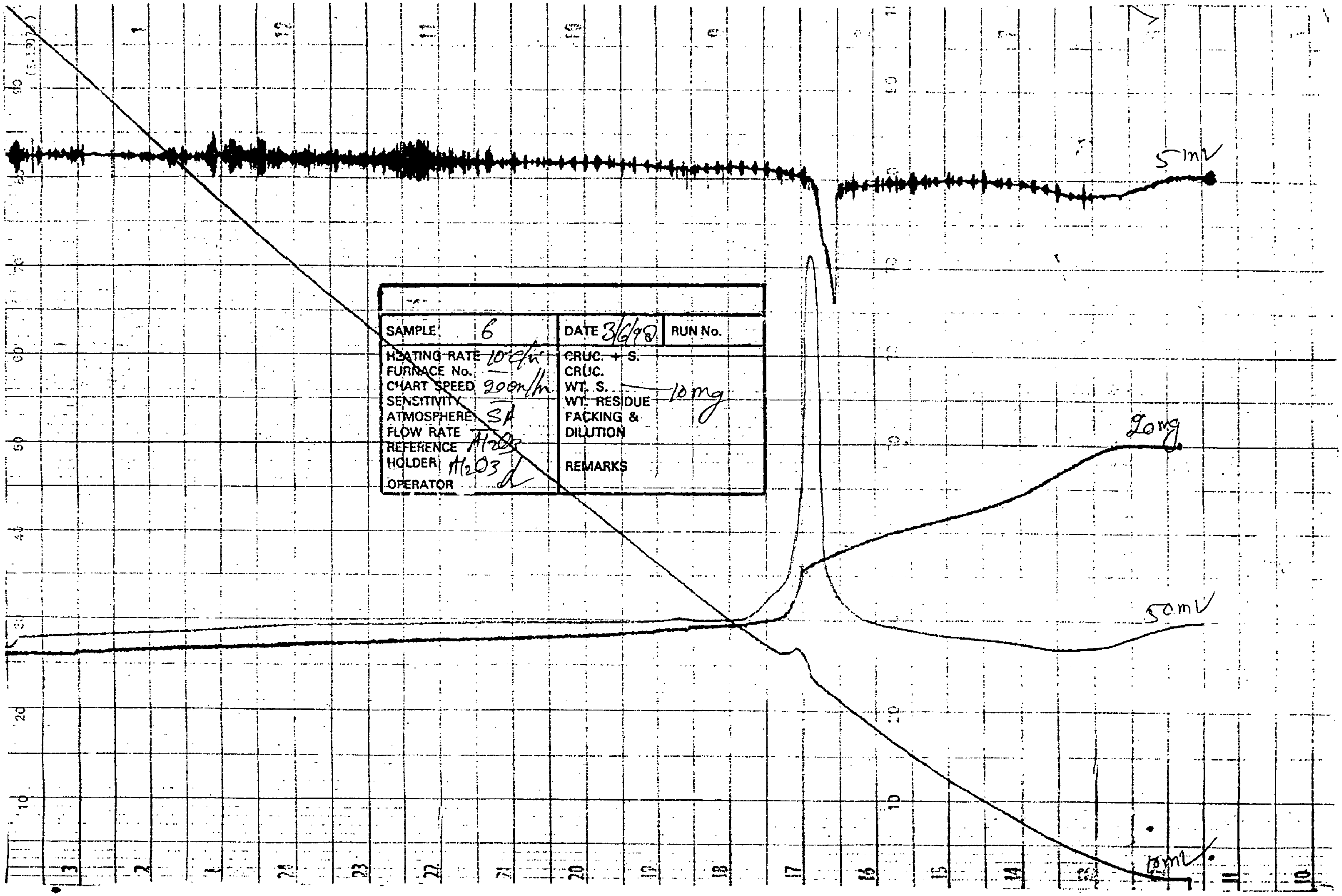
SAMPLE 4
DATE 29/5/98
RUN No.
HEATING RATE 10°/min
FURNACE No.
CHART SPEED 20cm/hr
SENSITIVITY —
ATMOSPHERE S.A.
FLOW RATE —
REFERENCE Al$_2$O$_3$
HOLDER Al$_2$O$_3$
OPERATOR
CRUC. + S.
CRUC.
WT. S. — 10mg
WT. RESIDUE
PACKING & DILUTION
REMARKS

FIG.17 THERMOGRAVIMETRIC PLOT FOR COBALT HEXACYANOMANGANATE(III)



SAMPLE (5)
DATE 1/6/98
RUN No.
HEATING RATE 10°C/min
FURNACE No. —
CHART-SPEED 20cm/hr.
SENSITIVITY —
ATMOSPHERE S. A.
FLOW RATE
REFERENCE Al_2O_3
HOLDER Al_2O_3
OPERATOR A
CRUC. + S.
CRUC.
WT. S. — 10mg
WT. RESIDUE
PACKING &
DILUTION
REMARKS

FIG.18 THERMOGRAVIMETRIC PLOT FOR POTASSIUM HEXACYANOCHROMATE(III)



SAMPLE 6

DATE 3/6/98

RUN No.

HEATING RATE 10°C/m

FURNACE No.

CHART SPEED 200m/h

SENSITIVITY

ATMOSPHERE SA

FLOW RATE

REFERENCE Al_2O_3

HOLDER Al_2O_3

OPERATOR

CRUC. + S.

CRUC.

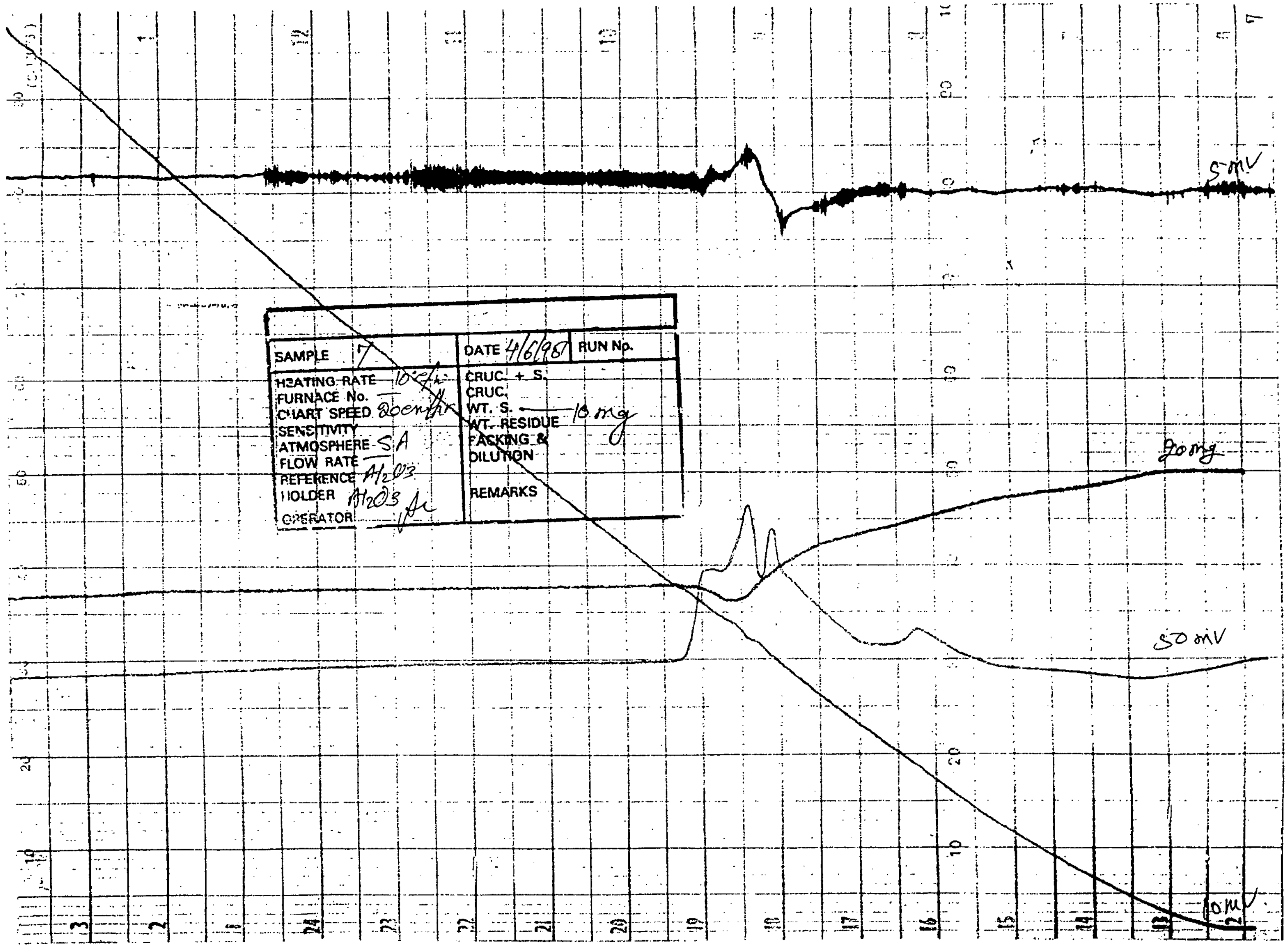
WT. S. 10mg

WT. RESIDUE

FACKING & DILUTION

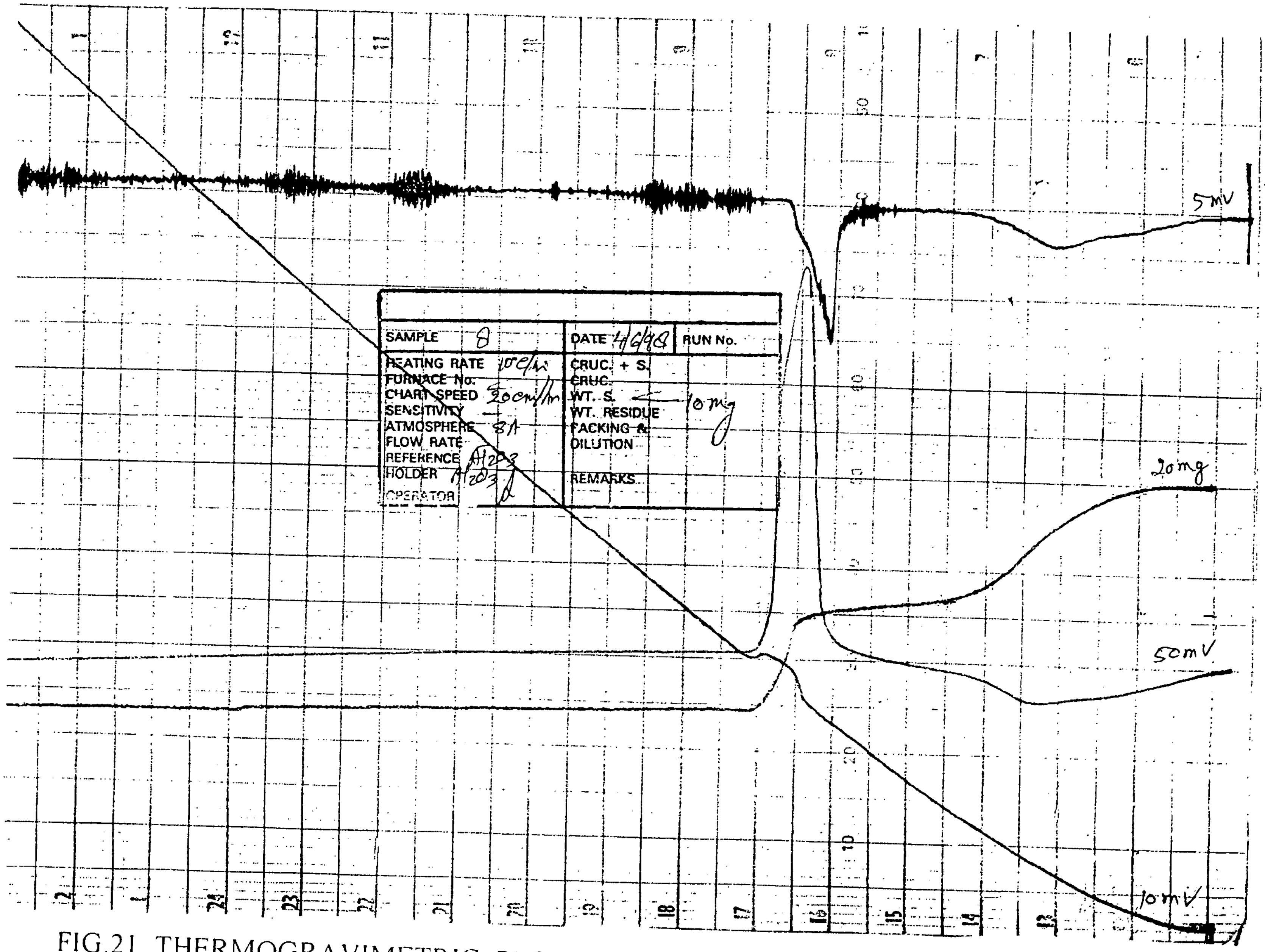
REMARKS

FIG.19 THERMOGRAVIMETRIC PLOT FOR ZINC HEXACYANOCHROMATE(III)



SAMPLE 7
DATE 4/6/98
RUN No.
HEATING RATE 10°C/m
FURNACE No. —
CHART SPEED 20cm/hr
SENSITIVITY
ATMOSPHERE SA
FLOW RATE —
REFERENCE Al_2O_3
HOLDER Al_2O_3
OPERATOR
CRUC. + S.
CRUC.
WT. S. — 10 mg
WT. RESIDUE
PACKING & DILUTION
REMARKS

FIG.20 THERMOGRAVIMETRIC PLOT FOR COPPER HEXACYANOCHROMATE(III)



SAMPLE 8

DATE 4/6/98

RUN No.

HEATING RATE 10°C/mi

FURNACE No.

CHART SPEED 20cm/hr

SENSITIVITY —

ATMOSPHERE 81

FLOW RATE

REFERENCE Al_2O_3

HOLDER Al_2O_3

OPERATOR d

CRUC. + S.

CRUC.

WT. S. 10 mg

WT. RESIDUE

PACKING & DILUTION

REMARKS

FIG.21 THERMOGRAVIMETRIC PLOT FOR COBALT HEXACYANOCHROMATE(III)

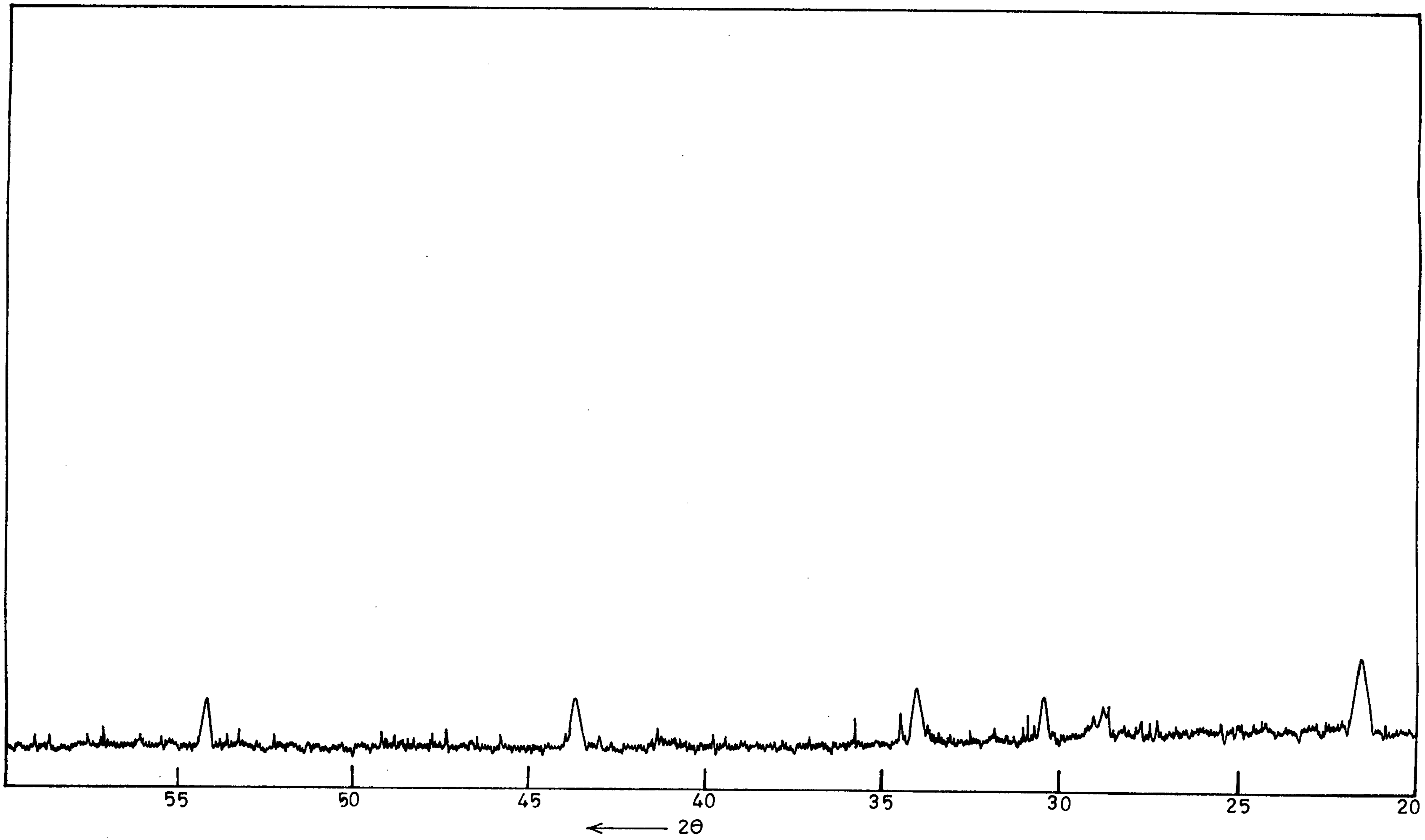


FIG.22 X-RAY DIFFRACTOGRAM FOR POTASSIUM HEXACYANOMANGANATE(III)

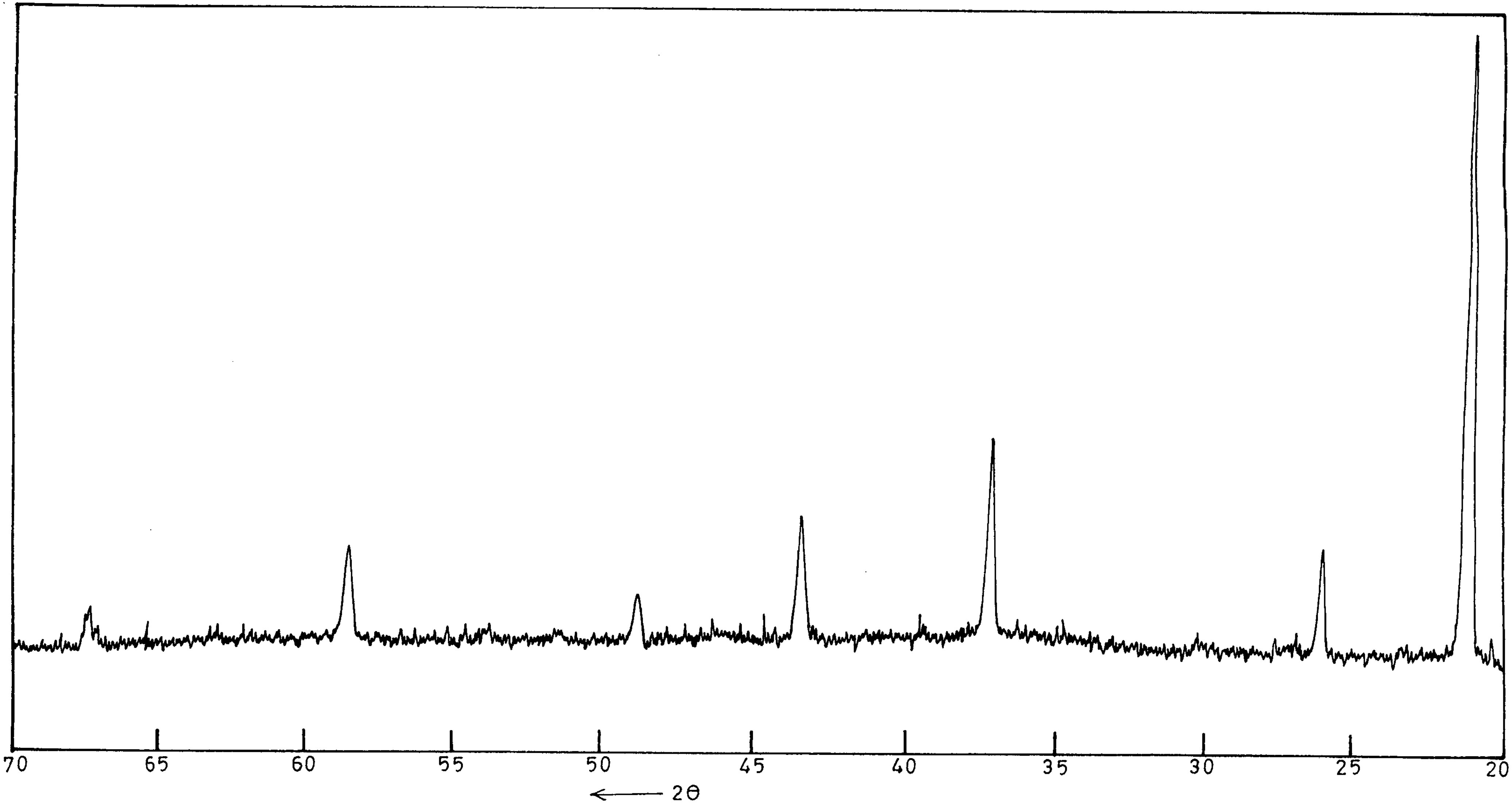


FIG.23 X-RAY DIFFRACTOGRAM FOR ZINC HEXACYANOMANGANATE(III)

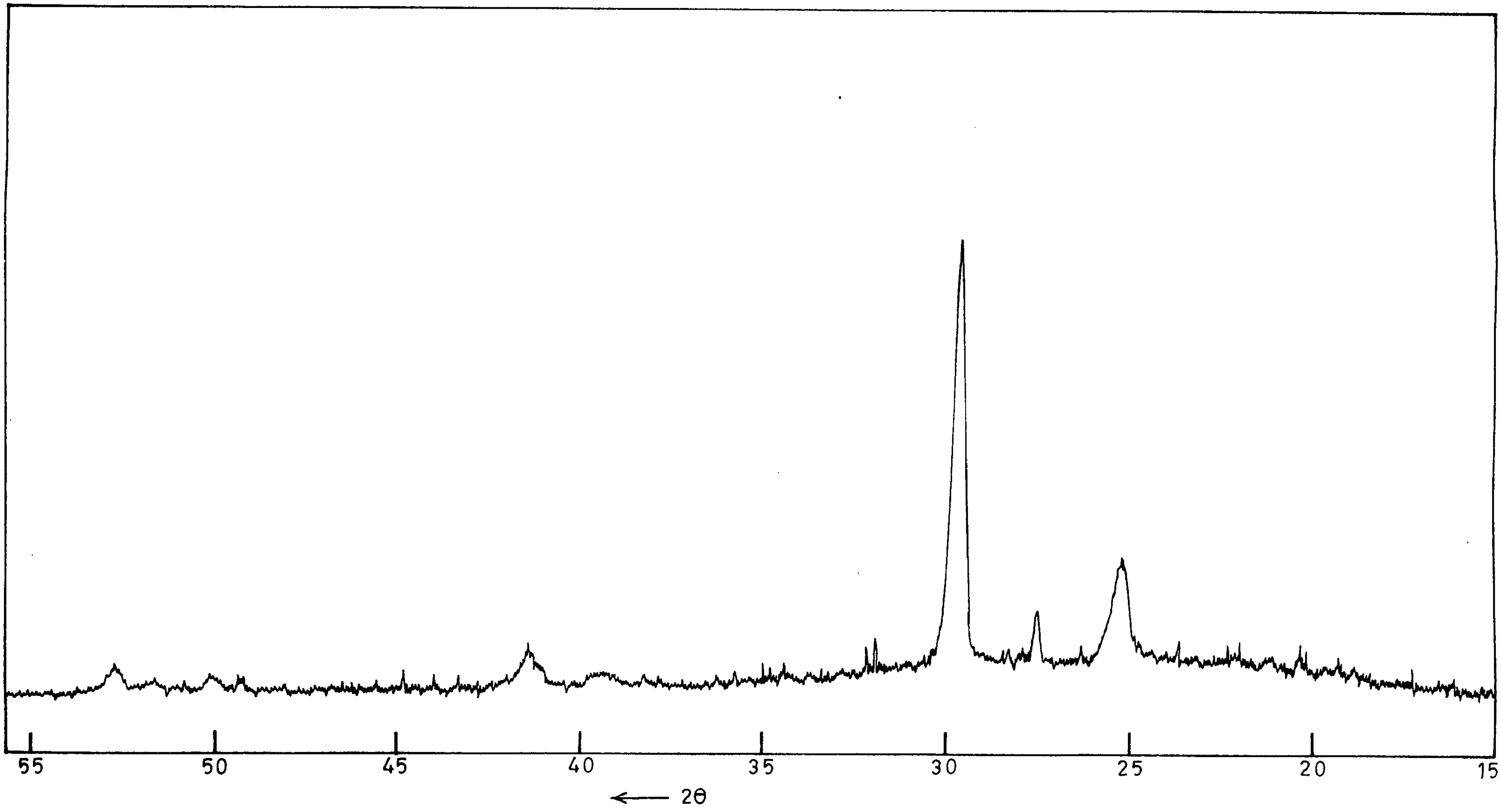


FIG.24 X-RAY DIFFRACTOGRAM FOR COPPER HEXACYANOMANGANATE(III)

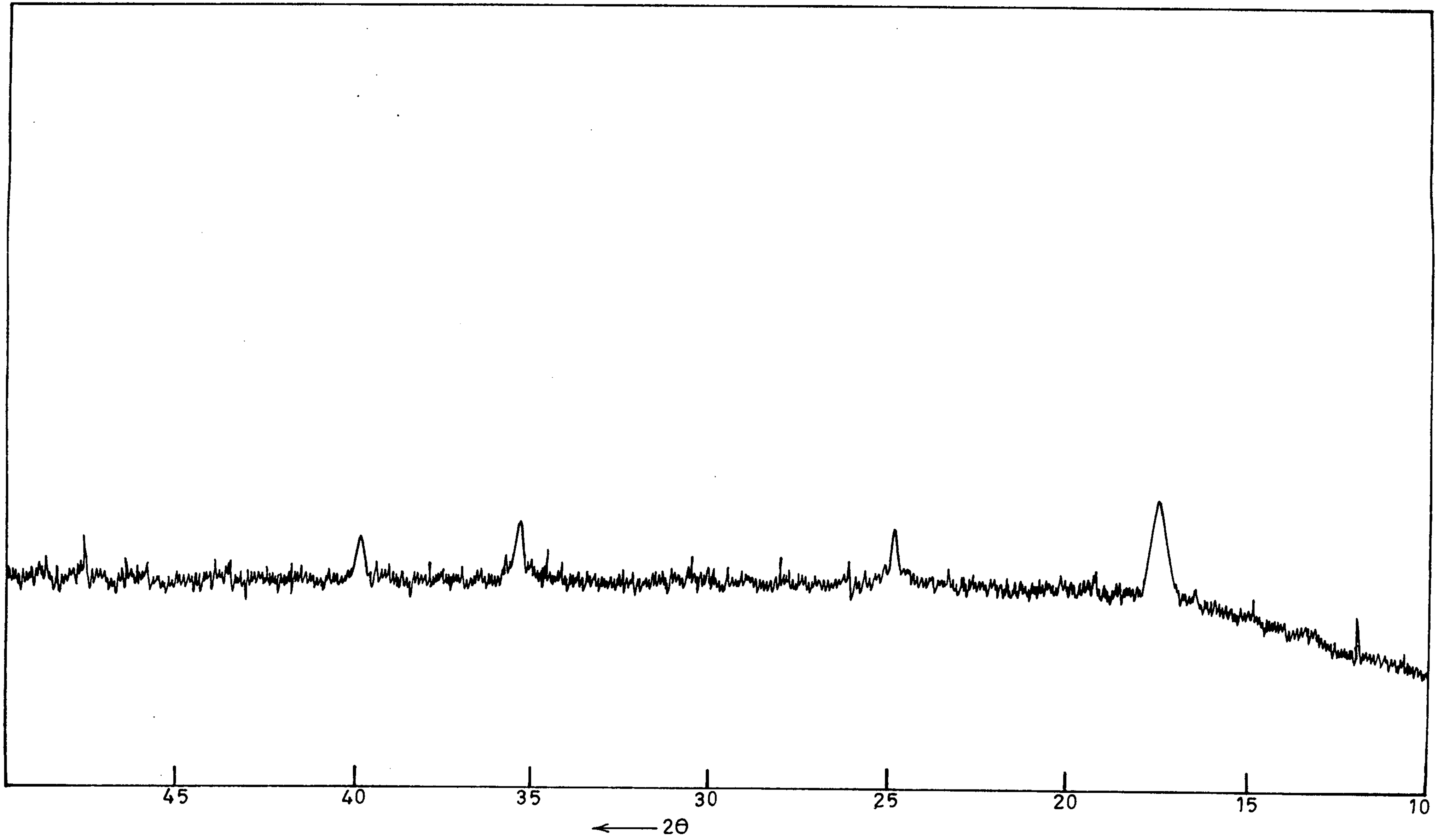


FIG.25 X-RAY DIFFRACTOGRAM FOR COBALT HEXACYANOMANGANATE(III)

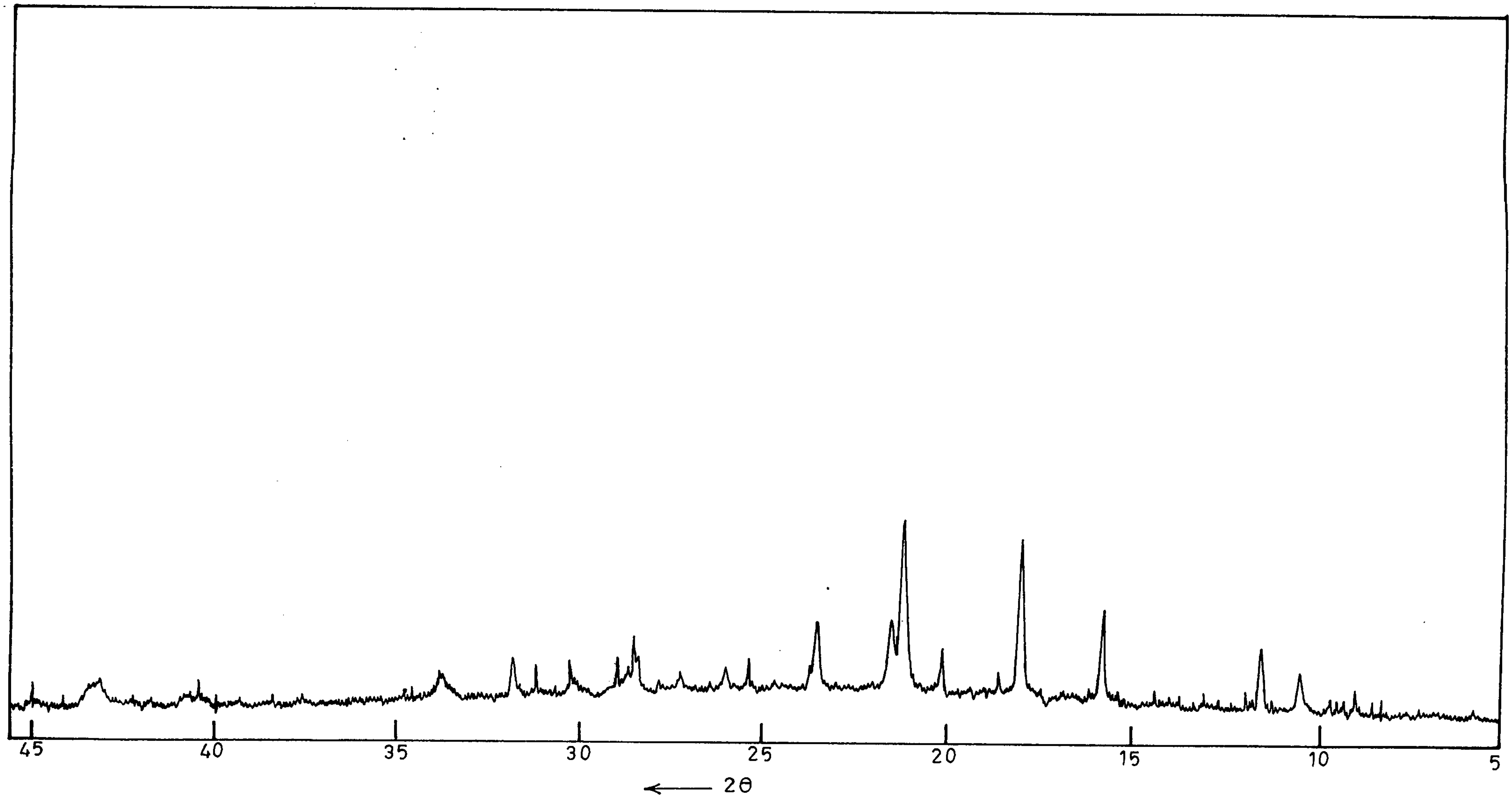


FIG.26 X-RAY DIFFRACTOGRAM FOR POTASSIUM HEXACYANOCHROMATE(III)

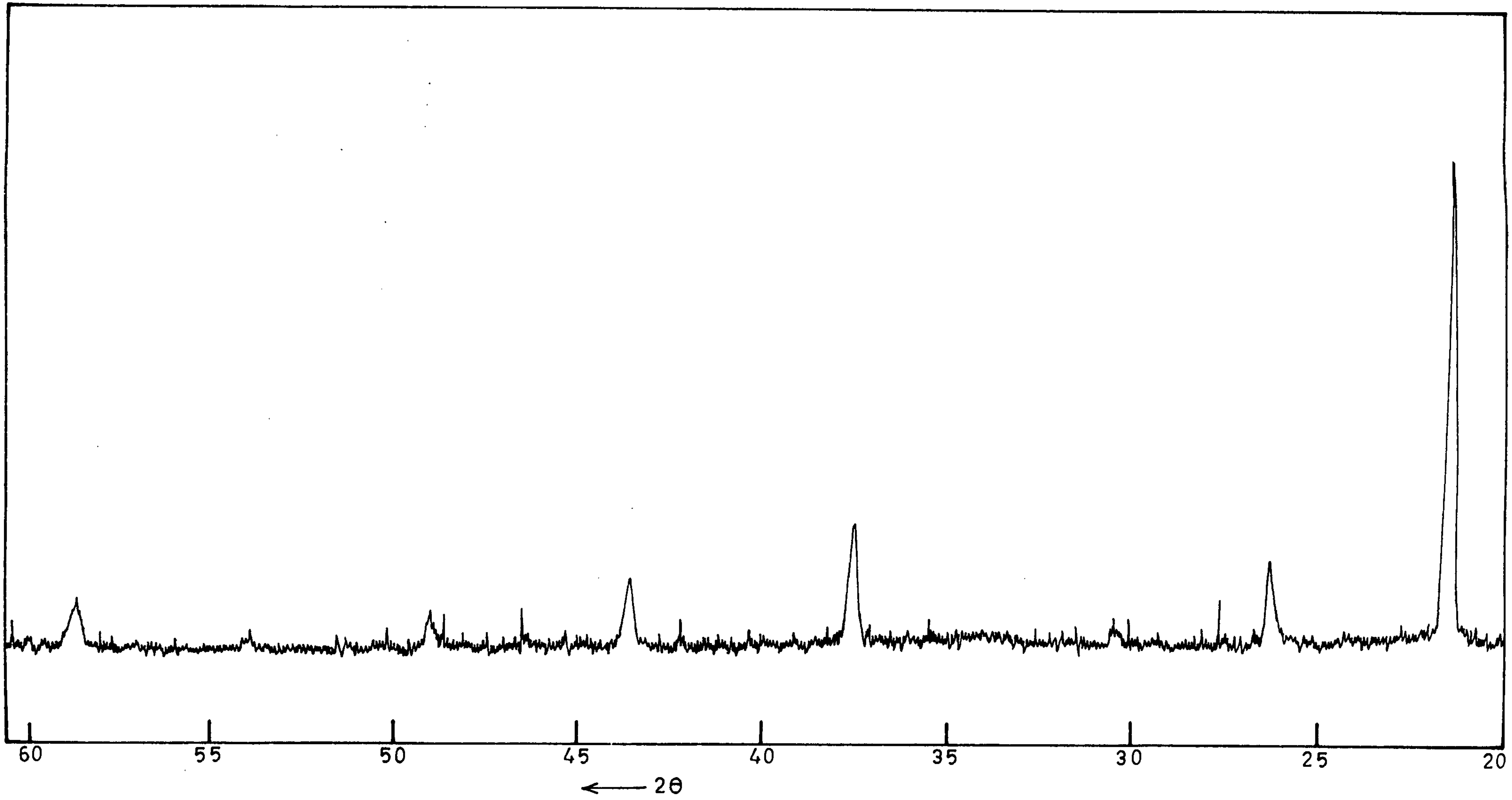


FIG.27 X-RAY DIFFRACTOGRAM FOR ZINC HEXACYANOCHROMATE(III)

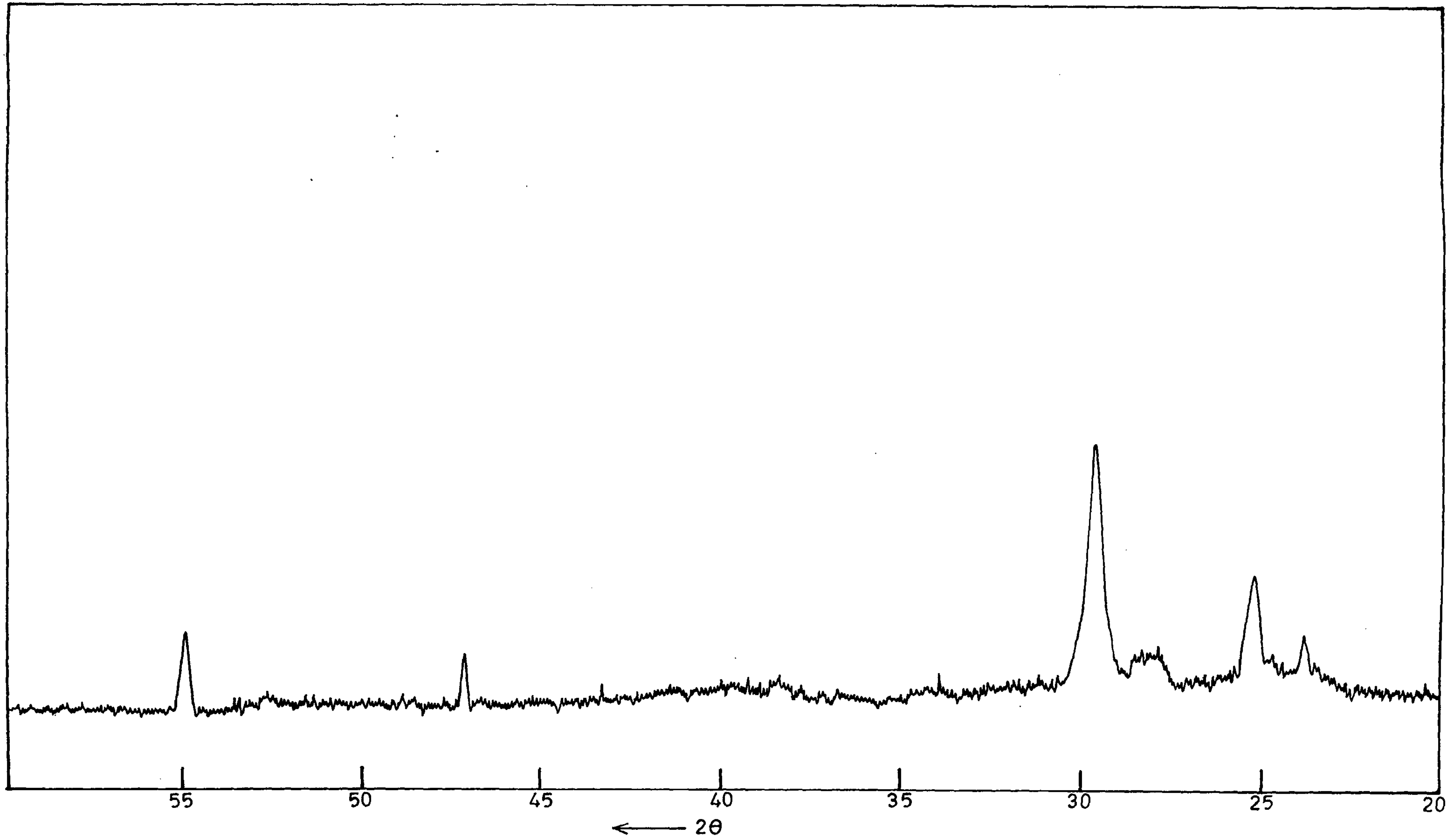


FIG.28 X-RAY DIFFRACTOGRAM FOR COPPER HEXACYANOCHROMATE(III)

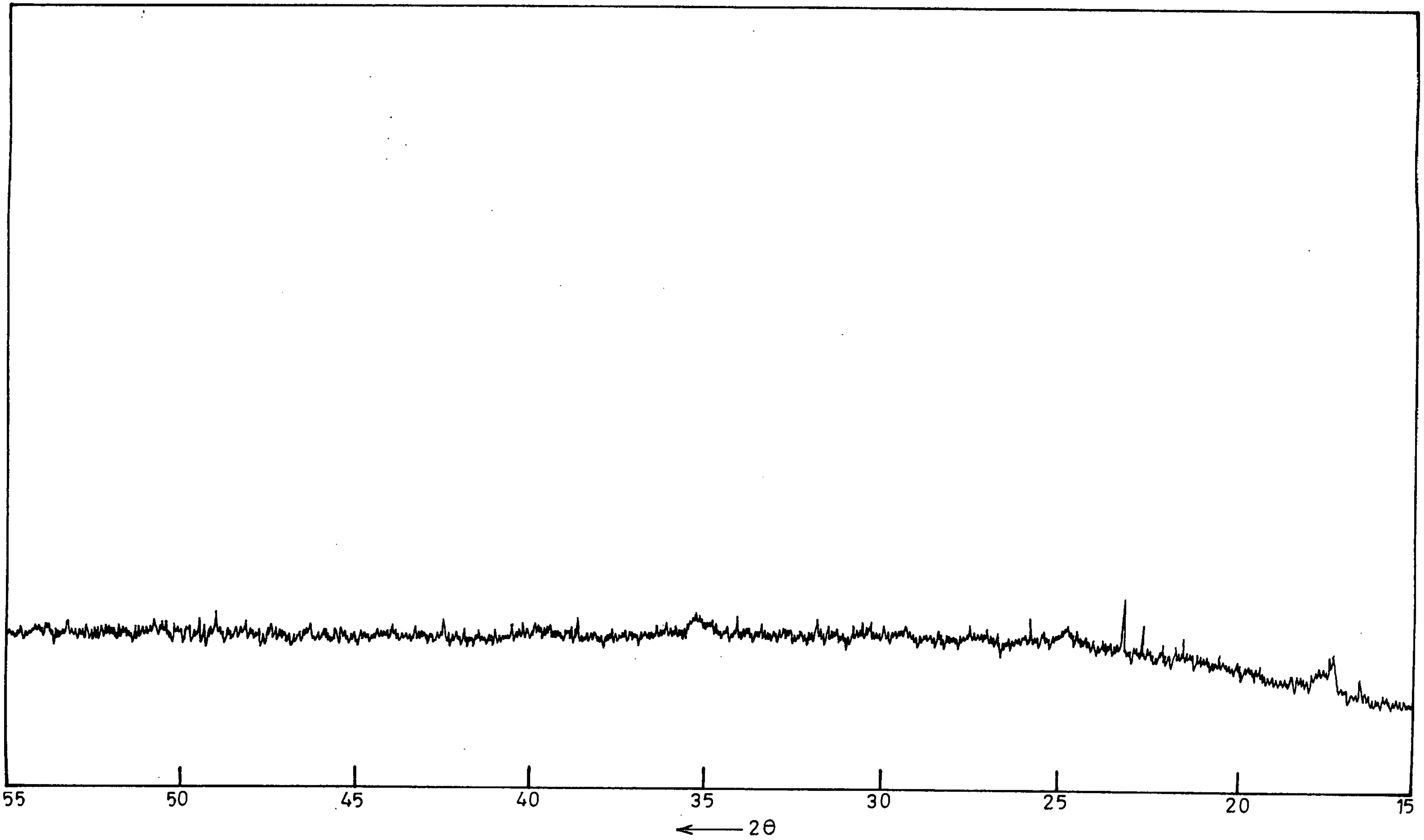


FIG.29 X-RAY DIFFRACTOGRAM FOR COBALT HEXACYANOCHROMATE(III

REFERENCES

REFERENCES

1. E.A. Heintz and D.N. Hume, Inorg. Synth., 7, 142 (1963); C.A. : 51, 11015a.

2. I.V. Tanandev and A.P. Korolkov, Izv. Akod. Nauk. SSSR Neorgan Mater, 1, 100 (1965); C.A. : 63, 4423b.

3. S. Kawamura, K. Kurotaki, H. Kuroku and M. Izawa, J. Chromatogr., 26, 557 (1967); C.A. : 66, 108569u.

4. S. Kawamura, K. Kurotaki and M. Izawo, Bull. Chem. Soc. Japan, 42, 30003 (1969); C.A. : 71, 72132a.

5. S. Kawamuro, H. Kuroku and K. Kurotaki, Anal. Chem. Acta, 49, 317 (1970); C.A. : 72, 71273p.

6. M.C. Mehra, Radiochem. Radioanal. Lett., 3, 20 (1970); C.A.: 72, 10018m .

7. M.Cole and M.T. Gangerli - Valentini, J. Inorg. Nucl. Chem., 8,5 (1972).

8. M.T. Gangerli - valentini, S. Meloni and V. Maxia, J. Inorg. Nucl. Chem., 34, 14279 (1972).

9. M.T. Gangerli-Valentini, U. Pisani, S. Meloni and V. Maxia, J. Inorg. chem., 37, 1269 (1975).

10. S. Vlasselaer, W.D. Olislager and M.D. Hont, J. Inorg. Nucl. Chem., 38, 327 (1976).

11. S. Vlasselaer, W.D. Olislager and M.D. Hont, J. Radioanal. Chem., 35, 211(1977); C.A. : 87, 54320m.

12. A. Samotus and B. Sieklucka, J. Inorg. Nucl. Chem., 40, 315 (1978); C.A. : 52, 2493g.

13. A. Samotus and Sieklucka, J. Inorg. Nucl. Chem., 42, 1003 (1980).

14. V. Kourim, R.J. Rais and B. Million, J. Inorg. Nucl. Chem., 26, 1111 (1964).

15. V. Kourim, R.J. Rais and Stejskal, J. Inorg. Nucl. Chem., 26, 1761 (1964).

16. V. Kourim and B. Million, Collection czech. Chem. Commun., 30, 2848 (1965); C.A. : 63, 182386h.

17. D.T. Cromer and R.M. Douglass, J. Phys. Chem., 61, 1388 (1957); C.A.:4,4792h.

18. H.J. Hrostowski, J. Acta Chem. Scand., 12, 1586 (1958); C.A.: 11,16042c.

19. N. A. Curry and W.A. Rurciman, Acta Cryst., 12, 674 (1959); C.A. : 53, 21023b.

20. G.W. Chantry and R.A. Plane, J. Chem. Phys., 35, 1027 (1961); C.A. : 55, 5123h.

21. A.A. Kalandiya, J. Inorg. Nucl. Chem., 19, 1635(1974).

22. A.W. Adamson and A.H. Sporer, J. Am. Chem. Soc., 80, 3865 (1958); C.A.:5, 16854h.

23. M.A. Malati and M.W. Rophall, J. Inorg. Nucl. Chem., 28, 915 (1966).

24. A.J. McDermid and N.F. Hall, ibid, 75, 5204 (1953); C.A.:2,8590g.

25. C.S. Sokol and C.H. Brubaker, J. Inorg. Nucl. Chem., 30, 3267 (1968).

26. P.J. Lucchesi and W.A. Glasson, J. Am. Chem. Soc., 78, 1347 (1956); C.A.:7,6320a.

27. K. Nakamoto, Infrared Spectra of Inorganic and Coordinate Compounds, John wiley, New York (1963) p. 160.

28. D.A. Dows, A. Haim and W.K. Wilmarth, J. Inorg·Nucl. Chem., 21, 33 (1961); C.A. : 55, 7778h.

29. D.F. Shriver, Structure and Bonding, Vol.I, Springer - Verlag, Berlin, 1961, p. 32.

30 M.H. Ford-Smith, Chemistry of Complex compounds, HMSO, 1964, p. 48.

31. R.L. McCullough, L.H. Jones and R.A. Penneman, J. Inorg. Nucl. Chem., 13, 286 (1960); C.A. : 51, 4821d.

32. D.F. Evans, D. Jones and G. Wilkinson, J. Chem. Soc.,21,3164 (1964).

33. D.F. Shriver, S.A. Shriver and S.E. Anderson, Inorg. Chem., 4, 725 (1965) ; C.A. : 62, 14030a.

34. K. Tarada, H. Hayakama, K. Sawada and T. Kiba, Talanta, 17, 955 (1970); C.A. : 72, 10096a.

35. T.R. Folson and R. Grismore, Trans. Nucl. Sci, 17, 202 (1970); C.A. : 72, 136174d.

36. W.E. Prout, E.R. Russell and H.J. Groh, J. Inorg. Nucl. Chem., 27, 473 (1965).

37. J. Krit, J. Inorg. Nucl. Chem., 27, 233 (1965).

38. L.H. Baetsle, D.V. Deysk and D. Huys, J. Inorg. Nucl. Chem., 27, 683 (1965).

39. V. Kourim, J. Rais and J. Stejskal, J. Inorg. Nucl. Chem., 26, 1761 (1964).

40. L.H. Baetsle, D. Huys and D.V. Deyck, J. Inorg. Nucl. Chem., 28, 2385 (1966).

41. B.B. Tewari and Kamaluddin, J. Colloid and Interface Science, 193, 167 (1997).

42. B.B. Tewari, D.Mohan and Kamaluddin, Colloids and Surfaces, 131, 89 (1998).

43. W.U. Malik and R. Bembi, Mikrochimica Acta, 1, 681 (1975); C.A.:6132530a.

44. W.U. Malik and R. Bembi, J. Anal. Chem., 274, 128 (1975).

45. W.U. Malik and K.D. Sharma, J. Anal. Chem., 276, 379 (1975).

46. M.T. Beck in Metal ions in Biological Systems, (Ed. Sigel) Marcel Dekker, New York, 1978, p.7.

47. L.E. Orgel in The Origins of Life and Evol. Biochem., (Ed. K. Dose, S.W. Fox, G.A. Deborin and T.E. Pavlovsky) Plenum Publishing Corporation, New York, 1974, p.369.

48. Kamaluddin, M. Nath and A. Sharma, Orig. Life Evol. Biosphere, 24, 469 (1994).

49. Kamaluddin, M. Nath, S.W. Deopujari and A. Sharma, Orig. Life Evol. Biosphere, 20, 259 (1990).

50. F.J. Scandrett, Nature, 186, 558 (1960); C.A. : 54, 18625d.

51. W.C. Fernelius, Inorg. Synth., Vol. (II), McGraw Hill Book Company, New York (London), 1946, p. 203; 214.

52. J.S. Yoo, E. Griswold and J. Kleinberg, Inorg. Chem., 4, 365 (1965); C.A.: 62, 8648g.

53. J.H. Bigelow, Inorg. Synth., 2, 123 (1946); C.A.: 3,7029.