A Thesis

submitted in partial fulfilment of the requirements for the

Master of Science Degree in Chemistry

of the

Royal University of Malta

Some Iron(II) Compounds with Thioether-Thiol Ligands

Noel Zarb Adami

Acknowledgements

I would like to thank:

Dr. A. P. Storace for suggesting the topic and for his very helpful suggestions during the project.

Prof. W. G. H. Edwards for his kind encouragement.

The laboratory staff of the Chemistry Department for their help.

Miss Adriana Tufigno for kindly typing out this script.

Dedication

This thesis is dedicated to my family, friends, the staff of the Chemistry Department of the Royal University of Malta and Miss Adriana Tufigno for having borne the smell of the ligands with little complaint.

CHAPTER 1

CONTENTS

Section A

Introduction

Sulphur and its compounds have long been known for their adverse effects in petroleum fuels and as poisons for various catalysts. Most of sulphur research, at the beginning of the century was directed at finding means of eliminating sulphur from fuels and reactants[1a]. Since then research into sulphur chemistry has been very active and thousands of sulphur-containing compounds[1b] and a number of complexes have been synthesised[2a]. Some of these compounds have found applications as anti-oxidants[3], inhibitors[4], analytical reagents[5], protein denaturants[6], pesticides[7], plasticisers[8], and in photographic emulsions[9]. More recently the discovery that the active site in non-haem iron proteins (NHIP's) contain an iron-sulphur linkage between a

central iron atom and an amino acid, probably cysteine-like, has provided an additional impetus for the synthesis of new sulphur ligands and iron complexes[10].

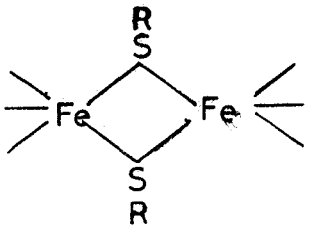
Complexes of iron with ligands having a sulphur atom as a donor are not as numerous as iron complexes with nitrogen and/or oxygen ligands. The sulphur atom has a relatively poor donating property[2b] and iron, except for manganese lies lowest in the Irving-Williams stability order[11a]. Hence, few iron-sulphur complexes are known and most of these are unstable towards oxidation and hydrolysis.

Iron-Sulphur Complexes

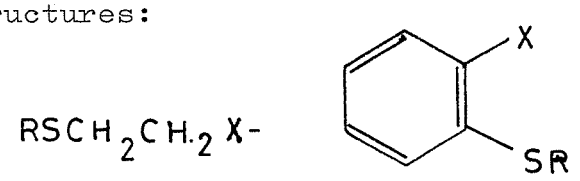
The majority of the known iron-sulphur complexes[1c, 2a, 12, 13a] can be classified into the following groups:

1) mercaptide salts, $Fe(II)(SR^-)_2$;

2) complexes having a bridging mercaptide group:



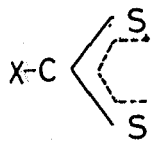
3) complexes with ligands having the skeletal structures:



where R is an alkyl group or hydrogen and X may be any donor atom or group, including a thioether or thiol group;

4) complexes with dithioacid type ligands;

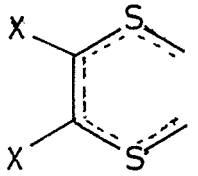
<u>i.e.</u>



where X may be R, RO, RS, R_2N, etc.;

5) complexes with dithiolene ligands:

<u>i.e.</u>



where X is usually CN or CF_3.

1) <u>Mercaptides</u>

The ability of thiols (mercaptans) to form salts with heavy metals, especially mercury, lead

and silver has been known almost since the discovery of thiols. The physical properties of the mercury salts, from which the name mercaptan (mercury capture) originates have been used for the identification of thiols[1c].

Most of the original work on metal complexes of thiols was carried out by Tschugaeff in 1908[14] and not much work has been done since[13b]. The known iron (II) mercaptide salts are green and highly insoluble. They are usually prepared by treating a solution of a ferrous salt with the thiol and adding the required amount of base to keep the solution near neutrality by neutralising the acid liberated during the reaction and suppress the decomposition of the mercaptide. The mercaptide is washed with water or alcohol, depending on the base used, containing a little of the free thiol to further minimise solvolysis[1c, 15].

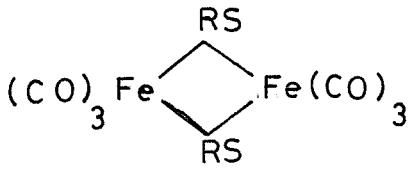
Ferric mercaptides cannot be obtained because of the spontaneous reaction:

$$2\,Fe^{III} + 2\,RSH = 2\,Fe^{II} + RSSR + 2H^{+}$$

It has however been found that solutions of Fe^{II}/Fe^{III} with thiol-acids provide a model of an oxidation/reduction system which is electromotively active, that is, the relative concentrations of ferrous to ferric ions depend on the direction of the applied current[16].

2) Bridging sulphur complexes

The best investigated complexes of this type are those obtained by treating triiron dodecacarbonyl with the required thiol to yield complexes with the structure:



where R may be both either alkyl or aryl[17]. It has been shown that when R is ethyl, then the complex when treated with bromine or iodine gives:

$$\left[Fe(CO)_3 S Et.X\right]_2$$

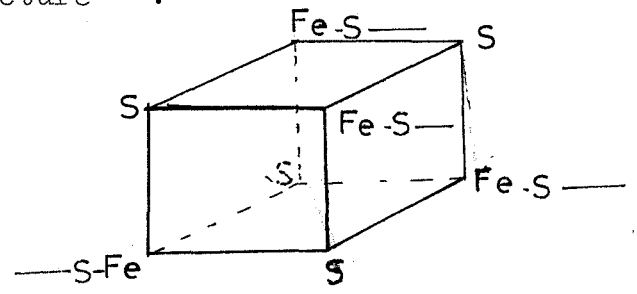
where X is respectively Br or I. If however the complex $[Fe(CO)_2P\emptyset_3.SEt]_2$ is treated with iodine the product then has the empirical formula[18]:

$$\left[Fe(CO)_2\ P\emptyset_3\ SEt\ I_{1/2}\right]^+\ I_3^-$$

The complex $[Fe(CO)_3.SEt]_2$ has also been obtained by treating an alkaline suspension of ferrous hydroxide and ethanethiol with a rapid stream of carbon monoxide[19].

Many new complexes containing sulphur bridging atoms have now been synthesised because of the growing interest in the series of electron-transfer proteins containing sulphur bound to iron in a non-haem environment. These NHIP's are characterised by two or more iron atoms bonded to the thiol group of the amino acid, cysteine[20]. These proteins occur widely in bacteria, plants and animals. Eighteen such proteins had been positively identified by 1969 and are known to play vital roles in respiration, nitrogen fixation and photosynthesis[10]. The structure of one of these proteins has recently

been determined by X-ray diffraction and has been found to contain tetrameric iron units as shown in the structure[11b]:



All NHIP's are known to contain an inorganic sulphur and a cysteine sulphur bound to an iron atom. They are characterized by the following physical properties:

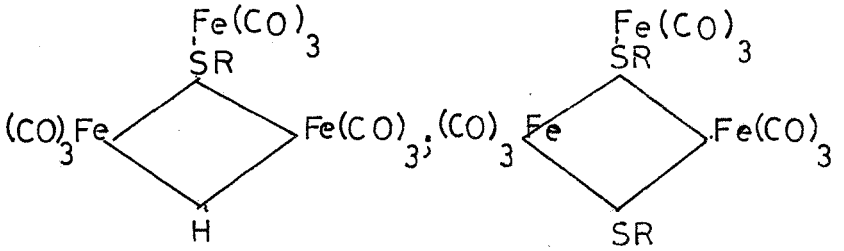
1) there is an equivalent amount of iron atoms and acid-labile sulphur groups;

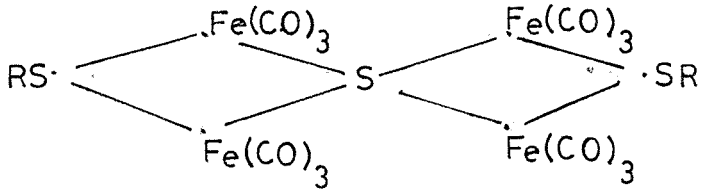
2) they function as electron carriers at low redox potentials;

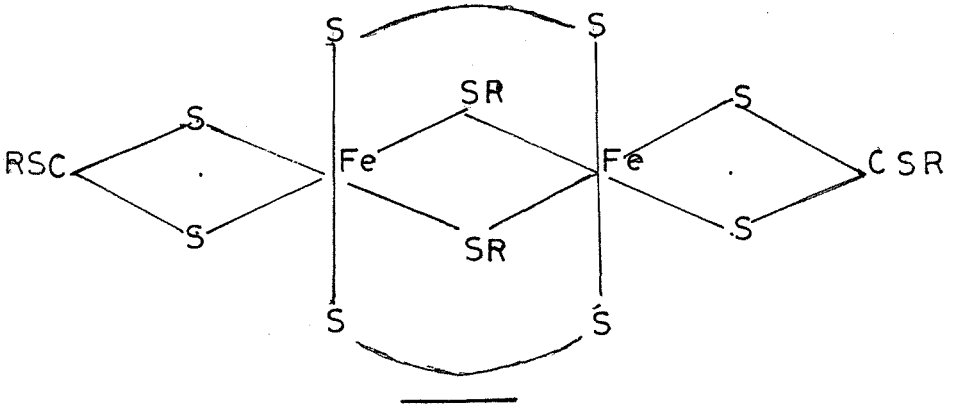
3) the 'g' value in the Electron Paramagnetic Resonance Spectrum is 1.94;

4) they show characteristic ultraviolet absorption at 315-335, 410-420 and 450-460 nm[21, 22].

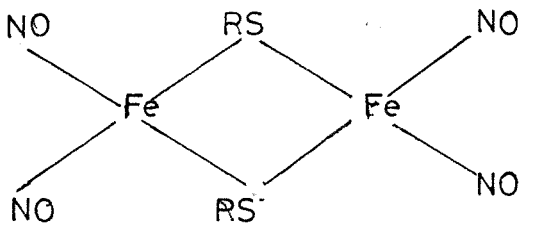
A variety of sulphur bridging compounds have been synthesised in the search of a behavioural model of NHIP. Most of these have novel structures[23-25]. Examples, illustrative of these types of structures are the following:







Nitrosyl compounds of iron with bridging sulphur ligands are also known. They may be prepared by either treating the ferrous mercaptide with nitric oxide or by treating a suspension of ferrous hydroxide and thiol with nitric oxide. The following structure has been proposed for the complexes obtained[26, 27]:



3) Complexes with $RSCH_2CH_2X$ and $\underline{o}\text{-}C_6H_4(SR)X$

Most of the complexes with these ligands are highly air-sensitive and some have not even been isolated, but their formation has been inferred by physical methods.

Iron complexes have been prepared where one of the donor atoms is a thiol or thioether

sulphur atom and the other donor, X, may be the appropriate atom in an amine, carboxylic acid, hydroxyl or less commonly another thiol or thioether group. However, when the ligand is an o-dithiol the complexes obtained behave like dithiolene complexes (see Section 5).

Ligands which have been used to form complexes of these types include o-mercaptobenzoic acid[28], o-aminobenzenethiol[29], cysteine[30], dimercaptopropane derivatives[31 - 33] and mercaptoethanol[22]. Some iron carbonyl and nitrosyl complexes with dithioether ligands are also well established[34, 35].

There appears to be only two references to iron-thioether complexes and these claim the synthesis of:

$$(C_7H_7)_2S.FeCl_3$$

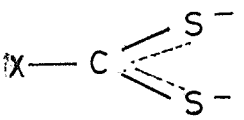
$$HFeCl_4(Et_2S)H_2O$$

but no attempt appears to have been made to determine their precise structure[36, 37].

In a comparative study of chelating monothiols and dithiols, it was found that the dithiols formed much more stable complexes. The same study also confirms the position of iron in the Irving-Williams order with respect to sulphur ligands[32].

4) Complexes with dithioacid-type ligands

These ligands must have the skeletal structure:



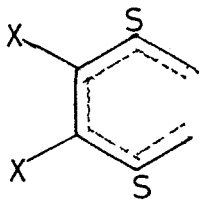
and include the dithioacids, xanthates, thioxanthates and the dithiocarbamates. These ligands and their complexes have been very extensively studied and the complex $Fe(Me_2dtc)_3$, (dtc = dithiocarbamate), has been found to have useful fungicidal properties. The literature on these compounds is very vast and reference should be

made to the reviews and articles which have appeared on the subject[1d, 2c, 38, 39].

Other ligands giving rise to chelates with four membered rings are the alpha dithiols and similar substituted compounds. The compound $(SH)_2CH(CH_2)_2Y$, where Y is a halogen is known to form strong iron(III) complexes[2d]. The dithiophosphates also form four-membered rings and these ligands and their complexes have been studied extensively[13c].

5) Complexes with dithiolene-type ligands

These ligands are either o-dithiols or contain an olefinic bond and have the skeletal structure:



The main interest in these complexes has been due to the fact that the six-coordinate complexes, like

their planar four-coordinate counterparts, undergo electron transfer reactions quite readily and that the tri-substituted systems have a trigonal prismatic arrangement of sulphur atoms around the central metal atom. The work done in this field is extensive and reference should be made to the detailed review by McCleverty[40].

Section B

Introduction

The literature survey of iron-sulphur complexes has shown that there appears to be no known complexes of iron with ligands containing both a coordinating thioether and a thiol group. Thioether-thiols are known but have been little studied as complexing agents. o-Methylthiobenzene-thiol gives complexes with nickel, palladium and

platinum whilst 2-ethylthiopropanethiol is known to give cobalt and palladium complexes[2e].

An attempt was made to synthesise iron complexes with ligands of the type $R.S.C_2H_4.SH$, where R is ethyl or n-propyl. These were expected to yield complexes whose stability would be between that of the known dithiol and dithioether complexes. They could also possess properties similar to NHIP's and if so could later be investigated as possible models of these proteins.

Thioether-thiols

A literature survey of 2-alkylthioethane-thiols indicated that the best known compound was the ethyl analogue, $Et.S.C_2H_4.SH$. This compound has been obtained in several different ways, including:

1) treatment of olefinic sulphide compounds with alkyl thiols in the presence of solid alkali metal alkylates or with hydrogen

sulphide under pressure[41 - 43];

2) high pressure hydrogenation of sulphurized olefinic compounds using a nickel catalyst[44];

3) halogenation of 2-ethylthioethanol by thionyl chloride and converting the chloride derivative into the thiol by thiourea[45];

4) conversion of 2-ethylthioethanol into the thiol by heating under reflux with hydrobromic acid and thiourea and then decomposing the thiouronium salt by alkali[46];

5) prolonged heating under reflux of diethyl sulphide and ethanethiol at a temperature gradient in the presence of a small quantity of hydroquinone[47];

6) reduction of 3,6-dithiaoctane with calcium in liquid ammonia[48].

2-Ethylthioethanethiol and similar compounds have been suggested as starting materials for dyes, textile acids, pharmaceuticals and vulcanization catalysts[41]. They have also been

investigated as possible antidotes for arsine poisoning but it has been found that intraveneous application may cause damage to the central nervous system[49]. However, the only known industrial application of 2-ethylthioethanethiol is in the preparation of esters of thiophosphoric acids which have been marketed under the names of Systox and MetaSystox as insecticides[46, 50]. Studies of the detection and analysis of these insecticides have resulted in the synthesis of a copper complex. Attempts to obtain iron, cobalt or nickel complexes were however unsuccessful[51].

2-n-Propylthioethanethiol and the isopropyl analogue have been less studied than the ethyl compound. These compounds have been prepared by:

1) conversion of the appropriate propylthioethanol to the thiol by using hydrogen sulphide in the presence of sodium ethoxide or sodium sulphide[52, 53];

2) reduction of 4,7-dithiadecane with calcium in liquid ammonia to give the n-propyl compound[48];

3) reduction of dithiolanes in the presence of boron trifluoride or aluminium trichloride to give the iso-propyl compound[54].

The method used for the preparation of the ethyl ligand was a slight adaptation of reaction 4 on page 15. An analogous method was used to prepare the propyl compound but this method has not been reported.

CHAPTER 2

Discussion

Ligand preparation

The reported[46] preparation of the ethyl ligand was carried out on various scales but the time under reflux condition was reduced from ten to seven hours. After the addition of the sodium hydroxide solution the ligand easily separated as the top layer and instead of further boiling under reflux it was removed. No more ligand could be obtained by further boiling under reflux or extraction with ether of the bottom layer. The yield of the product twice distilled at atmospheric pressure varied between 42 and 48 per cent in different preparations. The reported yield[46] is 66 per cent, but it is not stated whether this refers to the crude or the purified product. This adaptation, even though with a lower yield than claimed is still justified considering that the total preparation time is reduced by half since the final three hour boiling under reflux

after the addition of the sodium hydroxide and the extraction with ether are not carried out.

Elemental analysis

Analytical data indicate that the compound prepared from the ethyl ligand and iron tetracarbonyl diiodide has the stoichiometry $Fe(C_2H_5.S.C_2H_4.SH)_2I_2$. The carbon and hydrogen analyses of the two other compounds prepared do not agree well with FeL_2X_2 stoichiometry. A repeat duplicate analysis of the compounds at a different laboratory gave widely different results and this suggests that the method being used for analysis is unsuitable for these types of compounds. Moreover, the compound obtained from the propyl ligand seems to retain a carbonyl group (see page 35) but no reasonable formulation could be deduced from the analytical results. No attempt was made to analyse the compound presumed to be $Fe(SR)_2$ owing to its extreme ease of decomposition.

Conductivity measurements

The conductivity of the compounds in nitrobenzene (0.6-9.0 ohm^{-1}) indicates that these compounds are non-electrolytes as 1:1 electrolytes are expected to have a molar conductivity between 18-30 ohm^{-1} and 1:2 electrolytes conductivity of about 60 ohm^{-1} [55].

Infrared spectra

The infrared spectra of the ligands used in this work have not been reported but related compounds have been the subject of various detailed studies[56, 57] and many bands have been assigned even though there is still some disagreement.

Compounds having a skeletal $-S.C_2H_4.S-$ unit are known to exist as *trans* or *gauche* conformers. In the liquid state the *trans* conformer predominates and various strong bands in the spectra of these compounds have been assigned to vibrations of the *trans* conformer. On chelation the skeletal unit has

to assume a gauche configuration. This results in an increase in the intensity of the bands assigned to the gauche conformer and the disappearance of the bands assigned to the trans conformer[58].

The bands appearing at approximately 1130 and 1200 cm^{-1} (18, 22 in Table 2) have been assigned to a CH_2 twist and wag vibration respectively of the trans conformer[57]. Only weak bands appear in these regions in the spectra of the complexes prepared from the carbonyl halides whereas the 1200 cm^{-1} band appears quite strongly in the spectrum of the compound presumed to be $Fe(SR)_2$. The ethyl and propyl ligands show weak bands at 845 and 782 and 855 and 782 cm^{-1} respectively, (32, 34 in Table 2). In similar compounds these bands have been assigned to CH_2 rocking vibrations of the gauche conformer[56]. These bands appear quite strongly in the compounds prepared from the carbonyl halides but weakly in the compound presumed to be $Fe(SR)_2$.

On the basis of this evidence it can be stated that the ligand is chelating in the compounds prepared from the carbonyl halides and that it is either monodentate or bridging in the other compound as the trans conformer would be preferred in these situations[58].

The band appearing at 2430 cm^{-1} in the compounds prepared from the carbonyl halides (4, 5 in Table 2) can only be assigned to an SH vibration[59] (appearing at 2530 cm^{-1} in the ligands, 4 in Table 2) which has been shifted down due to coordination of the sulphur atom.

The compound prepared from the propyl ligand shows bands at 2089, 1970 and 1950 cm^{-1} (6, 7, 8 in Table 2). These bands can only be assigned to terminal carbonyl stretching frequencies[60]. The possibility that these arise from contamination by unchanged carbonyl halide was excluded as the bands remained unchanged in intensity and position after washing the compound with dichloromethane and light petroleum in both of which iron tetracarbonyl diiodide is soluble. It hence appears

that not all the carbon monoxide is displaced by the propyl ligand. Measurement of the volume of gas liberated during the reaction seemed to indicate that all the four moles of the carbon monoxide were liberated and this is in obvious contradiction to the infrared spectrum of the product. The possibility that some gas other than carbon monoxide was liberated cannot be excluded as no attempt was made to analyse the gas evolved. The problem is still unresolved and merits further attention.

Magnetic measurements

When d orbitals are placed in an octahedral environment, they split into a lower set of t_{2g} and an upper set of e_g orbitals which differ in energy by Δ , the ligand field splitting energy. According to Hund's first rule the distribution of electrons in the orbitals which gives the lowest energy arrangement is such

that all the spins are parallel. Complexes in which this situation holds are referred to as high-spin complexes. If however Δ is large enough so that the least energy arrangement is one in which some or all of the electrons pair up in the lower energy orbitals (*i.e.* the pairing up energy is lower than Δ) then low-spin complexes are obtained.

Since iron(II) is a d^6 system, high spin iron(II) complexes have four electrons in the t_{2g} orbitals, of which only two are paired and two other unpaired electrons in the e_g orbitals[11c]. The ground state of this electron distribution is $^5T_{2g}$ as indicated by the energy level diagram of a d^6 system. This gives rise to an appreciable orbital contribution because some orbital angular momentum is retained. Hence, the spin-only formula for magnetic moment (μ being 4.9 B.M. for 4 unpaired electrons) is not expected to hold accurately[61a], and moments in the range 5.0-5.6 B.M. have been

reported[61b]. Thus, the value of 5.7 B.M. for $Fe(C_2H_5.S.C_2H_4.SH)_2I_2$ is quite consistent with an iron(II) system in a pseudo-octahedral field.

The presence of iron as iron(II) was further ascertained by decomposing some of the complex with dilute hydrochloric acid and adding a few drops of ammonium thiocyanate solution. A deep red colour only developed after a few drops of concentrated nitric acid had been added.

Magnetic data for the other compounds prepared cannot be quoted as X_m values or as magnetic moments as no assumption can be made regarding their molecular weight. However, the X_g values are very similar to the one obtained for the ethyl iodo complex and this suggests that these compounds are also iron(II) complexes in a pseudo-octahedral environment. No magnetic measurements were made on the compound presumed to be $Fe(SR)_2$ because of the ease of its decomposition which would lead to inconsistent results.

Electronic spectra

Electronic transitions giving rise to absorption spectra in the ultraviolet and visible region can be attributed mainly to two different processes; transitions between orbitals localised mainly on the metal ion, i.e. d-d transitions and transitions between molecular orbitals localised on different atoms in the molecule, i.e. charge transfer spectra.

d-d Transitions occur between the free ion terms which are split energy-wise when placed in a ligand field. Various terms arise due to this but transitions between these terms are normally forbidden due to two selection rules. Transitions between terms having different multiplicities are forbidden (spin forbidden) and transitions between orbitals which behave similarly with respect to inversion (g to g, u to u) are also forbidden (Laporte forbidden).

Transitions between different molecular orbitals are not necessarily Laporte forbidden as

are d-d transitions. Charge transfer spectra are hence usually intense (ϵ being over 1000 and may be as high as 30,000). These spectra correspond to a transfer of charge from the central metal ion to the ligand atoms or vice versa and are best explained using the molecular orbital approach.

From the energy level diagram of a d^6 system in an octahedral field it is observed that only one transition is spin allowed, $^5T_{2g} \rightarrow {}^5E_g$ but this transition is Laporte forbidden. This should lead to no d-d bands appearing in the spectrum of a d^6 system. However, the Laporte selection rule may be slightly relaxed and a weak absorption band may be observed (ϵ approximately 10)[62a]. For example, the $^5T_{2g} \rightarrow {}^5E_g$ transition of aqueous ferrous perchlorate $Fe(H_2O)_6^{2+}$, appears at 10,000 cm^{-1} with an ϵ of 1.1[62b].

Iodine, bromine and sulphur ligands cause less splitting than water ligands[63]. This should cause any d-d transitions to appear below 10,000 cm^{-1}, i.e. in the infra-red region. Thus the five

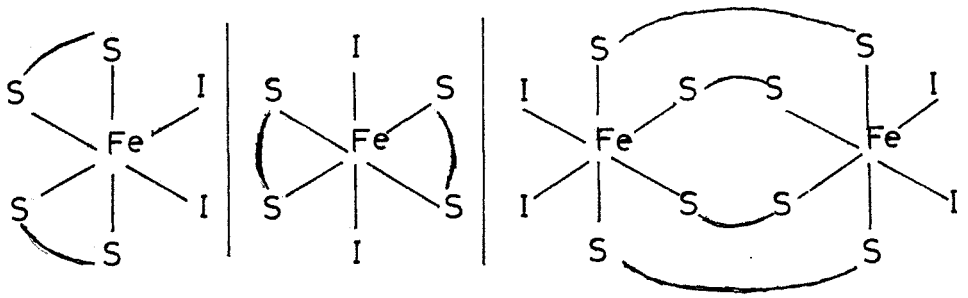
absorption bands in the ultraviolet and visible region shown by all the compounds prepared must be attributed to charge transfer transitions arising from iron to sulphur atomic orbitals or vice versa. The bands appearing at 680 and 468 nm in the compounds prepared from the carbonyl iodide and bromide respectively are however probably charge transfer transitions between the iron atom and the halogen ligand. The observed intensities (ϵ being 576-3400) further indicate that these bands are due to charge transfer transitions.

Conclusion

The best characterised compound is the one obtained from the ethyl ligand and iron tetracarbonyl diiodide. The physical properties are consistent with a high-spin ferrous ion in a pseudo-octahedral environment with two molecules of the sulphur ligand being bidentate, chelating, and retaining the thiol hydrogens. Recent studies on

iron tetracarbonyl diiodide seem to confirm a cis arrangement[64], even though a Mossbauer spectrum seems to suggest that the iron atom is bound to molecular iodine[65]. It has been observed that on standing the cis isomer converts to the trans isomer[66]. The possibility that this may occur during the reaction cannot be excluded even though it is improbable. No distinction could be made between the cis and trans forms from our data. The possibility of a cis and trans mixture also cannot be excluded.

Of the three possible structures for the complex:



1 2 3

structure 1 seems to be the most likely. This complex, cis- diiodobis(2-ethylthioethanethiol)iron(II).

appears to be unique in that the ligand molecules do not lose hydrogen ions to become ionic on coordination and hence the complex is not a mercaptide. The ligand is thence expected to behave more like thioether ligands than like thiols. However, Hieber[34] discovered that dithioethers failed to replace all the carbon monoxide molecules when treated with iron tetracarbonyl diiodide whilst the mixed thioether-thiol does so. This discrepancy may be accounted for by the less steric hindrance and perhaps the better donating properties, of the SH group compared to the C_2H_5S. group.

The compound presumed to be $Fe(SR)_2$ appears to be polymeric, possibly involving bridging ligand units as <u>trans</u> conformers, but no structure can be assigned to it from the studies made so far. In the two other compounds obtained, see Table 1, the ligands appear to be chelating and bidentate and the thiol hydrogen retained. The iron appears to be in the ferrous state. Not even tentative

structures can be assigned to them, but the propyl compound definitely appears to contain a terminal carbonyl group. Further studies have to be carried out to investigate the possibility that the compounds are mixtures and a full elemental analysis should be done to determine the stoichiometry of the compounds.

All the compounds prepared have ultra-violet-visible spectra similar to those of typical non-haem iron proteins, and these compounds may be investigated as models.

Further studies using other ligands where the alkyl group is methyl, iso-propyl and butyl should be carried out to determine whether the partial displacement of carbon monoxide by the propyl ligand is due to steric effects. Far infra-red spectra could be used to determine whether the compounds are <u>cis</u> or <u>trans</u>. Complexes of transitional metals other than iron might be easier to prepare and a comparative study of complexes obtained ought to be made.

CHAPTER 3

Experimental

Preparation of ligands

Preparation of 2-n-propylthioethanethiol

Sodium (23g; 1 mole) was dissolved in ethanol (250ml) and the solution cooled in an ice bath. n-Propanethiol (76g; 1 mole) was added to the solution and the mixture was stirred. 2-Chloroethanol (85g; 1 mole) was added dropwise to the mixture which was being continously stirred vigorously with a magnetic stirrer. The reaction proceeded exothermally and the mixture boiled under reflux. After all the 2-chloroethanol had been added the mixture was further boiled under reflux on a mantle for 30 minutes. The sodium chloride which deposited was filtered off and the alcohol removed by distillation on a water bath. The 2-n-propylthioethanol was purified by distillation at atmospheric pressure, b.p. 192°; n_D^{20} 1.475.

Yield 96g, 80 per cent.

2-n-Propylthioethanol (90g; 0.75 mole) was poured into a 1-litre three necked flask. Hydrobromic acid (350ml; 3 moles) was added, followed by thiourea (57g; 0.75 mole). A mechanical stirrer was inserted through the centre neck of the flask and a reflux condenser was attached to one of the other necks. A separating funnel containing sodium hydroxide solution (120g; 3 moles in 250ml water) was inserted in the remaining neck. The mixture was boiled under reflux for seven hours after which the sodium hydroxide solution was added dropwise. A light yellow oil separated as a top layer when the stirring was stopped. This was removed and dried over calcium chloride granules. After decanting, it was twice distilled under reduced pressure, b.p. 88°/15mm, 92°/18mm, (77°/11mm reported)[53]; n_D^{20} 1.580.

Yield 40g; 40 per cent.

Preparation of 2-ethylthioethanethiol

This was prepared as above using one mole of ethanethiol. For 2-ethylthioethanol, b.p. 184° (184° reported)[45]; n_D^{20} 1.480. Yield 92g; 85 per cent.

For 2-ethylthioethanethiol, b.p. 188°, (188° reported)[46]; n_D^{20} 1.525 (1.529 reported)[46]. Yield 42g; 45 per cent.

Reactions of ligands with iron compounds

2-Ethylthioethanethiol with ferric chloride

Anhydrous ferric chloride (1.63g; 0.01 mole) was dissolved in benzene (10ml) and the ligand (3.7g; 0.03 mole) was added. The brown solution immediately turned colourless and a grey powder precipitated. The infrared spectrum of the powder showed no ligand bands and the ultra-violet spectrum of the powder dissolved in ethanol

was the same as that of ferrous chloride. This result was expected due to the well known reducing behaviour of thiols with ferric compounds, (see page 4).

2-Ethylthioethanethiol with ferrous compounds

Anhydrous ferrous chloride (1.27g; 0.01 mole) was added to ethanol (10ml). The solution remained cloudy but on addition of ligand (3.7g; 0.03 mole) all the ferrous chloride dissolved. No precipitate could be obtained after prolonged boiling under reflux, prolonged cooling or reduction in the volume of solvent. On evaporating to dryness clear light green crystals were obtained. No ligand bands were observed in the infrared spectrum of the crystals after these were washed lightly with ethanol.

The same reaction was attempted using various solvents, an inert atmosphere, and various other different salts of iron(II) including

ferrous sulphate heptahydrate, ferrous perchlorate hexahydrate, hydrated ferrous bromide, as well as potassium trisoxalatoferrate(III) and trisacetylacetonatoiron(III). Tetraethylammonium chloride and tetraphenylarsonium chloride were also added to the reaction mixtures in the hope of precipitating a tris-complex anion. All attempts were unsuccessful.

2-Ethylthioethanethiol with ferrous compounds in the presence of a base

Ferrous chloride tetrahydrate (1.98g; 0.01 mole) was dissolved in ethanol (25ml) and the ligand (2.5g; 0.02 mole) was added. Addition of diethylamine (1.4g; 0.02 mole) caused the precipitation of a dark green powder, presumably ferrous mercaptide, $Fe(S.C_2H_4.S.C_2H_5)_2$. This was filtered off, washed with ethanol (25ml containing 0.5g of ligand) and with ether (15ml). It was then dried under vacuum.

Yield 2.4g; 80 per cent.

Attempts were made to crystallize the powder from 1,2-dichloroethane, dichloromethane and chloroform, but these were unsuccessful due to the almost spontaneous decomposition of the green powder. A brown powder showing no ligand bands in its infrared spectrum always deposited. This was probably some oxide of iron. The green product was insoluble in all other solvents (ethanol, methanol, acetone, benzene, water, etc.).

Other attempts to obtain a crystalline product using anhydrous ferrous chloride, ferrous sulphate heptahydrate, hydrated ferrous bromide, ferrous perchlorate hexahydrate as well as potassium trisoxolatoferrate(III) and trisacetylacetonato-iron(III) were unsuccessful. A variety of bases including aqueous ammonia, ammonia dissolved in ether, triethylamine and pyridine were also tried but failed to give any crystalline product. An addition of excess of base favoured the precipitation of ferrous hydroxide. Diethylamine was prefered as

the by-product diethylammonium chloride was soluble in ethanol.

2-Ethylthioethanethiol with iron tetracarbonyl diiodide

Iron tetracarbonyl diiodide (4.24g; 0.01 mole) prepared by the method of Hieber[67] was dissolved in 1,2-dichloroethane or diethyl ether (10ml). The ligand (2.5g; 0.02 mole) was added to the solution. The reaction flask was fitted with a reflux condenser and the outlet of the condenser was attached to a flask containing some of the solvent through which the carbon monoxide produced during the reaction was bubbled. The gas was then collected in a graduated gas jar. The system was hence sealed off from the atmosphere. Stirring was carried out using a magnetic stirrer.

All the carbon monoxide was given off at a rate dependent on the reaction temperature (15 minutes at 80°C, 4 hours at room temperature).

Stirring was continued for a short time after all the gas (0.04 mole) was given off. The physical properties of the product depended on the temperature and solvent used. Dark green crystals were obtained under reflux conditions using 1,2-dichloroethane and a light green powder was obtained at room temperature using diethyl ether.

Elemental analysis (see Table 1) and infrared spectra indicated that both products were $Fe(SH.C_2H_4.S.C_2H_5)_2I_2$.

Yield 2.5g; 45 per cent.

The product was found to be very moisture sensitive and was immediately decomposed by ethanol, methanol, acetone and water. It however remained undecomposed for days when stored in a sealed flask. Solutions of the product in 1,2-dichloroethane, dichloromethane and diethyl ether were found to be relatively stable at room temperature. Attempts at recrystallization proved fruitless due to the ease of decomposition at higher temperatures.

2-Ethylthioethanethiol with iron tetracarbonyl dibromide

Iron tetracarbonyl dibromide (3.66g; 0.01 mole) prepared by the method of Hieber[67] was added to dichloromethane (5ml). The suspension was cooled in an ice bath and the ligand (2.5g; 0.02 mole) was added. The experimental set up was the same as used in the previous reaction. The reaction proceeded immediately and rapidly. Stirring was carried on for 15 minutes after the evolution of carbon monoxide ceased. Filtration yielded a light greyish yellow powder. This was washed thrice with light petroleum and dried under vacuum.

Yield 3g; 70 per cent.

The product had similar solubility and stability properties to the iodo compound.

2-n-Propylthioethanethiol with iron tetracarbonyl diiodide

Iron tetracarbonyl diiodide (4.24g;

0.01 mole) was dissolved in diethyl ether (5ml) and the ligand (2.72g; 0.02 mole) was added. The experimental procedure was the same as used in the previous experiments except that when evolution of gas almost ceased diethyl ether (5ml) was added and stirring continued for some minutes.
Yield 1.8g; 30 per cent.
The product was more soluble than, but of similar stability to, the compounds prepared from the ethyl ligand.

Physical Measurements

Elemental analysis

The compound prepared from the ethyl ligand and iron tetracarbonyl diiodide (hereinafter referred to as Fe.Et.I.) was analysed by May and Baker Laboratories and the compounds prepared from the ethyl ligand and iron tetracarbonyl dibromide

(Fe.Et.Br.) and the propyl ligand and iron tetracarbonyl diiodide (Fe.Pr.I.) were analysed for carbon and hydrogen by the National Physical Laboratory, Teddington, United Kingdom.

Magnetic measurements

The magnetic properties of the three compounds obtained from the iron carbonyl halides were measured using a single temperature Gouy type balance calibrated against tris(ethylenediammine)-nickel(II) thiosulphate.

Conductivity measurements

The conductivity of the compounds in nitrobenzene was measured using a null point A.C. bridge.

Refractive index

Refractive indices of the ligands and the intermediate hydroxy compounds were measured using

a Hilger-Watts Abbe refractometer.

Melting point

The melting points of the compounds prepared were determined using a standard melting point apparatus.

Infrared spectra

These were recorded using nujol and hexachlorobutadiene mulls and sodium chloride plates. A Perkin Elmer 157 spectrophotometer was used at slow scanning speed and its calibration was periodically checked against a polystyrene film. Attenuation had to be employed whilst recording the spectra of the complexes due to the opacity of the mulls. Ligand spectra were recorded as liquid films. The spectrum of the compound presumed to be $Fe(SR)_2$, (SR = $.S.C_2H_4.S.C_2H_5$) was recorded using a Perkin Elmer 137 spectrophotometer.

Ultraviolet-visible spectra

Spectra in the region 250-800 nm were recorded in 1,2-dichloroethane using a Unicam SP800 spectrophotometer at fast scanning speed. The instrument was calibrated against a holmium and a didymium filter.

Table 1

Properties of compounds prepared

	Fe.Et.I	Fe.Et.Br	Fe.Pr.I
Melting point	92°	98-105°	73°
Gram susceptibility	23.8×10^{-6}	22.3×10^{-6}	19.3×10^{-6} cgs
Magnetic moment	5.7 B.M.		
Molar conductivity in nitrobenzene	7.0 ohm^{-1}	0.61 ohm^{-1}	8.9 ohm^{-1}
Elemental analysis Carbon (%)	16.6*	16.03	16.94
	16.6**	15.64	17.08
	(17.3)	(20.7)	(20.0)
Hydrogen (%)	3.55*	3.70	3.56
	3.50**	3.55	3.61
	(3.64)	(4.33)	(4.12)
Sulphur (%)	22.6*		
	22.4**		
	(23.1)		
Iodine (%)	46.7*		
	50.1**		
	(45.8)		
Iron	10.1*		
	9.6**		
	(10.1)		

For Fe.Et.I, * refers to the compound obtained from 1,2-dichloroethane and ** refers to the compound obtained from diethyl ether. For the other compounds the two values are for repeat analysis and value in brackets refers to estimated values for FeL_2X_2 stoichiometry.

Table 2

Infrared spectra

	$-S.C_2H_4.S-$	Ethyl Ligand	$Fe(SR)_2$	Fe.Et.X	Propyl Ligand	Fe.Pr.I
1		2950s		2950s	2950s	
2		2910s		2910s	2910s	
3		2860sh			2850sh	
4		2530w		2430w	2530w	
5						2430s
6						2089m
7						1970s
8						1950s
9	1452s	1450s		1445s	1458s	1450s
10	1424s	1425s		1420s	1450s	
11					1435s	
12					1425s	
13			1395s	1395s	1375s	1395s
14	1375m	1375m			1330w	
15		1290m			1290m	
16	1266s	1275s	1250sh		1270s	1260s
17	1260sh	1260s	1240s	1260s	1235s	1240m
18	1210s	1210s		1240s	1205s	1225s
19			1185s	1190vw		1190vw
20				1175w		1170w
21		1140m	1155vw	1155vw	1135m	1145vw
22	1129m			1145vw		1130m
23	1115sh			1125w		
24					1090w	1085w
25	1058m	1055w	1050w	1045w	1045vw	1051w
26	1051m		1010w	1030w		1030w
27				1010w		1010vw
28	980sh			990w		
29	970m	970m	978m	950w	965vw	
30		902w	925w		900w	
31		890vw	885vw	882s	890vw	890s
32	853w	845vw	855w	855m	855vw	850s
33			838w	838s		828m
34	783w	782w	785w	778m	780w	
35	763w	760w	755w	770s	770sh	
36	756sh			750m		
37	716m	710m	718w		725w	720w
38	688sh		695m		690m	

The values quoted for the vibrations of the $-S.C_2H_4.S-$ skeletal unit are from references 56 and 57. The ethyl bromo and iodo compounds have identical infrared spectra (see Fe.Et.X).

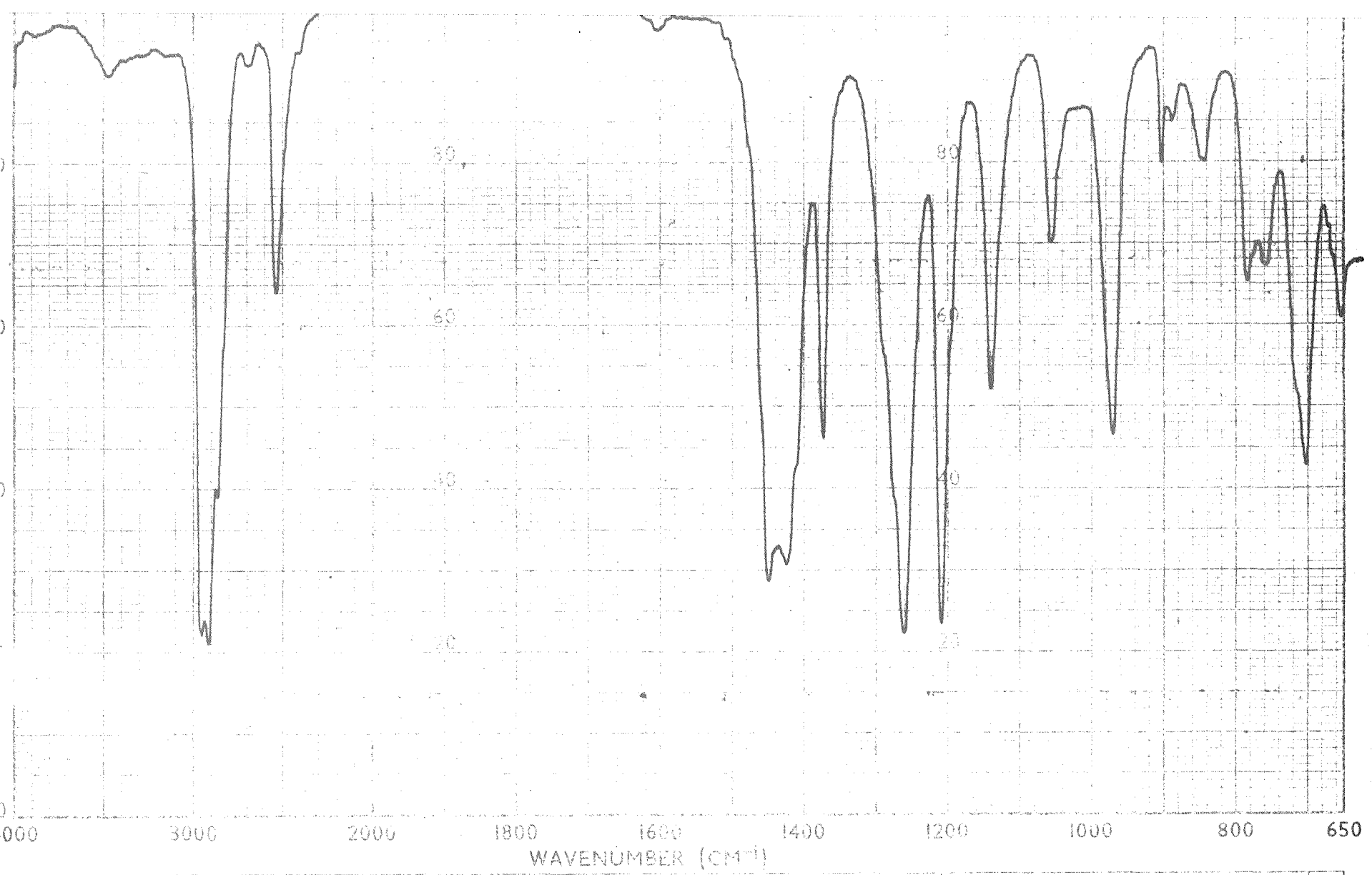
(s= strong, sh= shoulder, m= medium, w= weak, vw= very weak).

Table 3

Ultraviolet-visible spectra

	$Fe(SR)_2$		Fe.Et.I		Fe.Et.Br		Fe.Pr.I	
	λ (nm)	ϵ	λ (nm)	ϵ	λ (nm)	ϵ	λ (nm)	ϵ
1)	267	576	252	3150	280	1090	252	3375
2)	315	720	315	3106	288	1000	315	2250
3)	354	654	400	1610	395	700	400	1520
4)	395	576	480	1560	420	680	480	1480
5)	655	420	680	856	468	600	680	862

The extinction coefficient values are calculated on FeL_2X_2 stoichiometry for the compounds obtained from the carbonyl halides.



SAMPLE $C_2H_5 \cdot S \cdot C_2H_4SH$.

SOLVENT
CONC.
CELL PATH
REFERENCE

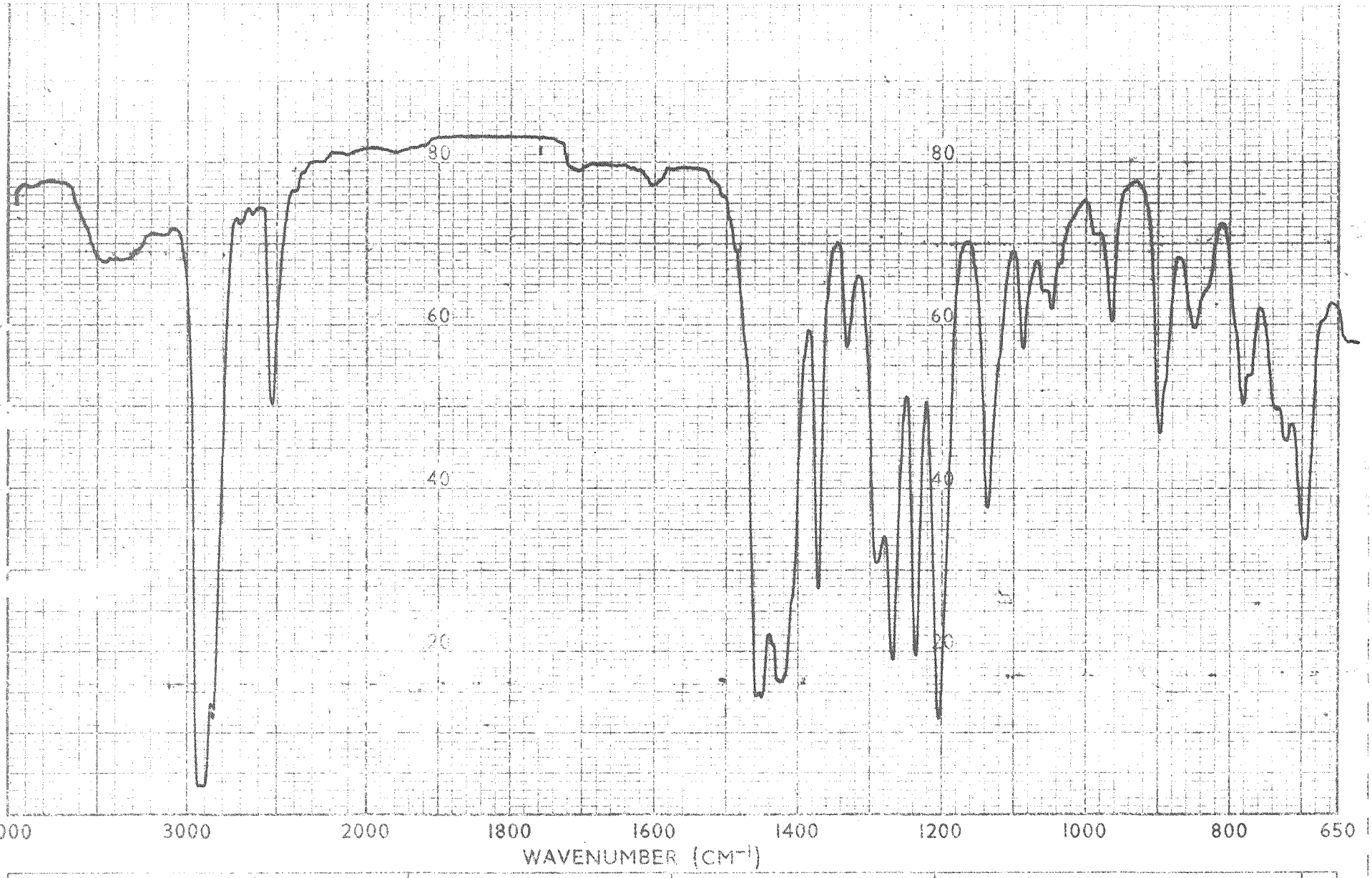
SCAN
SLIT
OPERATOR
DATE

REMARKS

No.

ORIGIN

PERKIN-ELMER PART No. 471-5049



SAMPLE

n-$C_3H_7 \cdot S \cdot C_2H_4SH$

SOLVENT

CONC.

CELL PATH

REFERENCE

SCAN

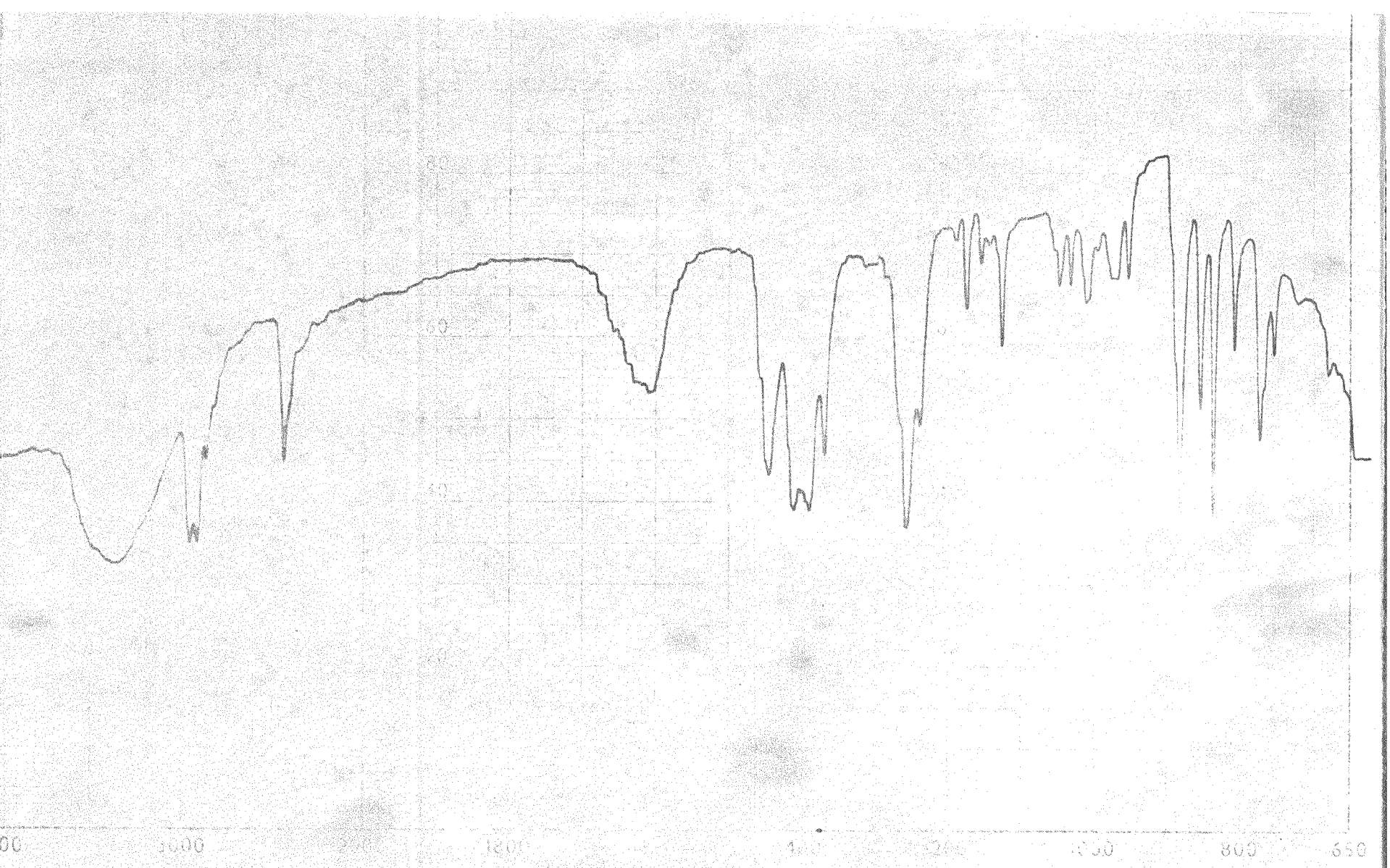
SLIT

OPERATOR

DATE

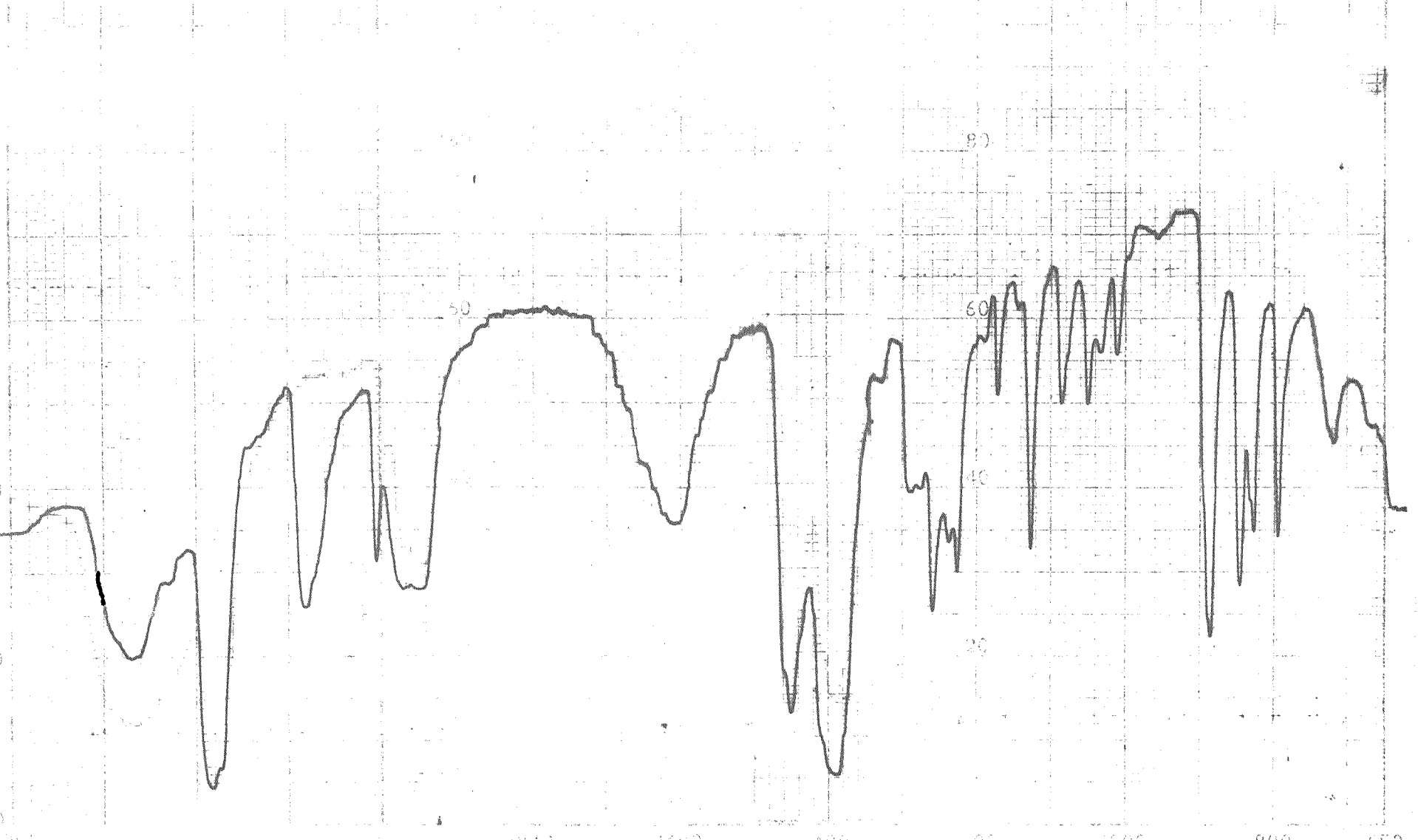
REMARKS

No.



Fe. Et. I
Fe. Et. Br

The regions 4000-2000 and 1500-1300 cm^{-1} were obtained by superimposing a thick chlorobutadiene mull spectrum.



SAMPLE Fe. Pr. I

SOLVENT

CONC.

CELL PATH

REFERENCE

ORIGIN

SCAN

SLIT

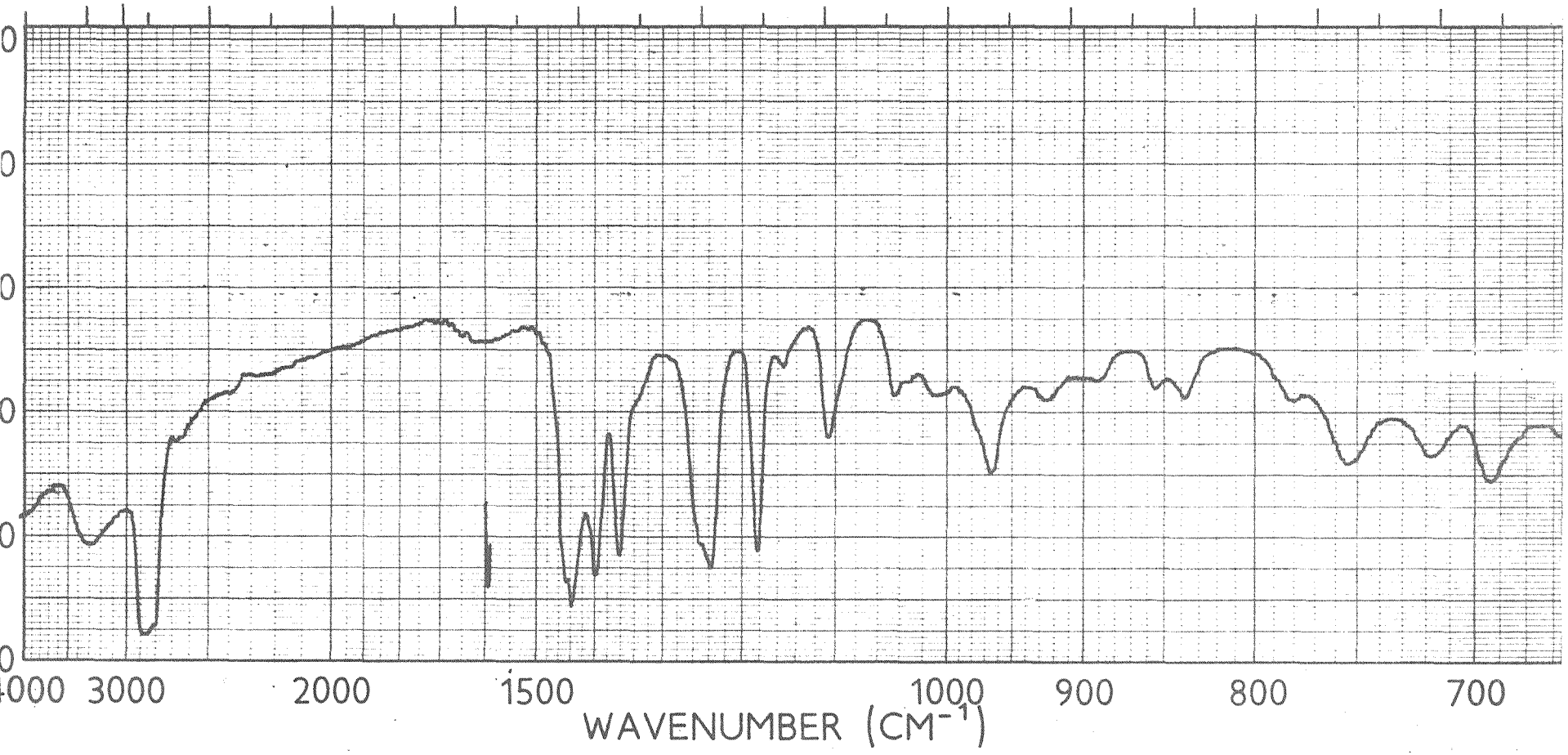
OPERATOR

DATE

REMARKS The regions 4000–2000 and 1500–1300 cm⁻¹ were obtained by superimposing a hexachlorobutadiene mull spectrum.

PERKIN-ELMER

PART No. 471-5049



SAMPLE

$Fe(RS^-)_2$

ORIGIN

PHASE

SOLVENT nujol.

CONC.

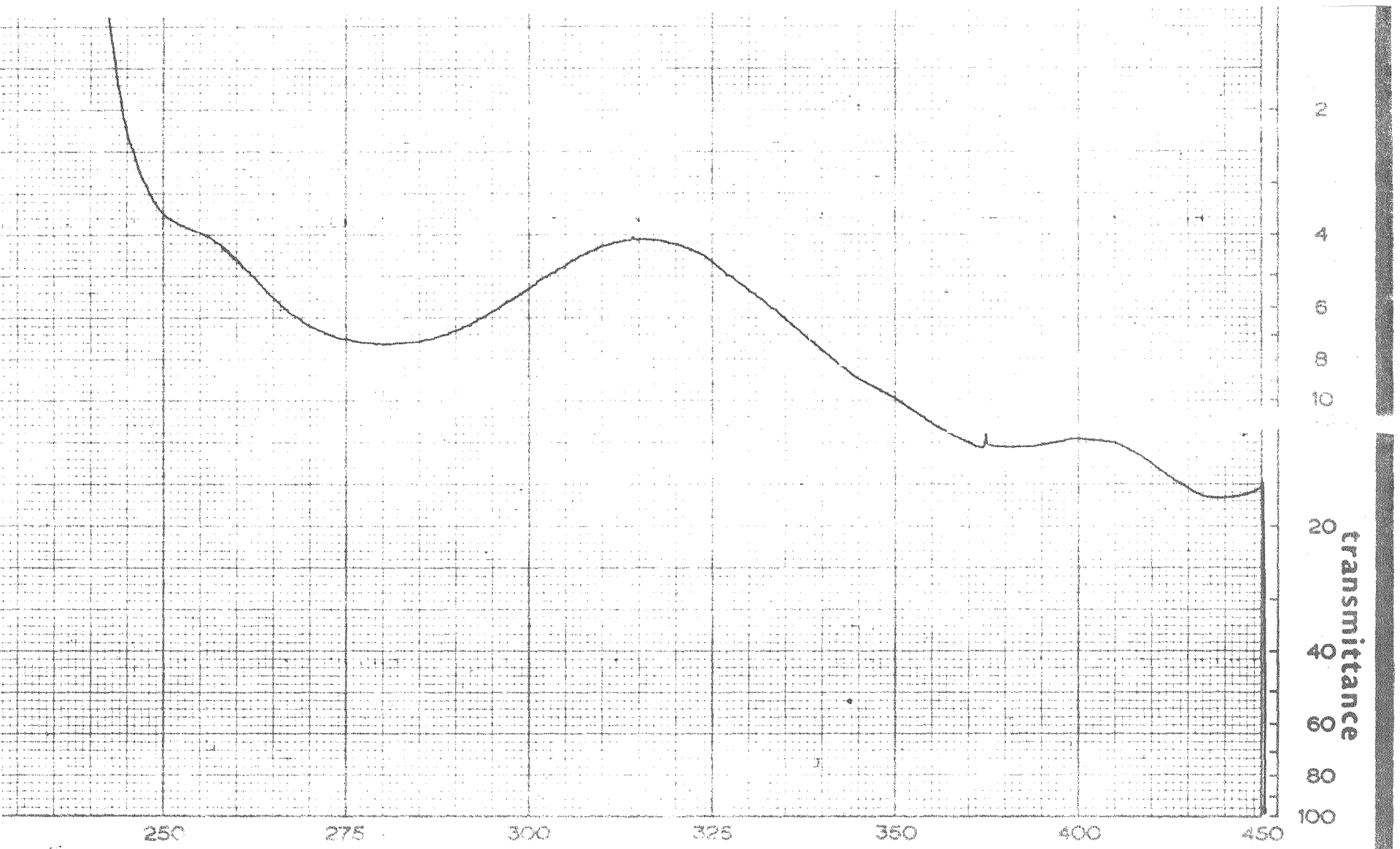
CELL PATH

REFERENCE

SCAN SPEED SLIT

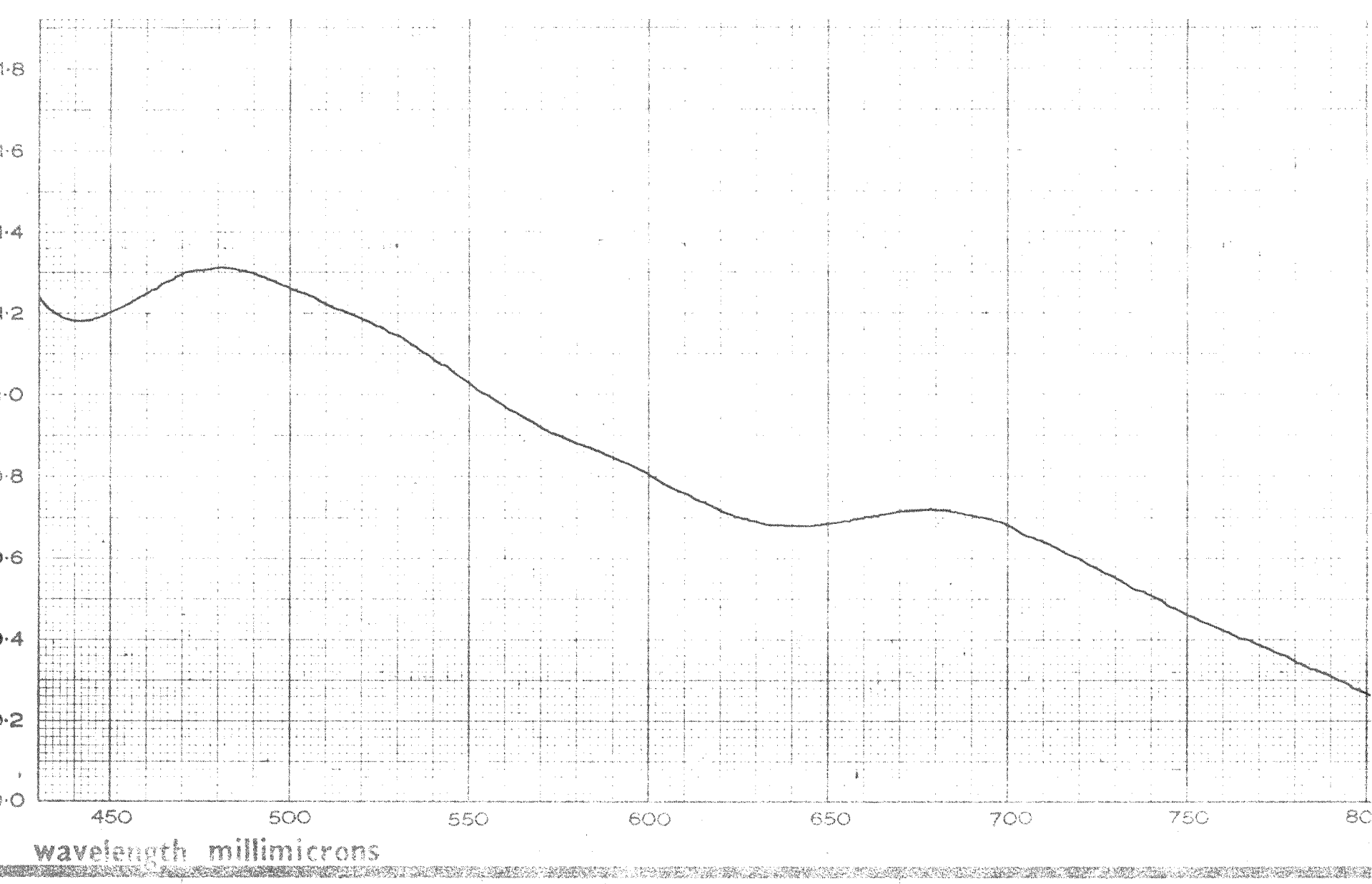
OPERATOR DATE

REMARKS



Fe. Pr. I.
Fe. Et. I.

CONCENTRATION
REFERENCE
SCAN SPEED FAST SLOW
DATE
REF. NO.



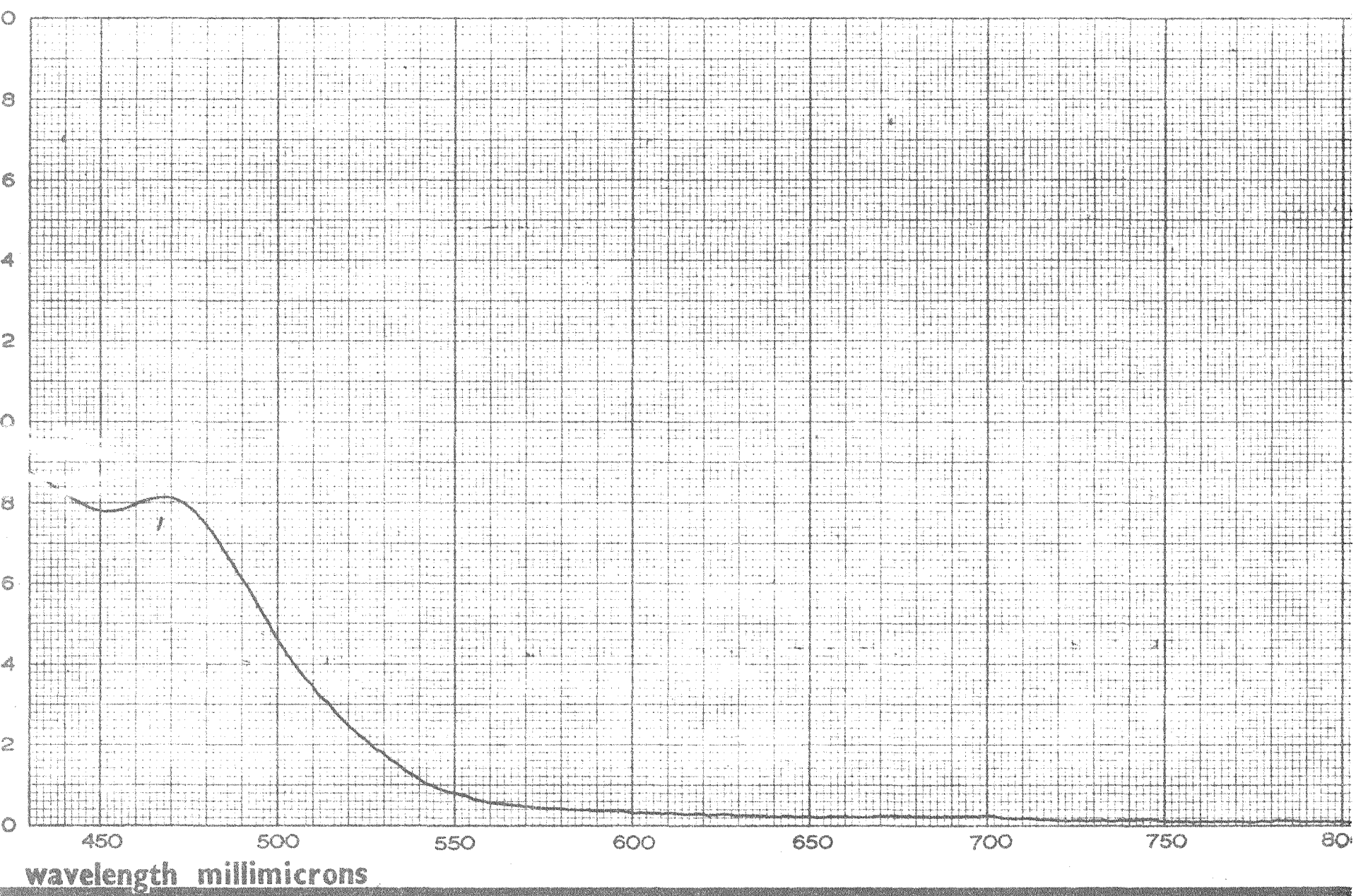
SIGN WITH INDEX
N THE RECORDER

SAMPLE NO. / FORMULA

Fe. Pr. I.
Fe. Et. I.

REFERENCE

DATE



SN WITH INDEX
THE RECORDER

SAMPLE AND FORMULA

Fl. Et. Bn.

CONCENTRATION

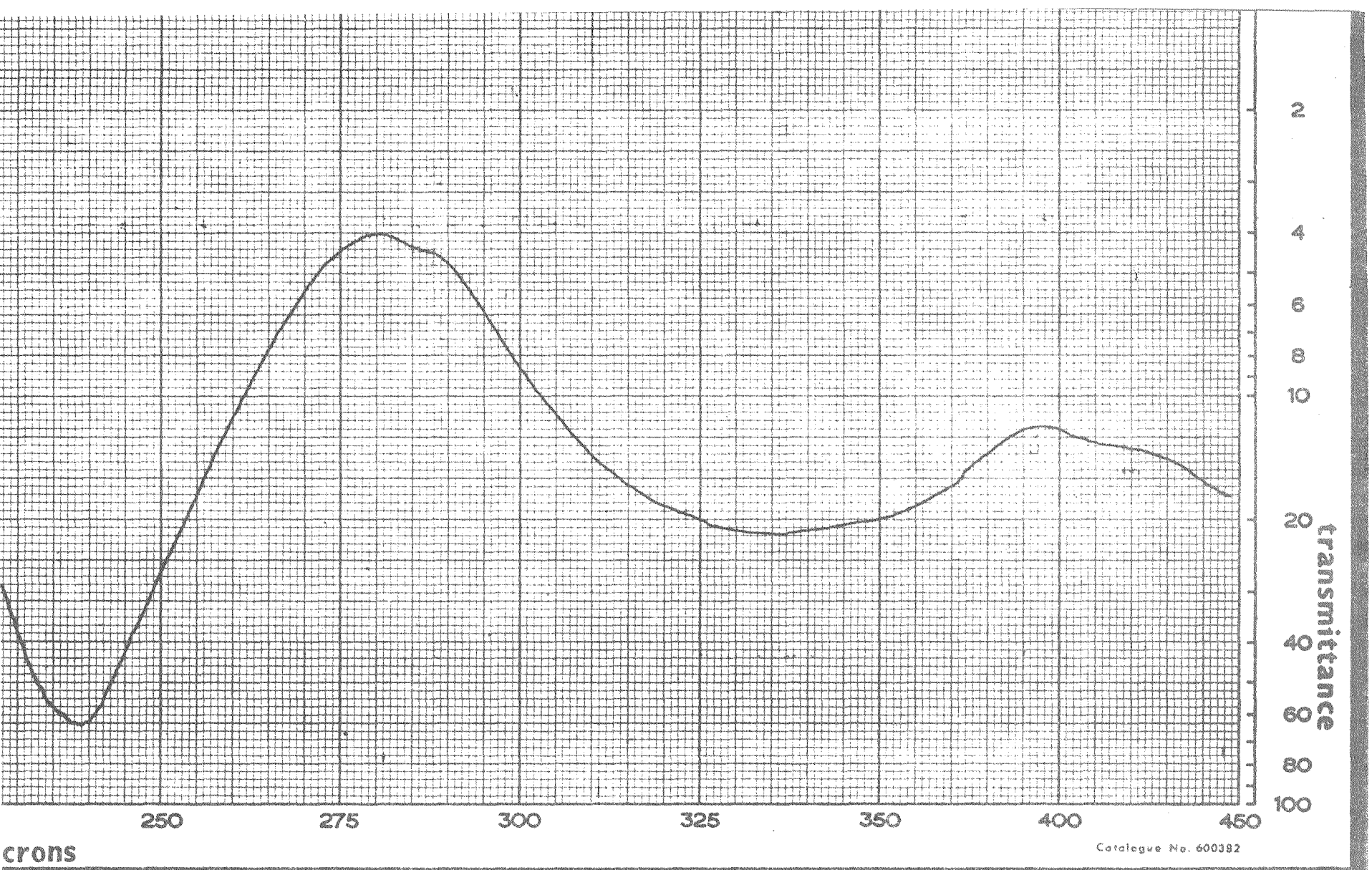
REFERENCE

PATH LENGTH M.M.

SCAN SPEED FAST

DATE

OPERATOR



Catalogue No. 600382

LA

Fe. et. Br.

CONCENTRATION

REFERENCE

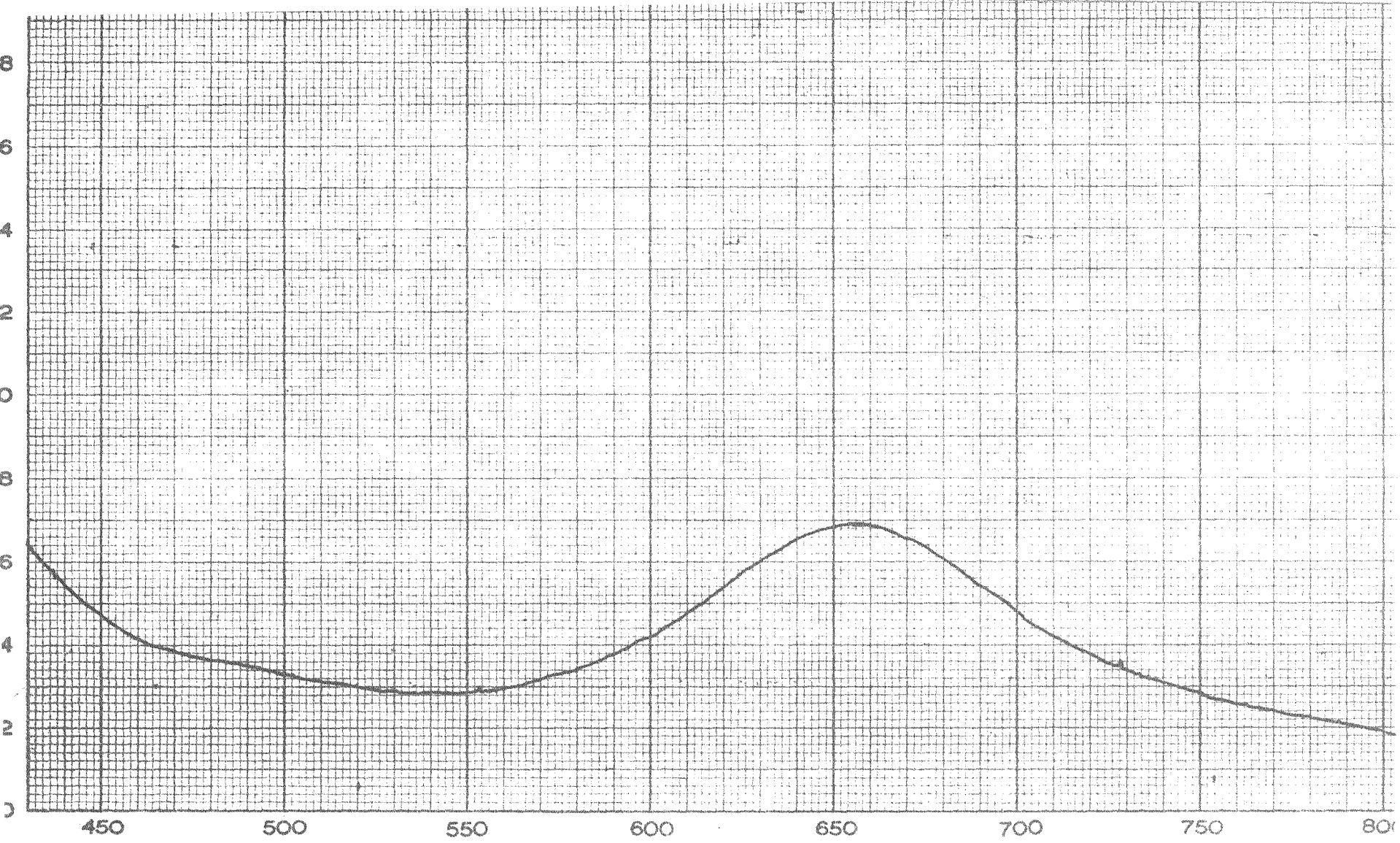
PATH LENGTH MM.

SCANSPEED FAST [X] SLOW [ ]

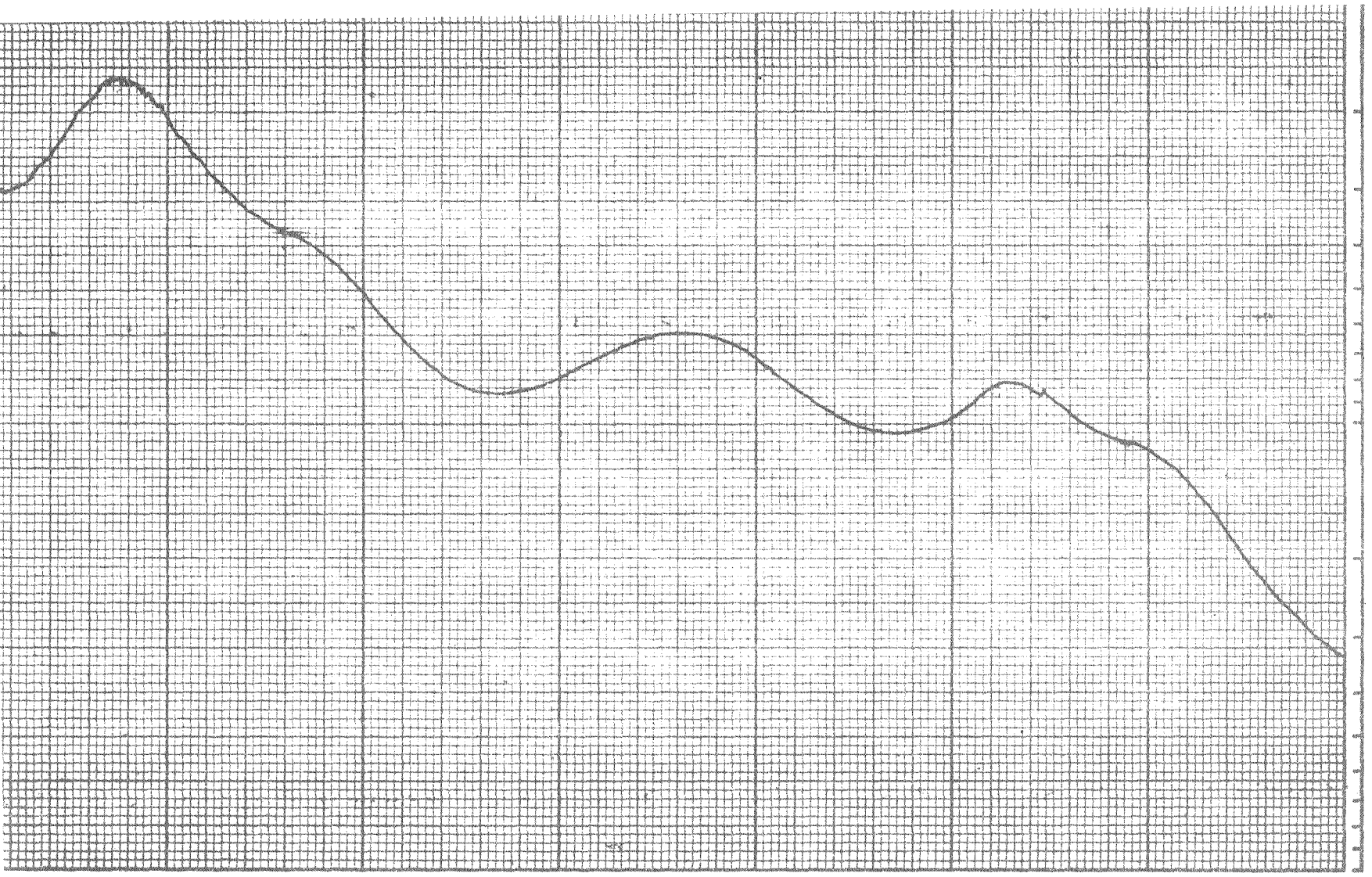
DATE

OPERATOR

REF. NO.



WITH INDEX HE RECORDER	SAMPLE AND FORMULA $Fe(RS^-)_2$	CONCENTRATION REFERENCE PATH LENGTH M.M.	SCAN SPEED FAST DATE OPERATOR



rons

Catalogue No. 600382

$Fe(RS^-)_2$.

CONCENTRATION

REFERENCE

PATH LENGTH MM.

SCANSPEED FAST ☐ SLOW ☐

DATE

OPERATOR

M.P. No.

Bibliography

1) Reid E., "Organic Chemistry of Bivalent Sulphur" Chemical Publishing Co., New York, 1, 1958, a) 108, b) 14, c) 142, d) 4, 1960, 208-33.

2) Livingstone S., Quart. Rev., 19, 1965, a) 386-425, b) 387-8, c) 416-422, d) 422, e) 413.

3) Kuzminskii A., Zaitzev V. and Lezhnev N., Rubber Chem. Technol., 1963, 541-6.

4) Calcoott W. and Lee I., U.S. Patent 1785513, Chem. Abs. 25, 1931, 483.

5) Mayr C. and Gebauer A., Chem. Abs. 33, 1939, 5320.

6) Weiss U., U.S. Patent 2520293, Chem. Abs. 46, 1952, 1344.

7) Richardson C. and Smith C., J. Agr. Chem., 1926, 598.

8) Imp. Chem. Ind. Ltd., Brit. Patent 520505, Chem. Abs. 36, 1942, 595.

9) Dimsdale W. and Robinson R., U.S. Patent 24328, Chem. Abs. 42, 1948, 2194.

10) Hall D. and Evans M., Nature, 223, 1969, 1342-8.

11) Cotton F. and Wilkinson G., "Advanced Inorganic Chemistry"., Interscience Publishers, New York, London, Sydney, 3rd Edition, 1972, a) 596, b) 872, c) 563.

12) Dwyer F. and Mellor D., "Chelating Agents and Metal Chelates", Academic Press: London and New York, 1963, 120-9.

13) Jorgensen C., "Inorganic Complexes", Academic Press, London and New York, 1963, a) 131-47, b) 139, c) 135.

14) Tschugaeff L., Ber. Dtsh. Chem. Ges., 1928, 2222.

15) Manchot W. and Gall H., Chem. Abs. 22, 1928, 2892.

16) Cannan R. and Richardson G., Biochem J., 1928, 1242-62.

17) Kettle S. and Orgel L., J. Chem. Soc. 1960, 3890-1.

18) Hieber W. and Kaiser K., Chem. Abs. 72, 1970, 38382.

19) Reihlen H., Friedolsheim A. and Oswald W., Chem. Abs. 22, 1928, 4476.

20) Coucouvanis D., Lippard S. and Zubieta J., J. Am. Chem. Soc. 91, 1969, 761-2.

21) Kimura T., "Structure and Bonding", Springer-Verlag, Berlin-Heidelberg New York, 5, 1968, 1-41.

22) Yang C. and Huennekens F., Biochemistry 1970, 2127-33.

23) De Beer J. and Haines R., J. Chem. Soc. (A) 1970, 288.

24) De Beer J. and Haines R., J. Organometal Chem., 1970, 757-67.

25) Coucouvanis D., Lippard S. and Zubieta J., J. Am. Chem. Soc. 92, 1970, 3342-7.

26) Manchot W. and Gall H., Chem. Abs. 23, 1929, 785.

27) Reihlen H. and Friedolsheim A., Ann. 457, 1927, 71-82.

28) Ramanani R. and Shanmuganathan S., Curr. Sci., 1968, 39-40.

29) Larkworthy L., Murphy J. and Phillip D., Inorg. Chem., 7, 1968, 1436-43.

30) Counter F., Duvall R., Foye W. and Vanderwyk R., J. Am. Pharm. Assoc., 49, 1960, 140 - 3.

31) Ospanov K. and Rozhdestvenskaya Z., Chem. Abs. 66, 1967, 25585.

32) Vasil'eva E. and Nedopekin T., Chem. Abs. 54, 1960, 24370.

33) Vol'f A., Chem Abs. 54, 1960, 18162.

34) Hieber W., Bader G. and Ries K., Chem. Abs. 26, 1932, 1209.

35) Hieber W. and Kaiser K., Chem. Abs. 69, 1968, 24095.

36) Ray P. and Mukherjee P., Chem. Abs. 24, 1930, 1814.

37) Forster A., Cooper C. and Yarrow G., J. Chem. Soc. 1917, 809.

38) Coucouvanis D., "Progress in Inorganic Chemistry", Interscience Publishers, 11, 1970, 233-357.

39) Thorn E. and Ludwig R., "The Dithiocarbamates and Related Compounds", Elsevier, New York, 1962.

40) McCleverty J., "Progress in Inorganic Chemistry", Interscience Publishers, London, New York, Sydney, 10, 1969, 49-222.

41) Korshunov M., Kuzovleva R. and Furawa I., Chem. Abs. 72, 1970, 3029.

42) Reppe W. and Freytag A., Chem. Abs. 35, 1941, 5909.

43) Lazier W., Signaigo F, and Werntz J., U.S. Patent 2402643, Chem. Abs. 40, 1946, 5765.

44) Shostakovskii M., Prilezhaeva E. and Uvarova N., Chem. Abs. 49, 1955, 9483.

45) Feher F. and Vogelbruch K., Chem. Abs. 54, 1960, 2152.

46) Kabachnik M., Godovikov N., Paikin D., Shabanova M., Efimova L and Gampu N., Chem. Abs. 54, 1960, 10830.

47) Reppe W. et al., Chem. Abs. 51, 1957, 9583.

48) Eliel E. and Naumann B., J. Org. Chem., 35, 1970, 3641-6.

49) Kensler J., Abels J. and Rhoads C., J. Pharmacology, 88, 1946,1947

50) Schrader G., U.S. Patent 2597534, Chem. Abs. 47, 1953, 4357.

51) Geldmacher M. and Mallinckrodt Weigel U., Chem. Abs. 59, 1963, 10708.

52) Goldsworthy L., Harding G. and Norris W., J. Chem. Soc. 1948, 2177-9.

53) Chadaeva N., Kamai G. and Mamkov K., Chem. Abs. 69, 1968, 106838.

54) Leggetter B. and Brown R., Canad. J. Chem., 1963, 2671-82.

55) Kaufmann G., Jorgensen C. et al., Inorg. Chem. 2, 1963, 1233.

56) Welti D. and Whittaker D., J. Chem. Soc., 1962, 4372.

57) Scott D. and McCullough J., J. Am. Chem. Soc. 80, 1958, 3555.

58) Cotton F., Oldham C. and Walton R., Inorg. Chem. 6, 1967, 220-1.

59) Bellamy L., "Infrared Spectra of Complex Molecules", Methuen, London, 1958, 350.

60) Adams D., "Metal Ligand and Related Vibrations", E. Arnold, London, 1967, 97-106.

61) Earnshaw A., "Introduction to Magnetochemistry", Academic Press, London and New York, 1968, a) 60-6, b) 34.

62) Figgis B., "Introduction to Ligand Fields", Interscience Publishers, New York, London, Sydney, 1966, a) 204-14, b) 225.

63) Jorgensen C., Adv. Chem. Phys., 1965, 52-3.

64) Butler I., and Spendjian H., J. Organometal. Chem. 18, 1969, 145.

65) Pettit R. and Collins R., J. Chem. Phys. 39, 1963, 3433.

66) Johnson B., et al., J. Chem. Soc. (A), 1968, 1043.

67) Hieber W. and Bader G., Chem. Abs. 23, 1928, 353.