SYNTHESIS AND CHARACTERIZATION OF SILVER(I) -ANTHRANILIC ACID;-N-PHENYL ANTHRANILIC ACID; -1-NITROSO-2-NAPHTHOL; AND -2-NITROSO-1-NAPHTHOL

SCHOOL OF GRADUATE STUDIES

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ELIZABETH YOHANNES

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by

Elizabeth Yohannes
Department of Chemistry
Science Faculty

Approved by:

Dr. Rimma Gridassova Advisor	Gridassova
Dr. M.F. Smith Examiner	
Dr.B.S. Chandravanshi Advisor	
Dr. Fikru Tafesse Examiner	Fikru Tafesse
Dr. Abdulkadir Examiner	A. Kadir

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ELIZABETH YOHANNES

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TO SCIENCE, GOD AND HUMANITY

AND

TO HUSSEN MOHAMMED

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ABBREVIATIONS

bipy	Bipyridine
phen	1,10-phenanthroline
DPP	4,7-Diphenyl phenanthroline
H_2DAMTNP	Diamine methylthio nitrosopyrimidine
tu	Thiourea
PT18C6	Pyridone thio 18 crown 6
$T_2$18C6	Dithio 18 crown 6
IR	Infrared
NMR	Nuclear magnetic resonance

ABSTRACT

Complexes of silver(I) with anthranilic acid, N-phenyl anthranilic acid, 1-nitroso-2-naphthol and 2-nitroso-1-naphthol have been synthesized. The yield of all the complexes have been found to be very good(>80%). The physical properties of the complexes have been studied. The complexes were found to be free from nitrate ion which indicated that the complexes were not in the form of ion pairs but were neutral species. All the complexes have been found to be insulators and not conductors. The composition of all the complexes were found to have a 1:1(M:L)molar ratio. All the complexes have been characterized by elemental analysis, electronic, infrared and nuclear magnetic resonance spectral studies and tentative structures of the complexes have been suggested.

1. INTRODUCTION

1.1. Occurrence and Application

Silver is very widely distributed in inanimate nature and is a major component of a wide range of minerals. It also occurs in smaller quantities in very many base metals ores. Sea water contains an estimated 0.01 ppm and the over all terrestrial concentration is considered to be ≈ 0.1 ppm. In contrast to the preceding group IB element Copper, it appears to be non-essential to life but is nevertheless found in trace quantities in wide range of living organisms, e.g. in the liver (-.005 - 0.001 %) and pancreas (0.0003 - 0.0001%) of cattle and in pacific marine organisms.

Silver is found native, usually associated with silver ores in the upper portions of the silver-bearing veins. In these environs native silver is of secondary origin, formed chemically in past ages by reduction of a portion of the ore body. Most of the world's source of native silver are exhausted and the most important minerals are: argentite or silver glance, Ag_2S; pyrargyrite or ruby silver, Ag_2S-Sb_2S_3; horn silver or chlorargyrite, AgCl; stromeverite, AgCuS and provsite, $3Ag_2S.As_2S_3$.

The germicidal properties of silver, although not recognized as such, have been utilized since the times of the ancient Mediterranean and Asiatic cultures, references being made to the use of silver vessels to prevent spoilage of beverages, and silver foil or plates in the surgical treatment of wounds and broken bones.

To primitive life forms silver is as toxic as the most powerful chemical disinfectants and this, coupled with its relative harmlessness to animate life, gives it great potential as disinfectant. The use of silver in agriculture as a potential fungicide,

as a seed disinfectant and as soil disinfectant have been investigated, but in these applications care has to be exercised as damage to the plants themselves is easily sustained.

Although silver is extremely toxic to low life forms, higher life forms are much more tolerant and several uses of silver, based on the antiseptic action of small concentrations of silver ions, have been developed in medicine. Continued ingestion of silver compounds in man leads to development of "Argyria",a condition in which a general discoloration of the skin, internal organs, mucous membranes, etc, is produced, caused by the deposition of silver particles in the tissues [1].

Silver also finds many industrial uses. It is used for silver plating vessels, for making mirrors, to measure radioactivity of the sample[2], to make materials which are used for purifying tap water [3]. On account of its softness it is alloyed with copper for making coins, it is used for jewellery and decorative purposes. Silver is also used to make light sensitive compounds for coating photographic plates, film and paper [4]. In electrical industry it is used for making electrical contacts and silver amalgam is used in filling teeth.

The majority of silver alloys of industrial importance are formed with the elements Cu, Au, Mg, Pd, Pt and Sn. Silver copper alloys are used in silver ware and until recently as coinage alloys. They are used where hardness and wear resistance greater than that of pure silver is required and to some extent for electrical contacts, for which purpose nickel in small amount is added; silver gold alloys are used for electrical contacts and jewellery. Copper containing silver gold alloys are used in industry; silver magnesium alloys have found application in the electronic industry particularly as a spring member in relays; silver palladium and silver platinum alloys

are used in electrical contacts; silver tin alloys are used in dental amalgams and low temperature solders [1].

1.2. General Properties and Chemistry of Silver.

Silver is a noble metal. It is a white, lustrous, soft and malleable metal (m.p. 961°c) with the highest known electrical and thermal conductivity [5], a very high reflectivity and probably the lowest emissivity (black body coefficients) of all the elements. Lying near the end of the transition metal series, silver has $4d^{10}\ 5s^{1}$ electron configuration with its small size and relatively large nuclear charges, this atom has little tendency to lose electrons and be oxidized. This low reactivity is evident in its positive reduction potentials.

$$Ag^{2+} \xrightarrow{+1.98V} Ag^{+} \xrightarrow{+0.80V} Ag$$

A relatively large positive reduction potential of silver explains why the element occur in the free state to some extent and do not react with non oxidizing acids except under extreme conditions [6].

Silver(I) is a mild oxidizing agent ($E^{0}_{Ag+/Ag} = 0.80$) reduced by a variety of substances to metallic silver. It has a strong tendency towards complex formation, even in the monovalent state, and compounds of silver when the metal is in its high valency state owe their existence, with few exceptions, to the stabilizing effect of complex ion formation. The donor atoms can be carbon, nitrogen, phosphorous, arsenic, oxygen, sulphur, the halogens and, in a few complexes metals [7]. It is one of the few metals to exhibit co-ordination number 2 characteristically when in the mono positive state, other coordination numbers favored being 3 and 4 [8 - 10]. Chelation in silver complexes is rare and is limited to systems where sulphur and /or oxygen and /or

nitrogen are the donor atoms. The affinity being much greater for sulphur than oxygen.

For monodentate ligands, the complex ions, $AgL+$, AgL_2+, AgL_3+, and AgL_4+ exist. The step wise stability constants K_1, K_2 are usually high whereas K_3 and K_4 are relatively small. The main species are hence, AgL_2+; which is linear. Because of this, chelating ligands can not form simple ions, and they give polynuclear complexes instead [11].

Silver(II)is too strong an oxidizing agent ($E^0_{Ag^{2+}/Ag^+} = +1.98$ V) to exist in the presence of many substances. Thus the compounds of divalent silver exhibit paramagnetic properties. The chemistry of divalent silver is often neglected although the argentic(II) ion is readily accessible and will give fairly stable aqueous solutions when strongly acidified with non reducing acids, e.g. an acidic solution of argentous salt can be oxidized by persulphate ion, fluorine or ozone to give the argentic(II) ion. In particular the oxidation by ozone of nitric acid solutions of argentous ion has been studied in detail[12-16]. The solutions are colored and paramagnetic, the color being dependent on the nature the acid used to acidify the argentous salt solution. This color effect, together with the result of kinetic studies, suggest that the argentic(II) ion is coordinated with the anion in solution.

Silver(II) is stabilized by coordination, particularly with nitrogen containing heterocycles. The complexes formed are usually four-coordinate with a square planar configuration. Typical examples are compounds with pyridine $[Agpy_4]X_2$[1], dipyridyl $[Ag(dipy)_2]X_2$[1], tripyridyl [AgtripyX]X[1], and ortho-phenanthroline $[Ag(o\text{-}phen)_2]X_2$[1]. A general method for preparing these complexes is to precipitate the persulphate as a sparingly water-soluble, yellow to dark, crystalline powder by oxidation of an argentous salt solution with potassium persulphate in the presence of

an excess of the appropriate ligand. Complexes of other anions are subsequently prepared from these persulphates by double decomposition reactions. Provided the ligand molecule is not oxidized, ozone can replace persulphate as the oxidizing agent in most preparations[14]. Alternatively the pyridyl and dipyridyl complexes have been obtained by anodic oxidation techniques[1].

Silver(III) (ionization potential 35.9 eV) electronic configuration [Kr] $4d^8$ $5s^0$ and the compounds of trivalent silver exhibit diamagnetic properties. It is extremely doubtful whether the uncomplexed silver(III) ion can exist, however it can be stabilized by coordination; for example, the stability of silver(III) is greatly increased when coordinated to ethylene bidiguanide and stable salts with the composition $[Agen(bigh)_2]X_3$[1] have been obtained, where X $=HSO_4^-$, ClO_4^-, NO_3^- and OH^-. Stabilization of silver(III) by coordination with biguanide $C_2H_7N_5$ has also been achieved and the brown, sparingly soluble crystalline compound $Ag(C_2H_7N_5)_2(OH)SO_4.7H_2O$ obtained by the $K_2S_2O_8$ oxidation a cold aqueous solution of silver nitrate and biguanide sulpahte at p^H 6.5-7.

Silver is commonly detected by adding sodium chloride (NaCl) solution to give an insoluble white precipitate of silver chloride(AgCl) in acidic media. It is most commonly determined volumetrically by the Mohr[17] and Volhard[17] methods.

1.3. The Relevance of Silver Complexes

Most of silver complexes have great potential as chemical disinfectants. In recent investigations silver(I) form better valuable antibacterial and antifungal drugs with norfloxacin[18] and p-aminobenzene sulphonyl derivatives of aminopyrimidines [19-20]. Silver(I) complexes of phosphino hydrocarbons have showed significant cytotoxicity and are found to be tumor cell growth inhibitors[21]. Silver(I) complex of diphenyl carbamodithiato-s,s' is used as liquid membrane in ion selective electrodes[27]. Therefore, it is worth synthesizing new silver complexes which may find important applications.

1.4. Objectives

The literature survey revealed that there is no report on the formation and/or characterization of silver(I) complexes with anthranilic acid, N-phenyl anthranilic acid, 1-nitroso-2-naphthol, and 2-nitroso-1-naphthol. Hence, the objectives of the present investigation were:

(i) to synthesize silver(I)-anthranilic acid; silver(I)-N-phenyl anthranilic acid; silver(I)-1-nitroso-2-naphthol and silver(I)-2-nitroso-1-naphthol complexes, and

(ii) to characterize the synthesized complexes by elemental analyses, electronic, infrared and NMR spectroscopic techniques.

2. LITERATURE SURVEY

The current intense interest in metal to ligand coordination chemistry of silver complexes[23] reflect their biological significance and structural diversity.

Silver(I) forms complexes mostly with ligands containing nitrogen, oxygen, sulphur, phosphorus and hydrocarbons.

2.1. Complexes of Silver(I) with Ligands Containing Nitrogen Donor Atoms

Silver(I) forms well defined complexes with ligands containing nitrogen donor atoms, such as 2-aminopyrimidine, 2,2'-bipyridine(2,2'-bipy),4,4'-bipyridine(4,4'-bipy) , 1,10-phenanthroline(phen) ,etc.

Silver(I) forms 1:2 complex with 2-aminopyridine[24]. Coordination occurs between Ag(I) and heterocyclic nitrogen atom and amino groups. The structure of the complex has been established based on infra Red and X-ray studies.

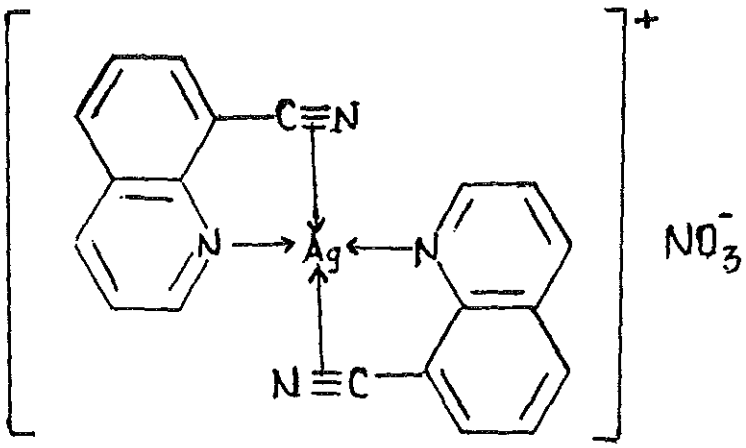
Silver (I) forms 1:1 complexes with the heterocyclic bases; 2,2'-bipyridine (2,2'bipy); 4,4'-bipyridine (4,4'bipy); 1,10 - phenanthroline (Phen) [25]. Coordination occurs between Ag(I) and heterocyclic nitrogen atoms. The structure of the complex have been established based on infrared [25] and laser mass spectrometry [26].

Silver (I) forms a polymeric complex with 4,6-diamine 2-methylthio-5-nitroso pyrimidine (H_2DAMTNP) [27]. Coordination occurs between Ag(I) and N(1) and N(3) atoms. Structure of the complex has been established based on ^{1}HNMR and IR - spectra.

A silver (I) complex of the bisamide ligand [$Ag(LH_2)NO_3.2H_2O$] (LH_2 = N,N'(dipicolyl)-1,8-naphthylene diamine) was prepared [28] and characterized by X -

ray powder patterns, conductometric measurements and infrared spectral data.

Silver (I) complex of the ligand 8-cyanoquinoline $[M(8\text{-cynoquinoline})_2]X$ ($M = Ag$, $X = NO^{3-}$) has been prepared [29]. In this complex coordination occurs between Ag(I) and heterocyclic nitrogen atom and cyano group. Up on coordination, the 8-cyanoquinoline shows small shifts to lower energy in the nitrile stretching frequency which are attributed to perpendicular nitrile - metal interaction. Structure of the complex has been established based on infrared, UV - visible and ESR spectroscopy.



8-Quinolinol forms silver (I) and silver (II) complexes with silver acetate [30]. The coordination occurs between silver and both heterocyclic nitrogen atom and oxygen atom. The oxidation state of silver in the complexes has been established to be Ag(I) and Ag(II) , respectively, based on the titration

f bromine with the complex. Whereas Block *et. al* [31] established the oxidation state of silver in both the complexes to be Ag(I). Their conclusions were based on the fact that the solid complex when placed in a modified curie - cheveneau balance, gave a deflection in the diamagnetic direction.

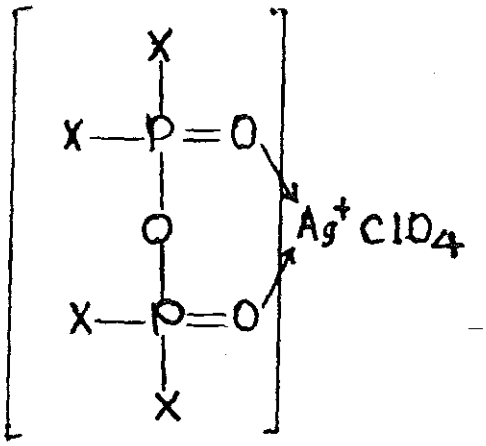
Silver (I) complexes of 1,8-diisocyano-p-menthane has been reported [32].

The complex is unidimensional polymeric rganometallic material $(AgL_2Y)_n$ where Y = PF_6^-, BF_4^-, or NO_3^-. Coordination occurs between Ag(I) and isocyano group. A structure has been assigned for this polymeric material based on X-ray powder diffraction studies.

2.2 Complexes of Silver (I) with Ligands Containing an Oxygen Donor Atom

Few complexes of silver(I) with ligands containing oxygen donor atoms are known. Typical oxygen silver(I) complexes which has been prepared are those with octamethylpyrophosphoramide, D-glucono-δ-lactone, ß-D-glucurono - τ - lactone and with 2, 6 - disubstituted aryl isocyanides.

Silver(I) forms a 1:2 complex with octalmethylpyr-ophoshoramide [33]. Octamethylpyrophosphoramide is believed to form a six-membred ring with the metal ion in which the phosphoryl oxygens are the donor atoms. The structure of the complex has been established based on UV-visible and infrared spectra.



Where X = NMe_2.

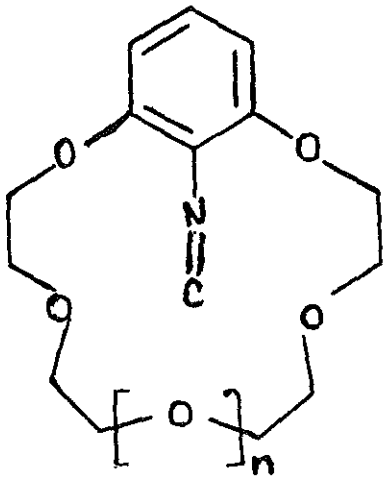
A silver(I) complex of D-glucono-δ-lactone has been prepared [34]. The

interaction between D-glucono-δ-lactone and Ag(I) ion was studied in aqueous solution and solid compounds of the type Ag(D-gluconolactone)NO_3 and Ag(D-gluconate) were isolated and characterized. Spectroscopic properties and other chemical evidence suggested that the Ag(I) ion, in the Ag(D-gluconolactone)NO_3 compound is double coordinated binding to a sugar molecule via carbonyl oxygen and the nitrate group, whereas the Ag(D-gluconate) is dimeric with each Ag(I) ion being bonded to ionized carboxyl oxygen of the first sugar anion and the carbonyl oxygen atom of the second sugar, resulting in a linear double coordination geometry around each Ag ion.

The silver(I) complex of ß-D-glucurono-τ-lactone has been prepared [35]. The interaction of ß-D-glucurono-τ lactone(L) with $AgNO_3$, $AgClO_4$, AgOAc, and Ag_2CO_3 was studied in aqueous solution and $AgLNO_3.H_2O$, $AgLClO_4.H_2O$ and AgL'(HL' = D-glucuronic acid) were prepared and characterized by means of Fourier-transform infrared spectroscopy, and X-ray powder diffraction. This and other evidences showed that in $AgLX.H_2O$(X = NO_3^- or ClO_4^-) Ag(I) is 2-coordinated, binding to a lactone carbonyl oxygen atom (06) and to a nitrate perchlorate oxygen atom, whereas AgL' is dimeric with each Ag(I) ion bonded to two sugar anions via O6 and O6' carboxyl oxygen atom resulting in linear 2-coordinate geometry around each Ag ion.

Silver forms a 1:1 complex with the isocyanide crown ether (2,6-disubstituted aryl isocyanide crown ether) [36]. 2,6-disubstituted aryl isocyanide crown ethers are attractive candidates for incorporation into cyclic ligands as they show both strong σ-donor and π-acceptor bonding to metal. Coordination occurs between Ag(I) and isocyanide group and ring ether oxygen. The structure of the complex has been

established based on its infrared and UV- visible spectra.

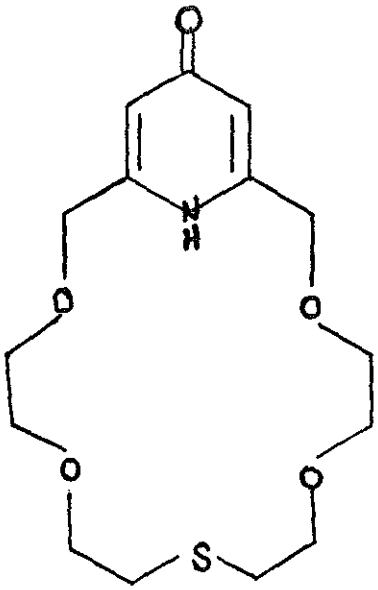


2,6-Disubstituted aryl isocyanide crown ether

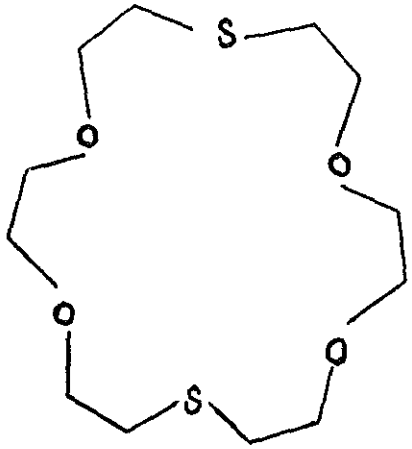
2.3. Complexes of Silver (I) with Ligands Containing Sulphur Donor Atom

Highly selective reagents for metal ions are of great importance to broad areas of analytical and separation chemistry. PT18C6 [37] was found to be a superior ligand which can discriminate Ag^+ from other strong thiophilic metal ions.

The normal selectivity order of Ag(I), Hg(II) and Pb(II) for most "soft", "border line" and even "hard" donor atoms and groups is: **Hg(II) > Pb(II) > Ag(I). But** successful reversal of this order of Hg(II) over Ag(I) was accompanied by insertion of a pyridone binding sub unit in the thiocrown ether ligand system



PT18C6



1,10-$T_2$18C6

Coordination occurs between Ag(I) and both heterocyclic nitrogen and sulphur and heterocyclic sulphur atoms in the two complexes, respectively. Three different techniques were used to investigate the metal ion - ligand binding equilibrium constant (K) for metal - ligand interaction were determined either potentiometrically or calorimetrically.[13] CNMR relaxation time (T1) and chemical shift (σ) measurements were made to provide information on ligand conformation, binding strength, and binding dynamics in solution.

Silver (I) complexes of thio- and seleno- semicarbizide ion complexes have been reported [38]. The IR spectra of AgLCl and $Ag_2L_3(NO_3)$ complexes were determined, and the ligand was found to be monodentate in Ag(I) complexes. Coordination occurs between Ag(I) and the sulphur or the selenium atom.

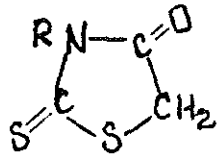
Silver(I) forms a 1:1 complex with 1,3,5-trithian [39]. Coordination occurs between silver(I) and sulphur atoms, in the 1:1 complex with 1,3,5trithian silver takes

up a tetrahedral and not a linear coordination. Since the maximum number of sulphur atoms available for coordination is three per silver atom it is necessary to complete the coordination spheres with water or the anion, which ever is the better ligand system. In the hydrated compounds tetrahedrally co-ordinated silver cations are bound by 1,3,5-trithian molecules to form polymeric sheets, neutral or cationic. In the anhydrous nitrate complex two kinds of crystallographically independent silver cations, one tetrahedrally, the other penta-co-ordinated, are bound by 1,3,5trithian molecules to form a cationic polymeric ribbon loosely associated to the anions. A structure has been assigned for this polymeric materials based on X-ray diffraction studies.

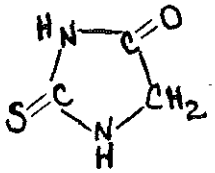
Silver forms a 1:2 complex with thiourea [40]. Thiourea (tu) is a chemically interesting ligand in that it has several different possible mode of binding to a metal ion. It may coordinate through the non bonding electron pairs of the nitrogen or via the sulphur atom. The sulphur itself may donate electrons by two different means: (a) electrons from the non-bonding sp^2 lobes or (b) electrons the S=C π molecular orbitals. Bis(thiourea)silver(I) chloride ($Ag(tu)_2Cl$) was first reported by Wardelli [40]. Although superficially the cation in this compound might be considered analogous to the ammoniated silver ion, particularly since a thiourea solution can be used to dissolve silver chloride. A preliminary communication has been published on this structure [41] and E.A. Vizzini et al.[40] presented the details of the analysis and the structure on the basis of X-ray diffraction studies.

Silver (I) complexes of rhodanine and a number of related heterocyclic compounds (I,II,III,IV,V,and VI) have been investigated by potentiometric titration and IR-spectroscopic studies [42]. A comparison of the behavior of suitably substituted compounds towards silver(I) ions has enable them to ascertain the function of each

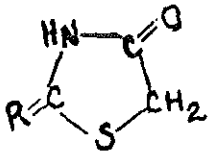
group in the rhodanine molecule with respect to silver, and to establish an analytical functional group for silver. A suggested structure that accords with the known composition and properties of silver rhodanide is given.



(I)



(II)



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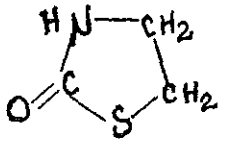

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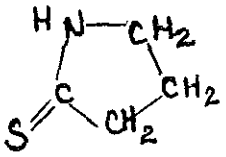
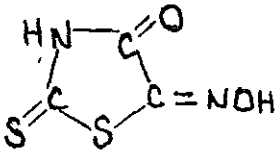
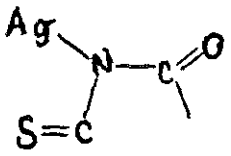


(V)

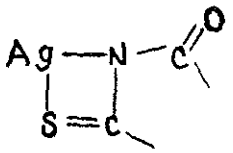


(VI)

The structures of silver rhodanide such as (VII) by Dubsky *et al*[42] and (VIII) by Yoe *et. al.* [42] and H. Lux *et al.* [42] are completely erroneous on the basis of W.I. Stephen *et al.* studies [42]. Therefore silver rhodanide would then have the structure (IX).



(VII)



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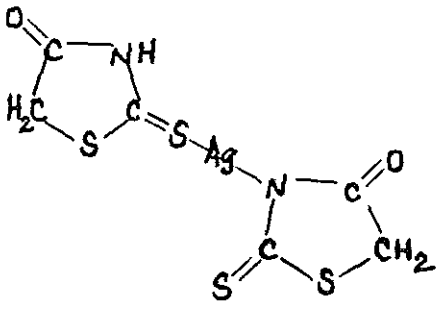


(IX)

2.4. Complexes of Silver (I) with Ligands Containing Phosphorus Donor Atoms

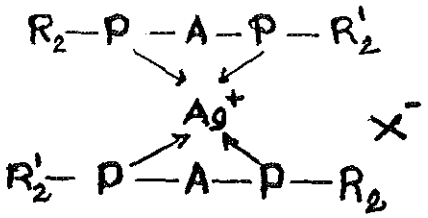
Silver (I) complexes of tri-p-tolyl phosphine and triethyl phosphite, have been elucidated primarily through analysis of ^{31}PNMR data [43]. The L_4Ag^+ cationic complex prevails in solutions at low temperatures for silver (I) salts except cyanide, iodide, bromide and chloride, provided that at least 4 equivalents of phosphorous ligands per silver salt are present. The ligands were labile in L_4Ag^+ as has been shown by loss of Ag-P coupling at temperatures above -70°C. The exchange was independent of free ligand concentration but dependent up on the nature of the counter an ion. Ligand lability was also found to be higher in the phosphine than in the phosphite system.

Silver(I) complexes of tetrakis(triphenyl phosphine) have been isolated by using metal salts with an ions having poor ligand properties, viz, ClO_4^-, BrO_3^-,NO_3^- [44]. All the complexes reported are white, stable solids. The complexes were characterized by IR spectroscopic studies.

Silver (I) complexes of triphenylphosphine and 5-phenyl dibenzophosphole $[Ag(L_n)]PF_6$ (n=1-4) have been prepared and characterized [45]. The step wise formation of $[Ag(L_n)]PF_6$ (n=1-4) was observed at 193 K by stopped-exchange solution ^{31}PNMR spectroscopy (L=5-phenyl dibenzophosphole, triphenyl phosphine). The 4 species observed as each ligand is gradually added to $AgPF_6$ in CH_2Cl_2 solution are identified by their characteristic chemical-shift and coupling constant data. The relative coordinating ability of the two ligands was further assessed by a comparison of the $^1J(M-^{31}P)$ coupling constant in some representative complexes.

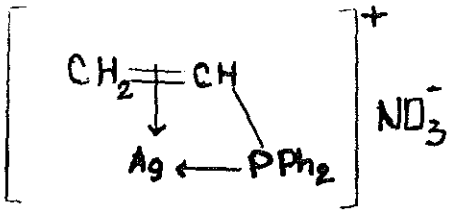
Silver(I) forms 1:2 complex with phosphinohydrocarbons [21]. Silver (I) is believed to form a tetrahedral coordination. The complex showed significant

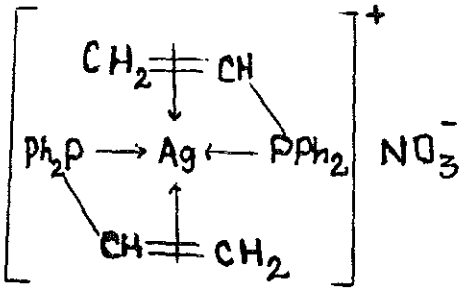
cytotoxicity and is also found to be a tumor cell-growth inhibitor.



[R,R' =Et(Un) substituted Ph, A=$(CH_2)_n$,cisCH:CH n=2,3, X=halogen, NO_{3^-},PF_{6^-}]

Silver(I) forms 1:1 and 2:1 complexes with vinyl diphenylphosphine [46]. In these complexes coordination occurs between Ag(I) and both the phosphorous atom and the vinyl double bond of the phosphine. The structure of the complexes has been established based on the infrared and ^1H and $^{31}PNMR$ spectral data.



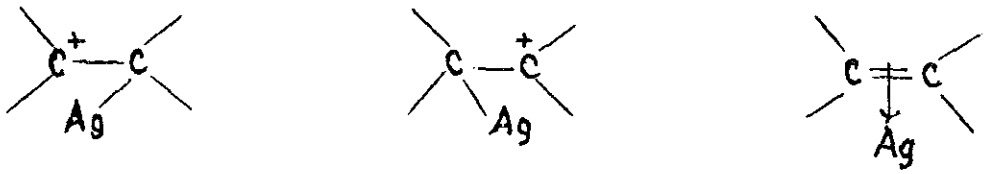


Silver(I) complex with triphenyl phosphine [47] $Ag(PPh_3)_3$ X was first reported by Alyea *et al.*[45]. and the formation of the complex was identified by stopped- exchange solution phosphorous $^{31}PNMR$ spectroscopy. Engelhardt *et al.* [47] presented the details of the analysis and the structure on the bases of X-ray crystallographic studies.

2.5 Complexes of Silver(I) with Hydrocarbons

Complexes between olefins and silver(I) have probably been more extensively studied by quantitative methods than those of any other metal ion [1]. Compounds between silver nitrate, perchlorate, fluoroborate, and straight and branched chain aliphatic olefins, cyclic olefins, diolefins, oxygenated olefin derivatives and aromatic hydrocarbons having been investigated.

In aqueous solution the reaction to form ethylenic complexes was found to be reversible and fast, and the more deeply buried the double bond the less stable the resulting complex [48]. Bonding is thought to be a resonant hybrid structure of and the



stability constants have been found to be much smaller for the silver(I) complexes than for the corresponding Pt(II) and Cu(II) complexes in cases where the comparison has been made [49,50]. In a recent investigation, Hewandos *et al.* [51] presented the details of the analysis and the structure on the basis of ^{1}HNMR spectroscopic studies.

Silver(I) forms complexes with a variety of aromatic hydrocarbons ranging from benzene itself through molecules of increasing complexity up to polycondensed benzenoid hydrocarbons.

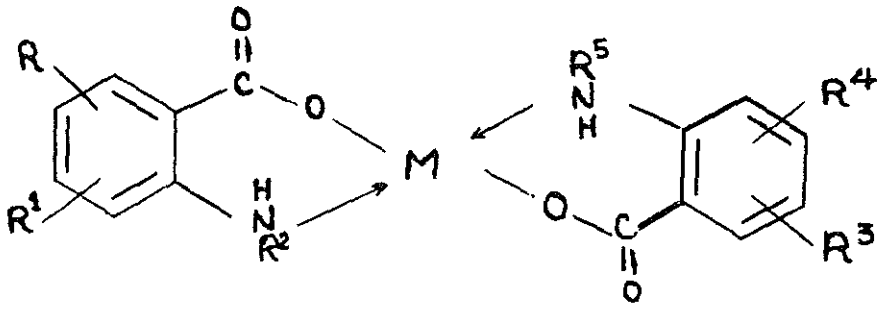
Coordination of polycyclic aromatic hydrocarbons with silver(I) is important in determining the carcinogenic potentials of the polycyclic aromatic hydrocarbons [52]. Furthermore, from a study of the crystal structure of the silver perchlorate- benzene complex it is evident that polarization of the π-bonding system leads to an increase in electron density in bonds nearest to Ag^+ ions and this effect is far more important

than charge transfer bonding in determining electron densities within the ring [53].

2.6. Complexes of Anthranilic and N-Phenyl Anthranilic Acid

Anthranilic acid and N-phenyl anthranilic acid form complexes with a variety of transition metal ion [54] with the exception of the rare metals; some examples are known for each periodic group, including the alkali [55] and alkaline earth elements [56].

Anthranilic and N-phenyl anthranilic acid complexes of divalent metal ion of the formula (I) are used as component of electrostatographic toner [56].



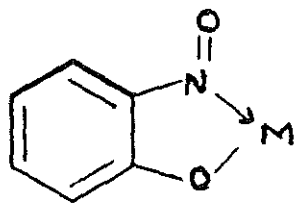
I

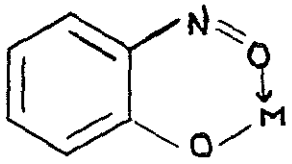
where R,R^1,R^3 and R^4=H,halo.,etc. and R^2 and R^5=H or Ph.

The two ligands are useful for toxicological drug analysis [57], as lubricating grease [58] and they promote the uptake of ferric Fe into Fe starved cell of R. leguminosarum [59].

2.7. Complexes of 1-Nitroso-2-naphthol and 2-Nitroso-1-naphthol

The ligands having a chelating site of 1-nitroso-2-hydroxy or 2-nitroso-1-hydroxy aryl group behave as a N,O-donating ligands toward metal ions such as Co(II), (III), Fe(II), Ni(II) and Pd(II) [60-62] whereas they behave as a O,O-donating ligand toward the other metals (e.g. Zr(IV)) [63]. The structures of each are schematically shown below.





3. EXPERIMENTAL

3.1. Apparatus and Chemicals

PYE UNICAM SP3-300 Infrared spectrophotometer Beckman Chem Mate pH-meter, Beckman Model 24 UV-visible spectrophot-ometer, Philips PM2517E multimeter and JEOL FX 90 Q FT NMR wereused. Silver nitrate (BDH), anthranilic acid (Hopkin and Williams), N-phenyl anthranilic acid (Hopkin and Williams), 1-nitroso-2-naphthol (Hopkin and Williams), 2-nitroso-1-naphthol (Hopkin and Williams), copper sulphate (BDH), potassium sulphate (BDH), sulphuric acid (BDH), sodium hydroxide (BDH, Analar), ethanol (Riedl-de Haen), diethyl ether (Riedel-de Haen), nitric acid (BDH), ammonia (BDH), potassium chromate (BDH), potassium hydrogen phthalate (BDH), borax (May and Baker), and sodium chloride (BDH) were used as received.

3.2. Synthesis of Silver(I)-Anthranilic acid Complex

Anthranilic acid, 2.8113 g(20.50 m moles), was dissolved in 10.25 ml of 2 M NaOH (20.50 m moles) solution. The pH of this solution was 6.8. The temperature of this mixture was raised to 70 °C. This mixture was added drop by drop, with stirring, to a warmed solution(70 °C) of 10.25 ml of 2 M $AgNO_3$ (20.50 m moles) solution. The white preci-pitate obtained was filtered while hot and was washed with small volumes of ice water, ethanol and diethyl ether, respectively. The product was dried at room temperature in a light protected desiccator. The yield was 4.800 g, 96%. The complex decomposed at 191.4 °C.

3 .3. Synthesis of Silver(I)-N-Phenylanthranilic Acid Complex

N-Phenyl anthranilic acid, 3.3265 g (15.6 m moles), was suspended in 10 ml of distilled water. The pH of this solution was brought to 10 with 2 ml of 2 M sodium hydroxide. The temperature of this solution was raised to 70 °C. This solution was added drop by drop to 7.8 ml of 2 M silver nitrate (15.6 m moles) solution. The white precipitate obtained was filtered and washed thoroughly with ice water and diethyl ether, respectively. The product was dried at room temperature in a light protected desiccator. The yield was 4.6500 g, 93%. The complex decomposed at 172 °C.

3.4 Synthesis of Silver(I)-1-nitroso-2-naphthol Complex

1-Nitroso-2-naphthol, 3.0906 g (17.85 m moles), was suspended in 15 ml of distilled water. The pH of this solution was brought to 11 with 5 ml of 2 M sodium hydroxide solution. This solution was added drop by drop to 8.93 ml of 2 M silver nitrate (17.85 m moles) solution. The brown precipitate obtained was filtered and washed thoroughly with water and diethyl ether, respectively. The product was dried at room temperature in a light protected desiccator. The yield was 4.7259 g, 94.52%. The complex decomposed at 152 °C.

3.5. Synthesis of Silver(I)-2-nitroso-1-naphthol Complex

2-Nitroso-1-naphthol, 3.0906 g (17.85 m moles), was suspended in 15 ml of distilled water. The pH of this solution was brought to 11 with 5 ml of 2 M sodium hydroxide solution. This solution was added drop by drop to 8.93 ml of 2 M silver nitrate (17.85 m moles) solution. The dark brown precipitate obtained was filtered and washed thoroughly with water and diethyl ether, respectively. The product was

dried at room temperature in a light protected desiccator. The yield was 4.3579 g, 87.16%. The complex decomposed at 155 °C.

3.6. Qualitative Tests for Silver and Nitrate Ions

3.6.1. Procedure for qualitative test of silver ion

All the complexes were decomposed in dilute sulphuric acid and each solution was divided into two portions. Sodium chloride solution was added in to each of the four portions of the solutions. A white precipitate was obtained in each case which indicated the presence of silver ion in each complex [64].

3.6.2. Procedure for qualitative test of nitrate ion

A few crystals of ferrous ammonium sulphate was added to each of the other four portions of the test solution, followed by the addition of one drop of concentrated sulphuric acid. There was no formation of brown ring around the ferrous sulphate crystals in each of the test solution which indicated the absence of nitrate ion in each of the test solutions [64]. The control test for the presence of nitrate ion was carried out by following the same procedure, replacing the test solution by silver nitrate solution. There was formation of brown ring around the ferrous crystals which indicated the presence of nitrate ion.

3.7. Procedure for Quantitative Determination of Silver(I) in the Complex

3.7.1. Silver(I)-anthranilic acid Complex

The complex (1.2198 g, 4.99 m moles) was decomposed in dilute nitric acid and the pH of the solution was adjusted to 7 with sodium hydroxide solution using glass stick dotting. This solution was diluted to 50 ml with distilled water. A 10ml aliquot of 0.10 N Nacl solution was pipeted out in to a 250 ml conical flask and 0.5 ml of 0.05 M potassium chromate indicator was added to it and titrated with silver(I)-anthranilic acid sample solution until the yellow color of the solution changed. The indicator blank was also determined by adding 0.5 ml of the indicator to about 25ml of water and then titerated with 10 times diluted silver(I)-anthranilic acid sample solution until the color corresponds to that of the sample solution which had just been titrated [17]. The titrations were done three times and the results are given in Table 1.

3.7.2. Silver(I)-N-phenyl anthranilic acid Complex

The complex (0.8002 g, 2.5 m moles) was decomposed in dilute nitric acid. This solution was diluted to 100 ml with distilled water. A 25ml aliquot of silver(I)-anthranilic acid sample solution was pipeted out in to a 250 ml conical flask. 5 ml of 6 N nitric acid and 1.0 ml of saturated ferric indicator solutions were added to the solution and the solution was titrated with 0.1040 N KSCN solution until a faint brown color of solution appeared [17]. The titrations were done four times and the results are given in Table 1.

3.7.3.Silver(I)-1-nitroso-2-naphthol Complex

The complex (0.6996 g, 2.495 m moles) was decomposed in dilute nitric acid. This solution was diluted to 100 ml with distilled water. A 25ml aliquot of silver(I)-anthranilic acid sample solution was pipeted out in to a 250 ml conical flask. 5 ml of 6 N nitric acid and 1.0 ml of saturated ferric indicator solutions were added to the solution and the solution was titrated with 0.1040 N KSCN solution until a faint brown color of solution appeared [17]. The titrations were done four times and the results are given in Table 1.

3.7.4.Silver(I)-2-nitroso-1-naphthol Complex

The complex (0.6996 g, 2.495 m moles) was decomposed in dilute nitric acid. This solution was diluted to 100 ml with distilled water. A 25ml aliquot of silver(I)-anthranilic acid sample solution was pipeted out in to a 250 ml conical flask. 5 ml of 6 N nitric acid and 1.0 ml of saturated ferric indicator solutions were added to the solution and the solution was titrated with 0.1040 N KSCN solution until a faint brown color of solution appeared [17]. The titrations were done four times and the results are given in Table 1.

3.8. Procedure for Quantitative Determination of Nitrogen in the Ligands and in the Complexes

The nitrogen content of the ligands and their complexes was determined by the Kjeldahl method [17].

The sample (0.5 g) was digested in concentrated sulphuric acid. The ammonia was distilled and collected in 50 ml of 0.05 M sulphuric acid. The excess acid was back titrated with 0.1 M sodium hydroxide solution using methyl red as indicator [17]. A blank determination for nitrogen was carried out by following the same procedure. The determination was done in triplicate.

The total nitrogen content in the complexes expressed as a percentage by mass, is given by the formula.

$$[((V_1 - V_2) - (V_3 - V_4))0.1401]/M$$

Where, V_1 is the volume, in millilitres, of the sulphuric acid solution used for the detetmination; V_2 is the volume, in millilitres, of the sodiun hydroxide solution used for the determination; V_3 is the volume, in millilitres, of the sulphuric acid solution used for the blank test and V_4 is the volume, in milliliters, of the sodium hydroxide solution used for the blank test.

Table 1. Volume of 0.1040 N KSCN used for the determination.

Complexes	Volume(ml) 0.1040 N KSCN	Average Volume (ml)	95% confidence limit
Ag-anthranilic acid	10.0[1]		
	10.1	10.1	10.1 ± 0.03
	10.2		
Ag-N-phenyl anthranilic	5.8		
	5.9	5.9	5.9 ± 0.13
	5.9		
	6.0		
Ag-1-nitroso-2-naphthol	5.8		
	5.9	5.9	5.9 ± 0.13
	5.9		
	6.0		
Ag-2-nitroso-1-naphthol	5.8		
	5.8	5.88	5.88 ± 0.14
	5.9		
	6.0		

[1]* Volume of unknown Ag-anthranilic acid.

Table 2. Volume of 0.1N NaOH used for the determination and for the blank test. The amount of silver complexes taken for the analysis in each case is 0.5 g.

Complexes	Volume(ml) 0.1N NaOH (m l)	$V_4 - V_2$	Average Volume	95% Confidence limit
Ag-anthranilic	6.2	19.2		
acid	6.3	19.3	19.3	19.3 ± 0.03
	6.4	19.4		
Blank-1	25.6			
Ag-N-phenyl	10.9	14.5		
anthranilic	11.0	14.6	14.6	14.6 ± 0.03
	11.1	14.7		
Blank-2	25.6			
Ag-1-nitroso-	8.9	17.3		
2-naphthol	9.0	17.4	17.4	17.4 ± 0.03
	9.1	17.5		
Blank-3	26.4			
Ag-2-nitroso-	9.0	17.3		
1-naphthol	9.1	17.3	17.33	17.33 ± 0.03
	9.1	17.4		
Blank-4	26.4			

Table 3. Determination of nitrogen in the ligands and the complexes

Ligand/ Complex	Sample Wt. (g)	N found (g)	N found (%)
Anthranilic acid	0.500	0.0493	9.86
Ag-anthranilic acid	0.500	0.0283	5.66
N-Phenyl anthranilic acid	0.500	0.0325	6.50
Ag-N-phenyl anthranilic acid	0.500	0.0214	4.28
1-Nitroso-2-naphthol	0.500	0.0400	8.00
Ag-1-nitorso-2-naphthol	0.500	0.0244	4.88
2-Nitroso-1-naphthol	0.500	0.0400	8.00
Ag-2-nitorso-1-naphthol	0.500	0.0243	4.86

3.9. Method for Recording the Infrared Spectra of the Ligands and Their Silver(I) Complexes

The infrared spectra of the ligands and the silver(I) complexes were recorded as solids (KBr discs).

3.10. Method for Recording the Visible Electronic Spectra of the Ligands and Their Silver(I) Complexes

All the complexes were insoluble in most common organic solvents but were soluble in DMSO. Thus the visible electronic spectra of the ligands and their silver(I) complexes were recorded in DMSO solution. The spectra of anthranilic acid and its silver(I) complex were recorded at 5.83×10^{-3} M and at 3.28×10^{-3} M, respectively; The spectra of N-phenyl anthranilic acid and its silver(I) complex were recorded at 3.75×10^{-3} M and at 2.49×10^{-3} M, respectively; The spectra of 1-nitroso-2-naphthol and its silver(I) complex were recorded at 4.62×10^{-3} M and at 2.86×10^{-3} M, respectively; The spectra of 2-nitroso-1-naphthol and its silver(I) complex were recorded at 4.62×10^{-3} M and at 2.86×10^{-3} M, respectively.

3.11. Method for Recording the ^{1}HNMR Spectra of the Ligands and Their Silver(I) Complexes

The ^{1}HNMR and ^{13}CNMR spectra of the ligands and the silver(I) complexes were recorded in DMSO-d_6 solution at 90 MHz.

3.12. Method for Measuring the Solid Conductivities of the Ligands and Their Silver(I) Complexes

The solid conductivities of the ligands and their silver(I) complexes were measured for pellets pressed at a pressure of 6 MPa.

4. RESULTS AND DISCUSSIONS

4.1. Physical Properties of the Complexes

The solubility of the complexes were examined in common organic solvents. The complexes were found to be insoluble in most of the common organic solvents such as ethanol, diethyl ether, acetone, chloroform, carbon tetrachloride, benzene, toluene, nitro benzene and dimethyl formamide. However, the complexes were found to be soluble in dimethyl sulphoxide. Attempt was also made to determine the melting point of the complexes, however, all the complexes decomposed before melting. The physical properties of the complexes are summarized in Table 4.

4.2. Qualitative Tests

Qualitative tests revealed the presence of silver ion and the absence of nitrate ion in all the complexes. These results indicate that the reaction products were not mixtures of silver nitrate and the ligands but were silver(I) complexes. The absence of nitrate ion in the complexes also indicates that the complexes were not in the form of ion pairs but were neutral species.

4.3. Elemental Analysis

The silver content of the complexes have been determined by the Mohr and Volhard methods. The results of the analysis are given in Table 5.

Table 4. Physical Properties of the Complexes

Complex	Formula	Color	% Yield	Solubility in DMSO	Decomp. temp.
Silver(I)-anthranilic acid	$Ag(C_7H_6NO_2)$	white	96.0	soluble	191.4°C
Silver(I)-N-phenyl anthranilic acid	$Ag(C_{13}H_{10}NO_2)$	white	93.0	soluble	172°C
Silver(I)-1-nitroso-2-naphthol	$Ag(C_{10}H_6NO_2)$	brown	94.52	soluble	152°C
Silver(I)-2-nitroso-1-naphthol	$Ag(C_{10}H_6NO_2)$	dark brown	87.16	soluble	155°C

Table 5. Percentages of silver calculated and found in the complexes

Complex			% Silver	
Name	Formula	M:L	Calculated	Found
Silver(I)-ant-	$Ag(C_7H_6NO_2)$	1:1	44.20	43.76
hranilic acid	$Ag(C_7H_6NO_2)_2$	1:2	28.37	
	$Ag_2(C_7H_6NO_2)$	2:1	61.31	
Silver(I)-N-phe-	$Ag(C_{13}H_{10}NO_2)$	1:1	33.69	33.08
nyl anthranilic	$Ag(C_{13}H_{10}NO_2)_2$	1:2	20.26	
acid	$Ag_2(C_{13}H_{10}NO_2)$	2:1	50.41	
Silver(I)-1-nit-	$Ag(C_{10}H_6NO_2)$	1:1	38.52	37.84
roso-2-naphthol	$Ag(C_{10}H_6NO_2)_2$	1:2	23.85	
	$Ag_2(C_{10}H_6NO_2)$	2:1	55.61	
Silver(I)-2-nit-	$Ag(C_{10}H_6NO_2)$	1:1	38.52	37.42
roso-1-naphthol	$Ag(C_{10}H_6NO_2)$	1:2	23.85	
	$Ag_2(C_{10}H_6NO_2)$	2:1	55.61	

The nitrogen content of the ligands and their silver(I) complexes have been determined by the Kjeldahl method. The results of the analysis are given in Table 6. These results clearly indicate that the experimental values are in good agreement with the calculated values of the proposed formula of the 1:1 (M:L) complexes (i.e. with the formation of 1:1 complex) and do not agree with the formation of 1:2 (M:L) or 2:1 (M:L) complexes.

Table 6. Percentages of nitrogen calculated and found in the ligands and their silver(I) complexes

Complex			% Nitrogen	
Name	Formula	M:L	Calculated	Found
Anthranilic acid	$C_7H_7NO_2$		10.20	9.86
Silver(I)-anthranilic acid	$Ag(C_7H_6NO_2)$	1:1	5.73	5.66
	$Ag(C_7H_6NO_2)_2$	1:2	7.36	
	$Ag_2(C_7H_6NO_2)$	2:1	3.97	
N-Phenyl anthranilic acid	$C_{13}H_{11}NO_2$		6.56	6.50
Silver(I)-N-phe-	$Ag(C_{13}H_{10}NO_2)$	1:1	4.37	4.28

nyl anthranilic	$Ag(C_{13}H_{10}NO_2)_2$	1:2	5.25	
acid	$Ag_2(C_{13}H_{10}NO_2)$	2:1	3.27	
1-Nitroso-2-				
naphthol	$C_{10}H_7NO_2$		8.08	8.00
Silver(I)-1-nit-	$Ag(C_{10}H_6NO_2)$	1:1	4.99	4.88
roso-2-naphthol	$Ag(C_{10}H_6NO_2)_2$	1:2	6.19	
	$Ag_2(C_{10}H_6NO_2)$	2:1	3.60	
2-Nitroso-1-				
naphthol	$C_{10}H_7NO_2$		8.08	8.01
Silver(I)-2-nit-	$Ag(C_{10}H_6NO_2)$	1:1	4.99	4.86
roso-1-naphthol	$Ag(C_{10}H_6NO_2)$	1:2	6.19	
	$Ag_2(C_{10}H_6NO_2)$	2:1	3.60	

The ratio of silver to nitrogen found is relatively greater than the ratio calculated in all the complexes. These clearly show that the amounts of nitrogen found are smaller than the amounts calculated. The possible sources of loss of nitrogen are probably due to the nature of the method used for its determination, i.e the Kjeldahl method, which involves three steps namely digetion, distillation and titration.

Table 7. Ratio of silver to nitrogen calculated and found in the complexes

Complexes	Ag/N ratio Calculated	Found
Ag-anthranilicacid	7.71	7.73
Ag-N-phenylanthranilic acid	7.71	7.73
Ag-1-nitroso-2-naphthol	7.71	7.75
Ag-2-nitroso-1-naphthol	7.71	7.75

4.4. Visible Electronic Spectra of the Ligands and Their Silver(I) Complexes

The visible electronic spectra of the ligands and their silver(I) complexes were recorded in the wavelength range 700-350 nm. The spectra of the complexes were recorded at different concentrations in DMSO and it was found that there is a shift in the wavelength of maximum absorption with changes in concentration. The shift in λ_{max} with dilution may probably be due to dissociation of the complexes. Thus it was not possible to determine the extinction coefficient accurately. Therefore it was not possible to determine the type of electronic transition in the complexes. The wavelength of maximum absorption (λ_{max}) of the complexse are given in Table 8. Comparison of the spectra of the ligands with that of their silver(I) complexes clearly indicates the complex formation between silver(I) and the ligands.

Table 8. The Wavelength of Maximum Absorption in Their Visible Electronic Spectra (λ_{max}) of the Ligands and Their Silver(I) Complexes

Ligand/Complex	λ_{max} (nm)
Anthranilic acid	*
Silver(I)-anthranilic acid	460
N-Phenyl anthranilic acid	350
Silver(I)-N-phenyl anthranilic acid	450
1-Nitroso-2-naphthol	352
Silver(I)-1-nitroso-2-naphthol	417
2-Nitroso-naphthol	*
Silver(I)-2-nitroso-1-naphthol	447

* Donot exhibit absorption maximum in the visible region (700-350 nm).

4.5. Infrared Spectra of the Ligands and Their Silver(I) Complexes

4.5.1. Infrared spectra of anthranilic acid and its silver(I) complex

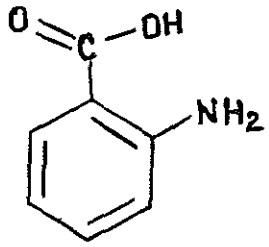
The most significant infrared spectral data of the ligand and its silver(I) complex are summarized in Table 9.

The IR spectrum of anthranilic acid showed all the characteristic frequencies. The most important characteristic frequencies are: sharp and medium intensity bands at 3480 and 3370 cm^{-1} due to N-H symmetric and asymmetric stretchings, characteristic of primary amines; a broad band between 3100-2400 cm^{-1} with maxima around 3000 and 2600 cm^{-1} due to O-H stretching and a band at 1660 cm^{-1} due to C=O stretching, characteristic of aromatic carboxylic acids; two bands at 1410 and 1300 cm^{-1} due to O-H deformation and C-O stretching coupled vibration; two bands at 1250 and 1162 cm^{-1} due to C-N stretching of aromatic amine and a band at 920 cm^{-1} due to O-H out of plane bending characteristic of carboxylic acid.

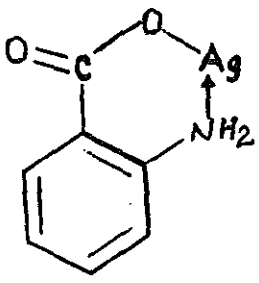
The IR spectrum of the silver(I) complex of anthranilic acid was found to be different from that of anthranilic acid and showed either a shift or disappearance of some characteristic frequencies. The bands at 3480 and 3370 cm^{-1} (due to N-H streching in the ligand) disappeared in the spectrum of the complex. Instead a broad band between 3600-3000 cm^{-1} with maxima around 3420 and 3300 cm^{-1} due to N-H streching of amine salts appeared. This suggest that the NH_2 group is involved in coordination through its nitrogen atom. The broad band in the region 3100-2400 cm^{-1} (due to O-H stretching in the ligand) also disappeared in the spectrum of the complex. The band at 1660 cm^{-1} (due to C=O stretching of carboxylic acid function in the ligand) disappeared in the spectrum of the complex. Instead a doublet at 1580 and

1380 cm^{-1}, which are characteristic of carboxylate ion, appeared in the spectrum of the complex. This suggest that the COO^- group is involved in coordination through its oxygen atom. The band at 1162 cm^{-1} (due to C-N stretching of aromatic amine in the spectrum of the ligand) shifted to 1148 cm^{-1} in the spectrum of the complex. Further, the bands at 1410 and 920 cm^{-1} (due to O-H deformation and O-H out of plane bending, respectively) disappeared in the spectrum of the complex. These further suggest that both nitrogen ($-NH_2$) and oxygen(-OH) or (O=C-O-)are involved in coordination. The appearance of two new bands at 420 and 390 cm^{-1} in the spectrum of the complex are assigned to Ag-N and Ag-O stretchings, respectively. The assignment of Ag-N and Ag-O bands was based on a similar assignment by Nakamoto et al where the M-N stretchings are assigned to the higher frequency band and the M-O stretchings to the lower frequency band (M = metal) (65).

These results are consistent with the following structures of the ligand and the complex, respectively.



Anthranilic acid



Silver(I)-anthranilic acid

4.5.2. Infrared spectra of n-phenyl anthranilic acid and its silver(I) complex

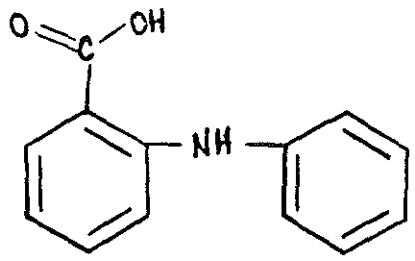
The most significant infrared spectral data of the ligand and its silver(I) complex are summarized in Table 10.

The IR spectrum of N-phenyl anthranilic acid showed all the characteristic frequencies. The most important characteristic frequencies are: sharp and medium intensity band at 3320 cm^{-1} due to N-H stretchings, characteristic of secondary amines; a broad band between 3100-2400 cm^{-1} with maxima around 3000 and 2600 cm^{-1} due to O-H stretching and a band at 1650 cm^{-1} due to C=O stretching, characteristic of aromatic carboxylic acids; two bands at 1408 and 1320 cm^{-1} due to O-H deformation and C-O stretching coupled vibration; two bands at 1250 and 1162 cm^{-1} due to C-N stretching of aromatic amine and a band at 900 cm^{-1} due to O-H out of plane bending characteristic of carboxylic acid.

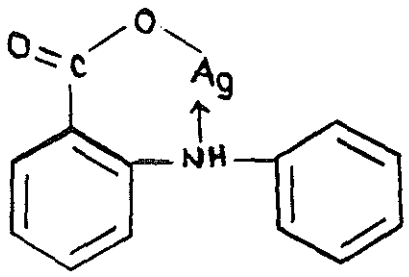
The IR spectrum of the silver(I) complex of N-phenyl anthranilic acid was found to be different from that of N-phenyl anthranilic acid and showed either a shift or disappearance of some characteristic frequencies. The band at 3320 cm^{-1} (due to N-H stretching in the ligand) disappeared in the spectrum of the complex. Instead a broad band between 3700-3000 cm^{-1} with maxima around 3420 and 3300 cm^{-1} due to N-H streching of amine salts appeared. This suggests that the N-H group is involved in coord-dination through its nitrogen atom. The broad band in the region 3100-2400 cm^{-1} (due to O-H stretching in the ligand) also disappeared in the spectrum of the complex. The band at 1650 cm^{-1} (due to C=O stretching of carboxylic acid function in the ligand) disappeared in the spectrum of the complex. Instead a doublet at 1572 and 1378 cm^{-1}, which are characteristic of carboxylate ion, appeared in the spectrum of the

complex. This suggest that the COO^- group is involved in coordination through its oxygen atom. The band at 1160 cm^{-1} (due to C-N stretching of aromatic amine in the spectrum of the ligand) shifted to 1156 cm^{-1} in the spectrum of the complex. Further, the bands at 1408 and 900 cm^{-1} (due to O-H deformation and O-H out of plane bending, respectively) disappeared in the spectrum of the complex. These further suggest that both nitrogen ($-NH_2$) and oxygen (-OH) or ($O=C-O^-$) are involved in coordination. The appearance of two new bands at 525 and 418 cm^{-1} in the spectrum of the complex are assigned to Ag-N and Ag-O stretchings, respectively (65).

These results are consistent with the following structures of the ligand and the complex, respectively.



N-Phenyl-anthranilic acid



Silver(I)-N-phenyl anthranilic acid

4.5.3.Infrared spectra of 1-nitroso-2-naphthol and its silver(I) complex

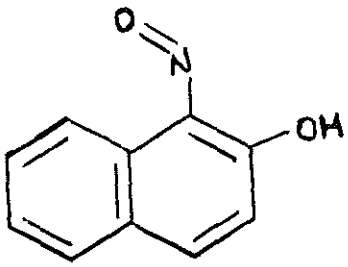
The most significant infrared spectral data of the ligand and its silver(I) complex are summarized in Table 11.

The IR spectrum of 1-nitroso-2-naphthol showed all the characteristic frequencies. Some of the important characteristic frequencies are: a band at 1520 cm^{-1} due to N=O stretching, characteristic of aromatic nitroso groups; the absence a broad band between 3200-2500 cm^{-1} due to O-H stretching was observed (this was also observed by Amstutz et al (66); two bands at 1410 and 1215 cm^{-1} due to O-H deformation and C-O stretching coupled vibration; and a band at 1070 cm^{-1} due to C-N stretching of C-N=O group.

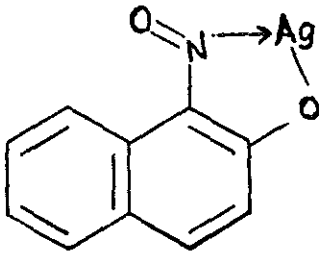
The IR spectrum of the silver(I) complex of 1-nitroso-2-naphthol was found to be different from that of 1-nitroso-2-naphthol and showed either a shift or disappearance of some characteristic frequencies. The broad band between 3200-2500 cm^{-1} due to O-H streching is absent in the spectrum of the complex. The broad band in the region 3600-3300 cm^{-1} with maxima around 3450 cm^{-1} was observed which is probably due to O-H stretching of absorbed water and due to that of hydroxyl group (this is confirmed by the appearance of the band at 1610 cm^{-1} which is due to O-H deformation of water, silver(I) complexe of 1-nitroso-2-naphthol was found to be hygroscopic). The band at 1520 cm^{-1} (due to N=O stretching) in the spectrum of the ligand shifted to 1280 cm^{-1}, in the spectrum of the complex. This suggest that the N=O group is involved in coordination through its nitrogen atom. Further more, the band at 1410 cm^{-1} (due to O-H deformation of the hydroxyl group in the ligand) disappeared in the spectrum of the complex. This suggest that the oxygen atom of the hydroxyl

group is involved in coordination. The band at 1215 cm^{-1} (due to C-O stretching) and the band at 1070 cm^{-1} (due to C-N stretching) in the spectrum of the ligand shifted to 1200 cm^{-1} and 1080 cm^{-1}, respectively in the spectrum of the complex. The appearance of two new bands at 520 and 435 cm^{-1} in the spectrum of the complex are assigned to Ag-N and Ag-O stretchings, respectively (65).

These results are consistent with the following structures of the ligand and the complex, respectively.



1-Nitroso-2-naphthol



Silver(I)-1-nitroso-2-naphthol

4.5.4. Infrared spectra of 2-nitroso-1-naphthol and its silver(I) complex

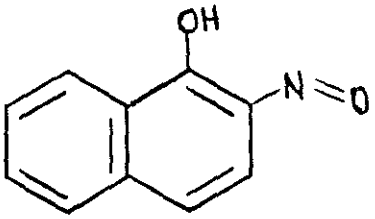
The most significant infrared spectral data of the ligand and its silver(I) complex is summarized in Table 12.

The IR spectrum of 2-nitroso-1-naphthol showed all the characteristic frequencies. Some of the important characteristic frequencies are: a band at 1660 cm^{-1} due to N=O stretching, characteristic of aromatic nitroso groups; a broad band between 3400-2800 cm^{-1} with maxima around 3240 cm^{-1} due to O-H stretching; two bands at 1380 and 1310 cm^{-1} due to O-H deformation and C-O stretching coupled vibration; and two bands at 1110 cm^{-1} and 1065 cm^{-1} due to C-N stretching of C-N=O group.

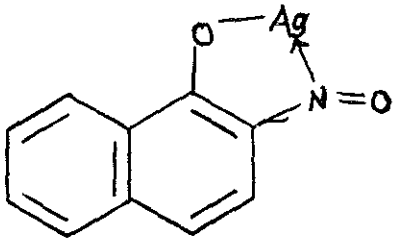
The IR spectrum of the silver(I) complex of 2-nitroso-1-naphthol was found to be different from that of 2-nitroso-1-naphthol and showed either a shift or disappearance of some characteristic frequencies. The broad band between 3400-2800 cm^{-1} due to O-H streching disappeared in the spectrum of the complex. This suggest that oxygen is involved in coordination. The broad band in the region 3600-3300 cm^{-1} with maxima around 3450 cm^{-1} was observed which is due to O-H stretching of absorbed water and due to that of hydroxyl group (this is confirmed by the appearance of the band at 1610 cm^{-1} which is due to O-H deformation of water. The silver(I) complex of 2-nitroso-1-naphthol was found to be hygroscopic). The band at 1660 cm^{-1} (due to N=O stretching) in the spectrum of the ligand shifted to 1270 cm^{-1}, in the spectrum of the complex. This suggest that the N=O group is involved in coordination through its nitrogen atom. The band at 1310 cm^{-1} (due to C-O stretching) and the band at 1110 cm^{-1} (due to C-N stretching) in the spectrum of the ligand shifted to 1300 cm^{-1}

and 1140 cm^{-1}, respectively in the spectrum of the complex. Further more, the band at 1380 cm^{-1} (due to O-H deformation in the ligand) disappeared in the spectrum of the complex showing that oxygen of the hydroxyl group is involved in coordination. The appearance of two new bands at 470 and 360 cm^{-1} in the spectrum of the complex are assigned to Ag-N and Ag-O stretchings, respectively (65).

These results are consistent with the following structures of the ligand and the complex, respectively.



2-Nitroso-1-naphthol



Silver(I)-2-nitroso-1-naphthol

Table 9. Some characteristic IR frequencies(cm^{-1}) of anthranilic acid and its silver(I) complex

Characteristic frequencies, cm^{-1}		
Anthranilic acid	Silver(I)-anthranilic acid complex	Assignment
3480(m), 3370(m) (sharp)	3600-3000 (v. broad with maxima around 3420 and 3300)	N-H streching
3100-2400 (broad with maxima around 3000 and 2600)	---	O-H str. of COOH
1660(s)	---	C=O str. of COOH
---	1580,1380(s)	C-O str. of C=O-O$^-$
1410,1300(s)	---,1310(s)	O-H def. C-O str. coupled
1250,1162(m)	1250,1148(m)	C-N str. of aromatic amine
920(m)	---	O-H out of plane bending
---	420(m)	Ag-N streching
---	390(w)	Ag-O streching

Table 10. Some characteristic IR frequencies(cm^{-1})of N-phenyl anthranilic acid and its silver(I) complex

Characteristic frequencies, cm^{-1}		
N-phenyl anthranilic acid	Silver(I)-N-phenyl anthranilic acid	Assignment
3320(m)	3700-3000 (v. broad)	N-H streching
3100-2400 (maxima around 3000 and 2600)	---	O-H str. of COOH
1650(s)	---	C=O str. of COOH
---	1572, 1378(s)	C-O str. of O=C-O^-
1408,1320(s)	---,1285(s)	O-H def. and C-O str. coupled
1160(s)	1155(w)	C-N str. of aromatic amine
900(m)	---	O-H out of plane bending
---	525(w)	Ag-N streching
---	418(w)	Ag-O streching

Table 11. Some characteristic IR frequencies(cm^{-1}) of 1-nitroso-2-naphthol and its silver(I) complex

Characteristic freguencies, cm^1		
1-nitroso-2-naphthol	Silver(I)-1-nitroso-2-naphthol complex	Assignment
1520(s)	1280(s)	N=O streching
1405(m)	---	O-H deformation
1215(m)	1200(s)	C-O streching
1070(s)	1080(m)	C-N streching
---	520(w)	Ag-N streching
---	435(w)	Ag-O streching

Table 12. Some characteristic IR frequencies(cm^{-1}) of 2-nitroso-1-naphthol and its silver(I) complex

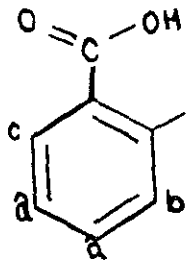
Characteristic frequencies, cm^{-1}		
2-Nitroso-1-naphthol	Silver(I)-2-nitroso-1-naphthol complex	Assignment
3400-2800[2]	---	O-H streching
1660(m)	1270(s)	N=O streching
1380(m)	---	O-H deformation
1310(w)	1300(m)	C-O streching
1110(m)	1140(w)	C-N streching
---	470(w)	Ag-N streching
---	368(w)	Ag-O streching

Note: In tables 9-12 ring vibrations (C-C str., =C-H str. and =C-H deformation) have not been listed since they appeared in the spectra of both the ligands and the complexes with out shifts since they are not affected by complex formation.

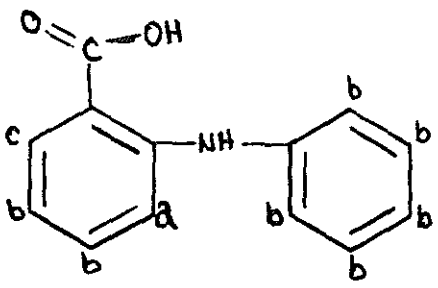
[2]Very broad with maxima around 3240, 3090, 2980 and 2850.

4.6. Nuclear Magnetic Resonance Spectra of the Ligands and Their Silver(I) Complexes

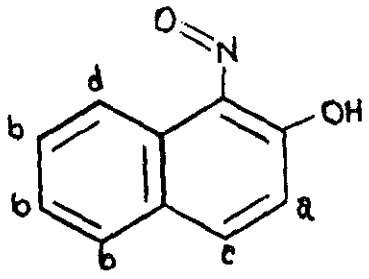
The ^{1}H and ^{13}C NMR signals in the complexes are shifted only slightly either down or up fields relative to the signals of the proton and ^{13}C signals of the parent ligands as shown in Table 13 and 14. This clearly indicate the absence of unpaired electrons in the four silver complexes which is a characteristic of diamagnetism. Therefore, the oxidation state of silver in the complexes is +1 (i.e. Ag^{+1}) and not +2 or +3 (i.e. Ag^{2+} or Ag^{3+}). If the oxidation state of silver in the complaxes were +2, the local magnetic field generated by silver ion would have led to a substantial shift of signals. The assignment of the ^{1}H and ^{13}C NMR signals is based on Sadtler and substituent additivity, respectively.



Anthranilic acid



N-Phenyl anthranilic acid



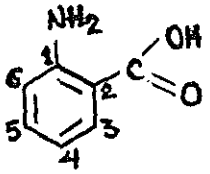
1-Nitroso-2-naphthol

Table 13. ^{1}HNMR chemical shifts of the ligands and their silver(I) complexes

Ligand	Assignment[3]	Chemical Shift (ppm) In the ligand	Chemical Shift (ppm) In the complex
Anthranilic acid	a (2H)	6.6	6.6
	b (1H)	7.2	7.1
	c (1H)	7.7	7.8
N-Phenyl anthranilic acid	a (1H)	6.75	6.70
	b (7H)	7.25	7.15
	c (1H)	7.90	7.97
1-Nitroso-2-naphthol	a (1H)	6.4	6.6
	b (3H)	7.6	7.55
	c (1H)	7.8	7.82
	d (1H)	8.8	9.3

[3] The acid, hydroxyl, and amine protons are unobserved.

Table 14: ^{13}CNMR chemical shift of anthranilic acid and its silver(I) complex

Assignment	Chemical Shift (ppm)		
	Anthranilic acid		Silver(I)-anthranilic acid complex
	Calc.	Obs.	Obs.
C1	148.0	151.4	149.8
C2	117.3	114.6	114.3
C3	130.9	131.1	130.9
C4	118.7	116.3	114.8
C5	134.5	133.6	132.0
C6	115.2	109.9	111.3
C7		169.5	172.2

4.7. Solid Conductivities of the Ligands and the Complexes

The solid conductivities of the ligands and their silver(I) complexes were measured as pellets pressed at a pressure of 6 MPa. All the ligands and their silver(I) the complexes were found to be highly resistive (>100 M ohm). If the complexes were solid conductors, they may find very important applications in science and technology for example they may have many uses in galvanic cells. The technical applications include batteries with solid electrolytes, high temperature fuelcells for measuring partial pressures or activities.

CONCLUSION

Complexes of silver(I) with anthranilic acid, N-phenyl anthranilic acid, 1-nitroso-2-naphthol and 2-nitroso-1-naphthol have been synthesized, isolated and characterized. The complexes were found to be neutral species and non conductors (insulators). Further studies are necessary to fully establish the structures of the complexes and to find their possible applications.

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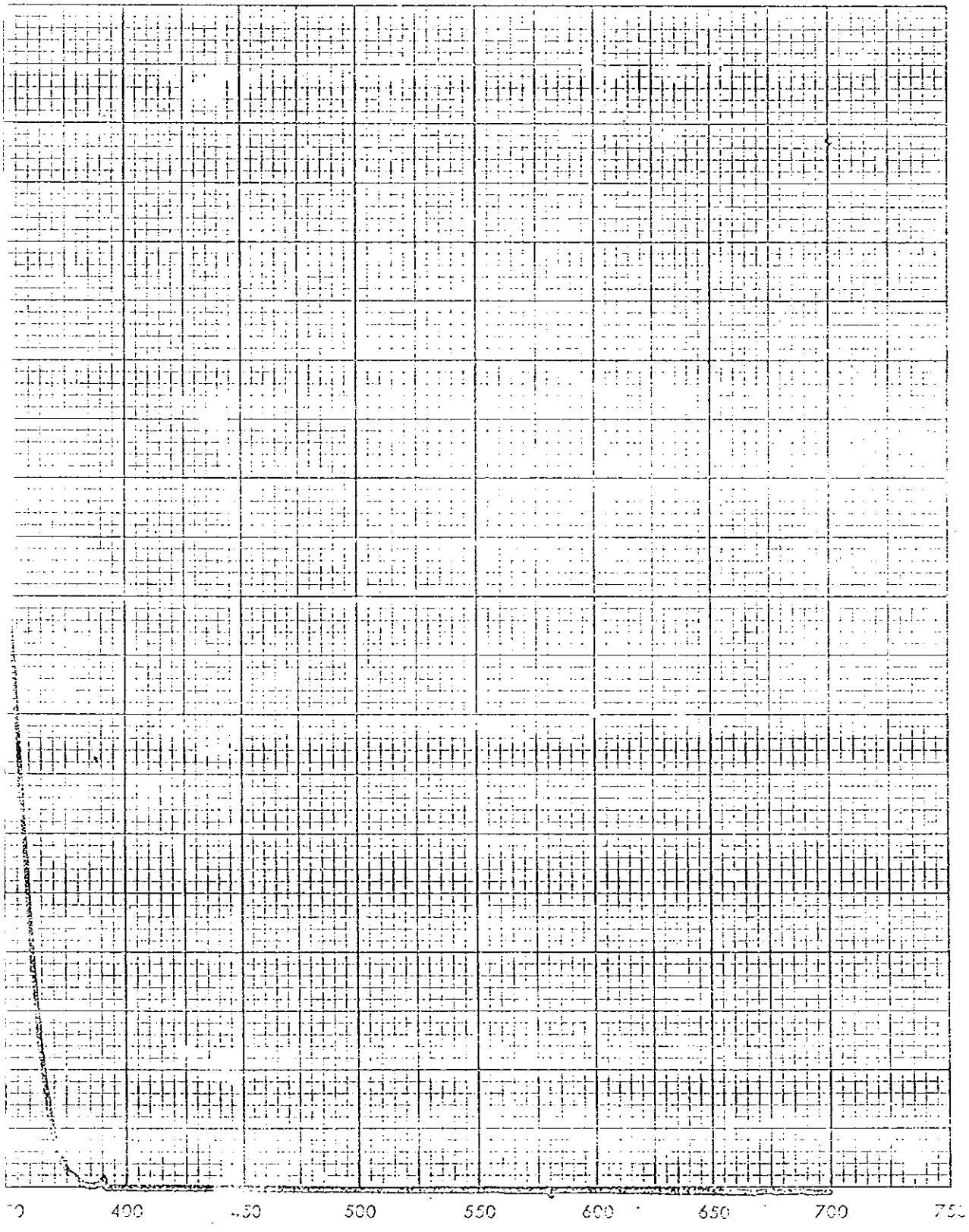
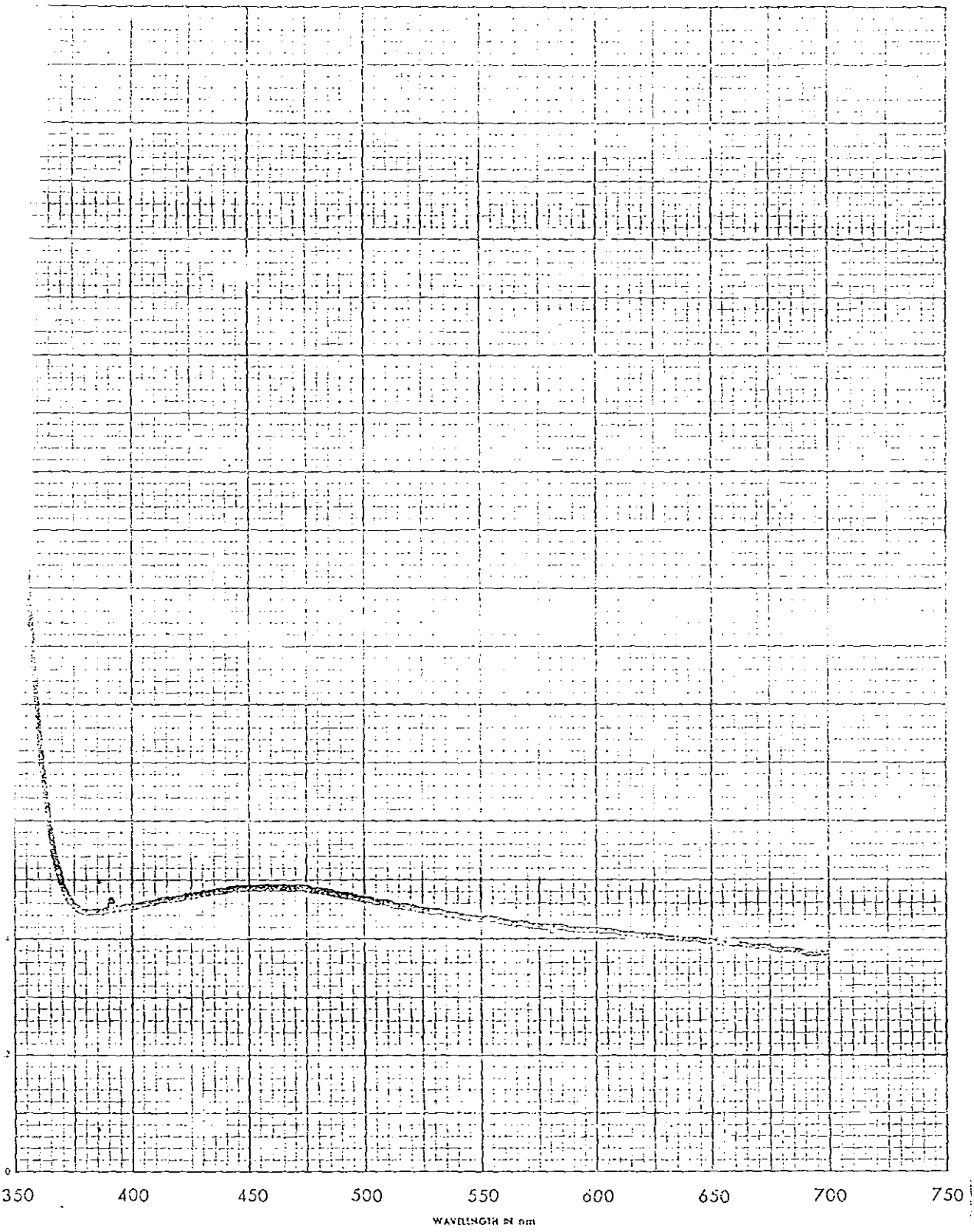
APPENDIX

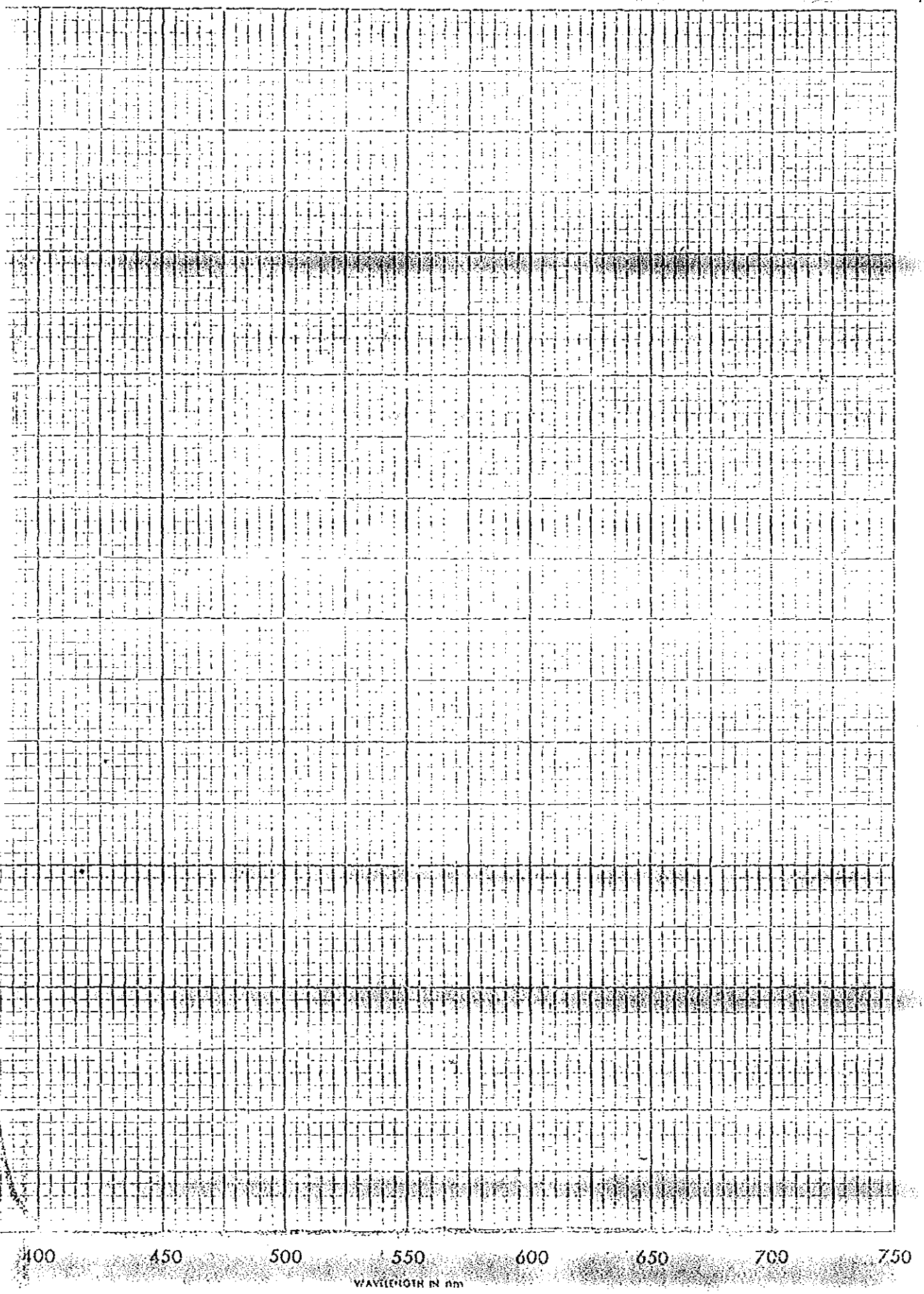
1. Electronic spectrum of anthranilic acid.



2. Electronic spectrum of silver(I)-anthranilic acid.



3. Electronic spectrum of N-phenyl anthranilic acid.



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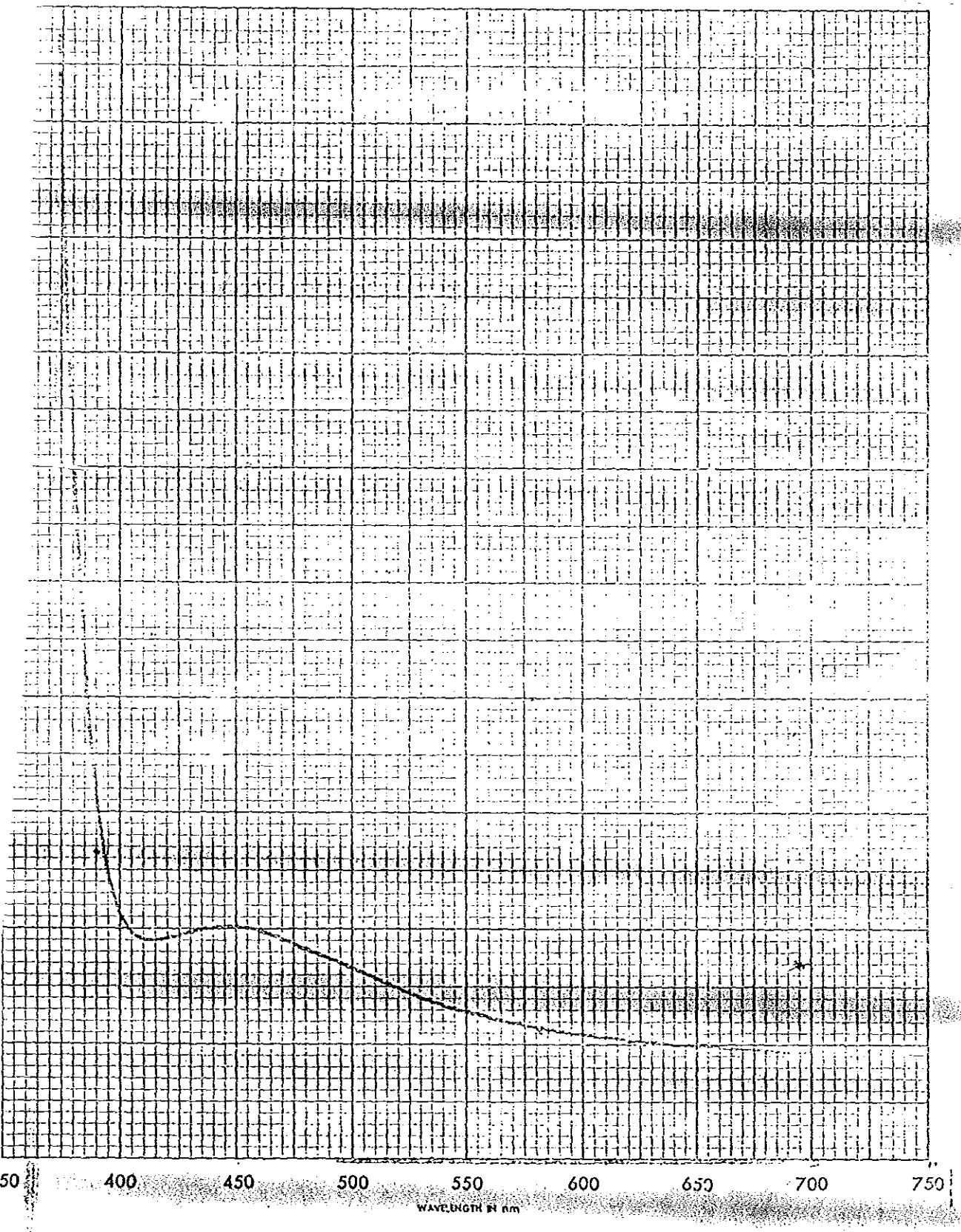
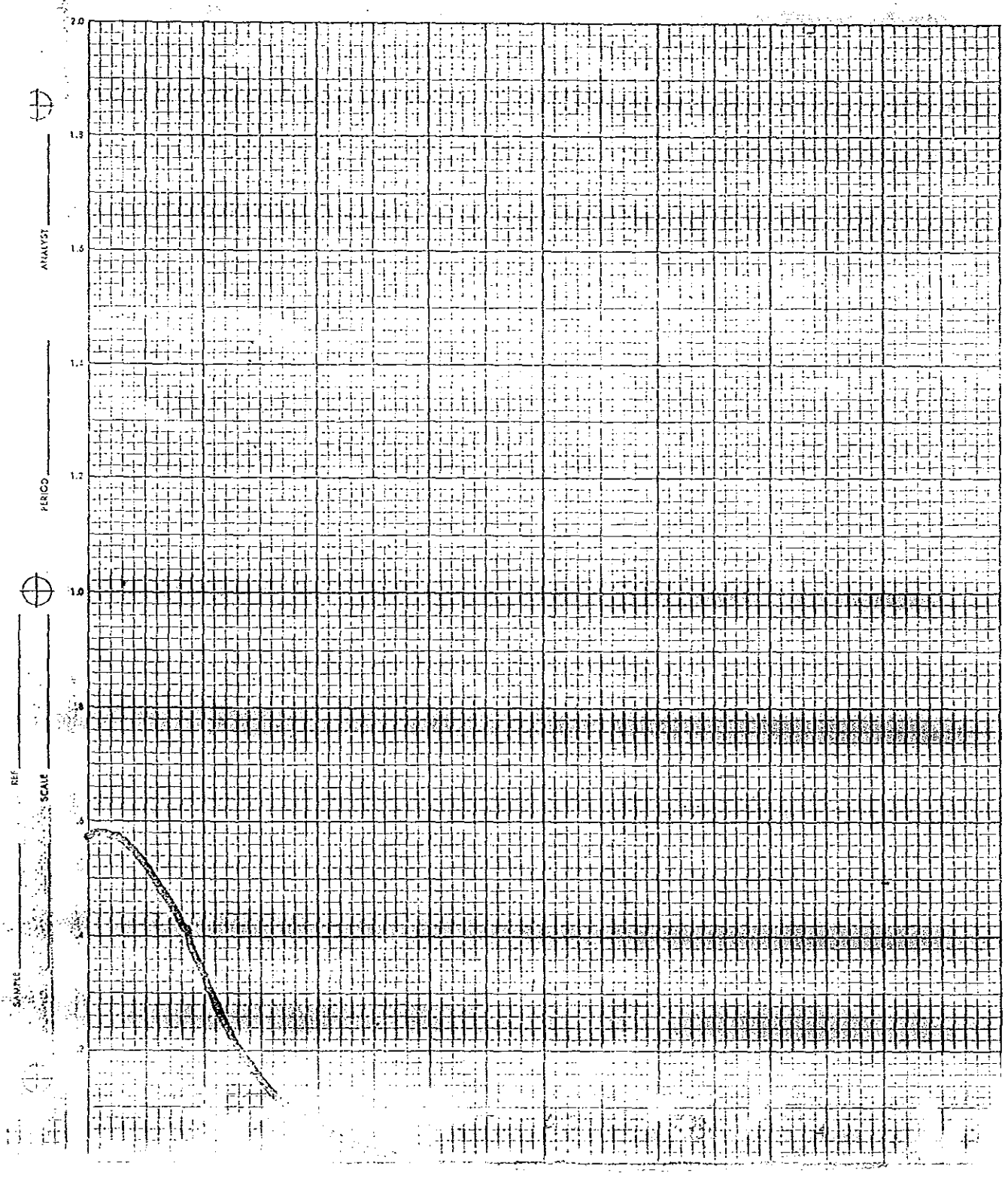
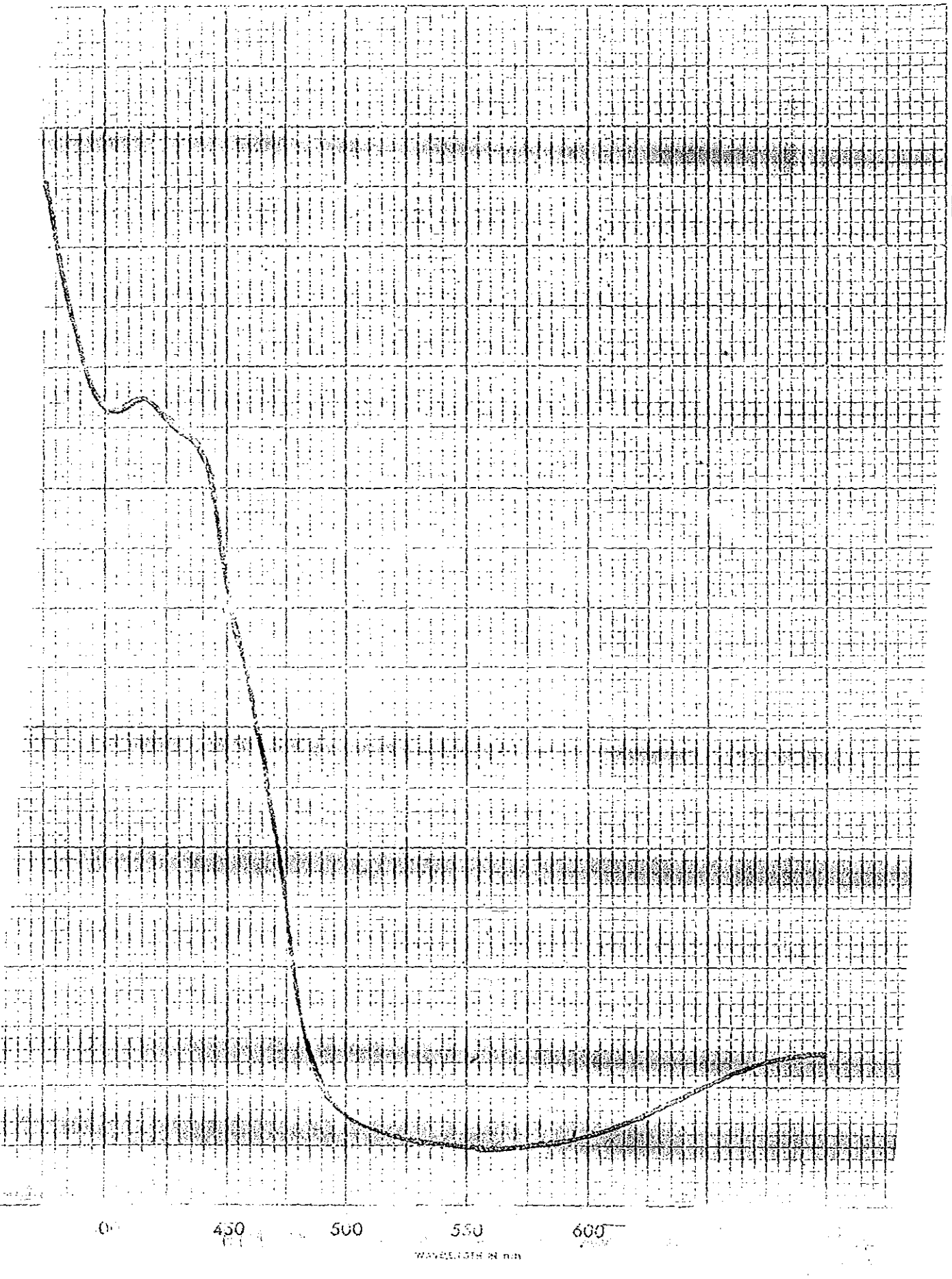


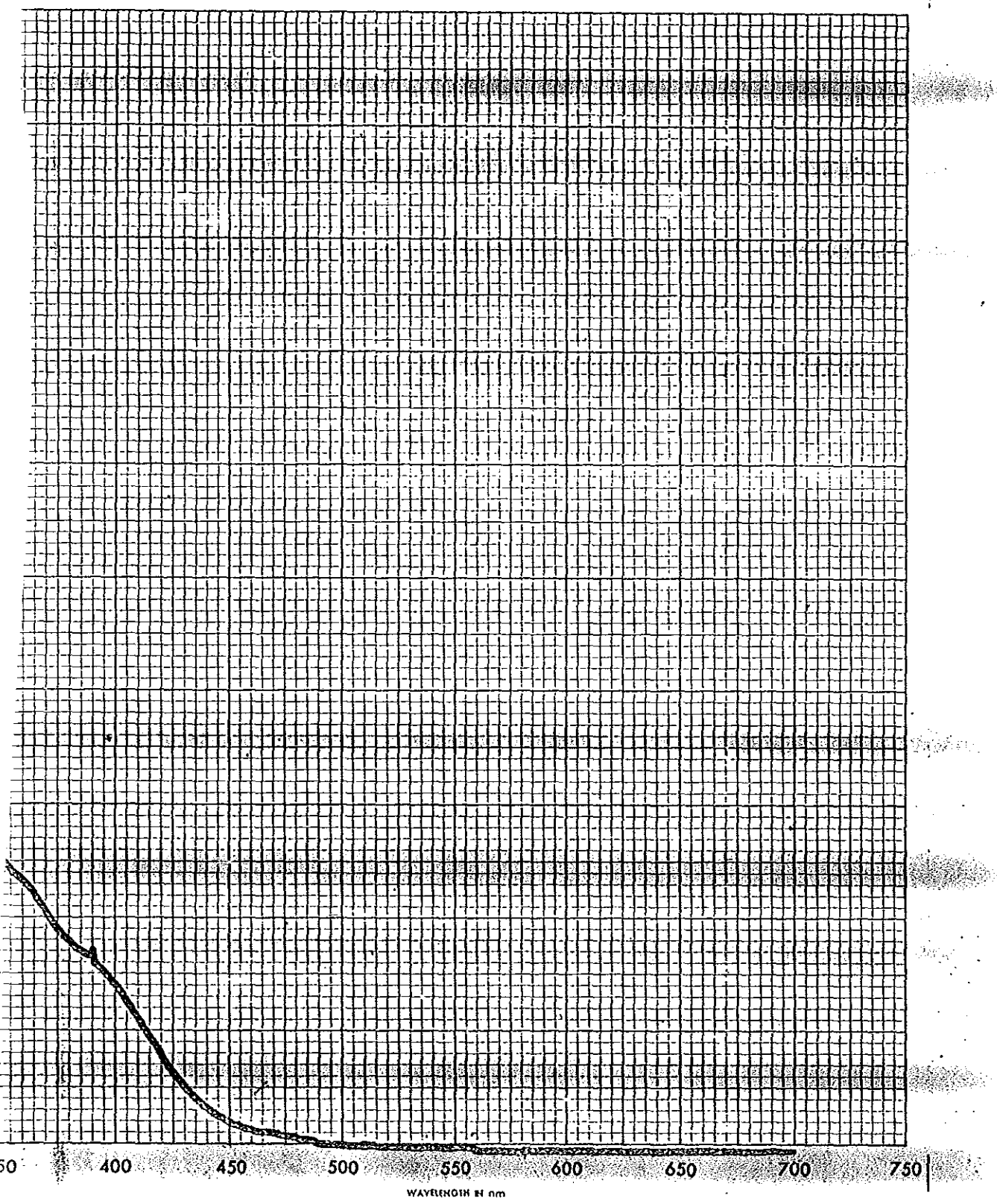
Fig. 5. Electronic spectrum of 1-nitroso-2-naphthol.



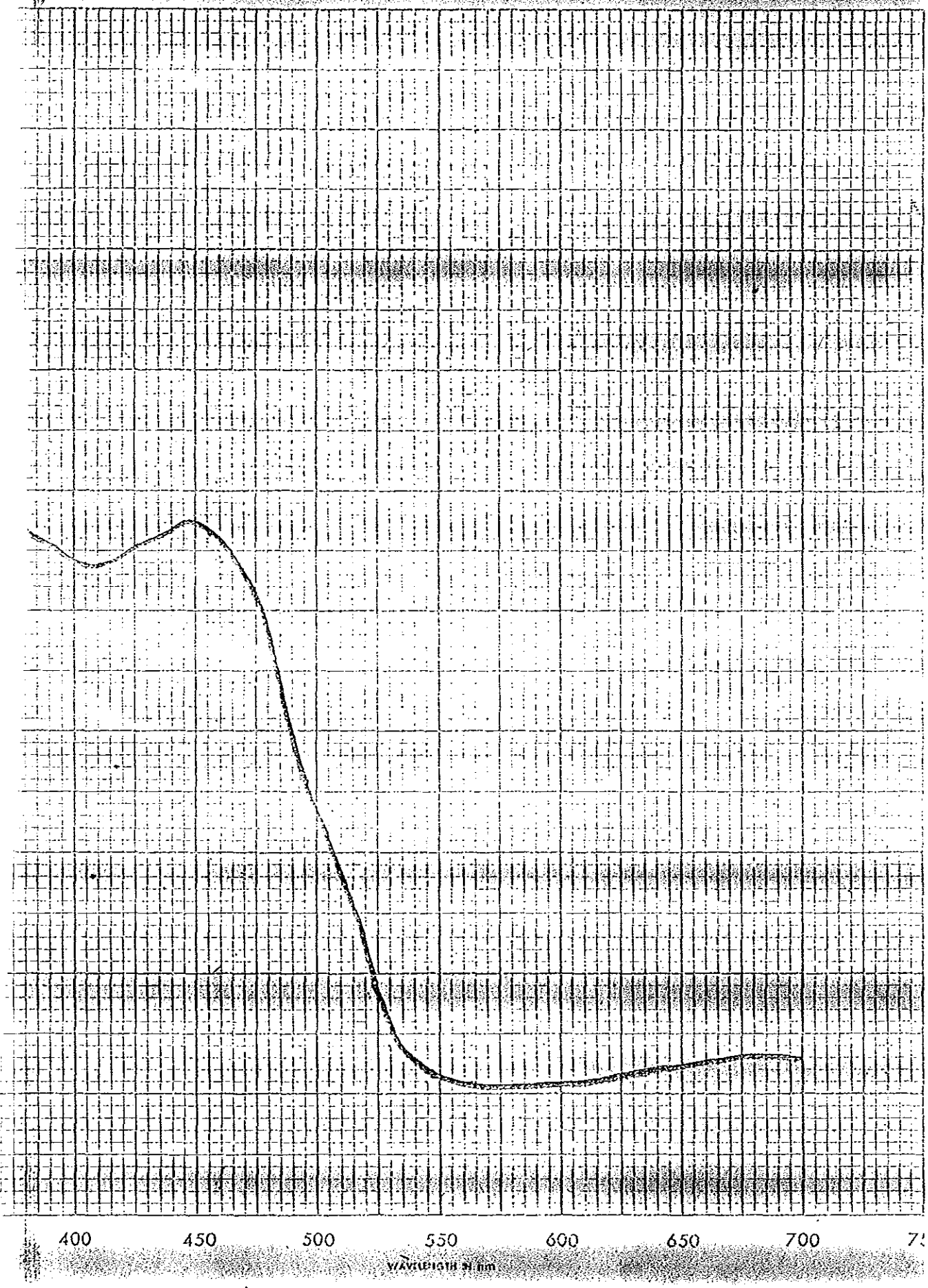
. 6. Electronic spectrum of silver(I)-1-nitroso-2-naphthol.



7. Electronic spectrum of 2-nitroso-1-naphthol.



8. Electronic spectrum of silver(I)-2-nitroso-1-naphthol.



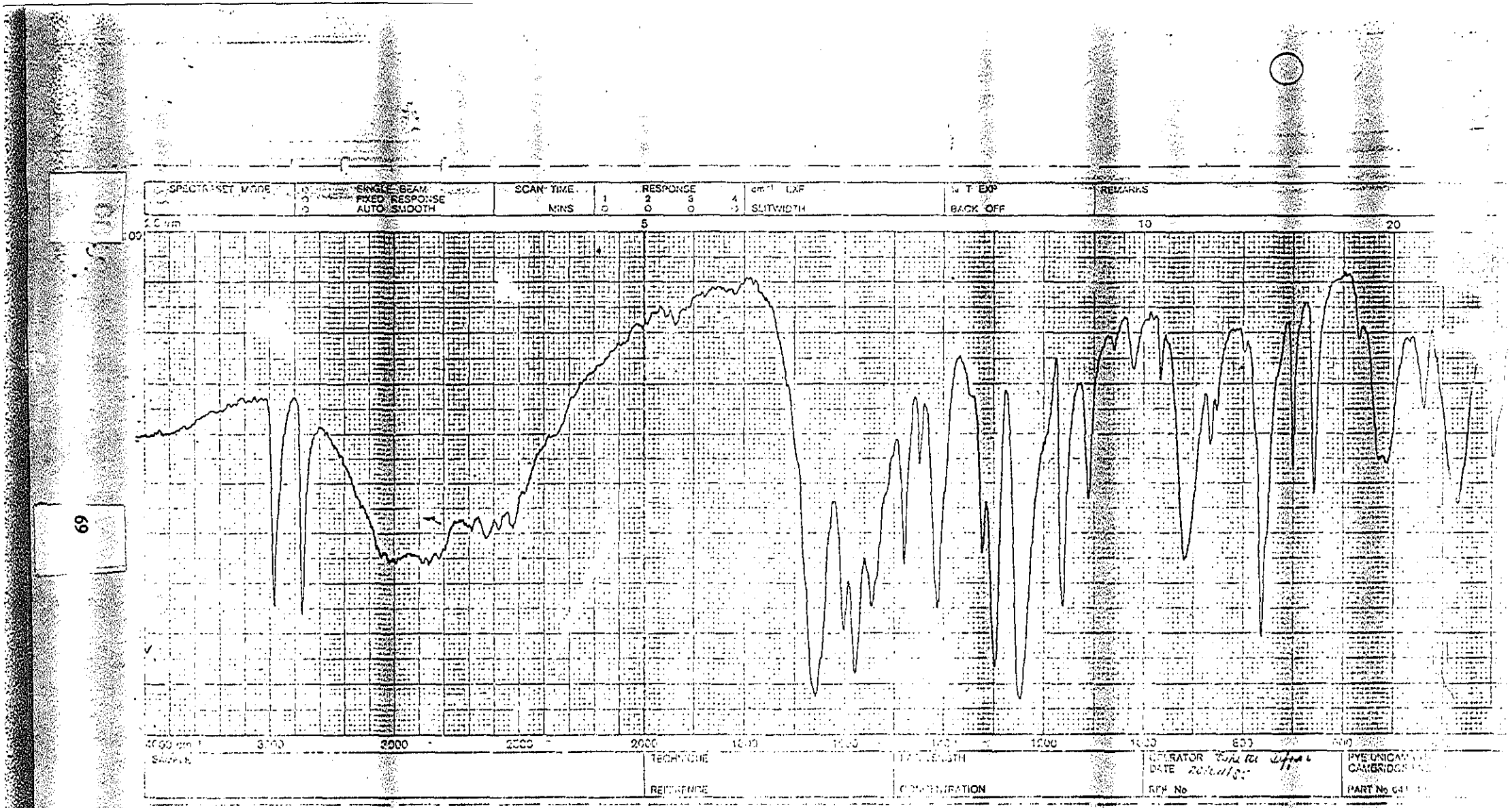


Fig. 9. Infra Red spectrum of anthranilic acid.

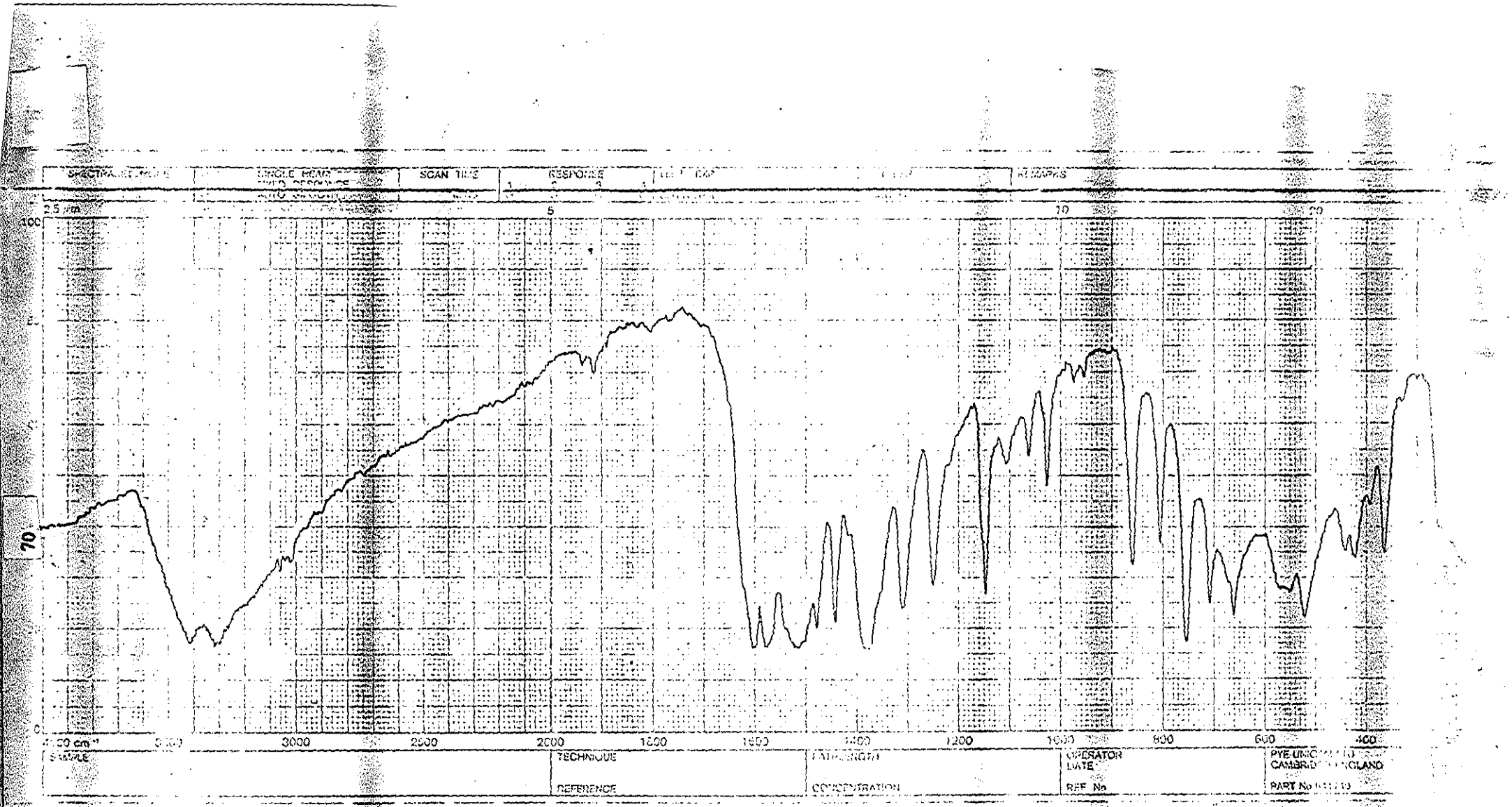


Fig. 10. Infra Red spectrum of silver(I)-anthranilic acid.

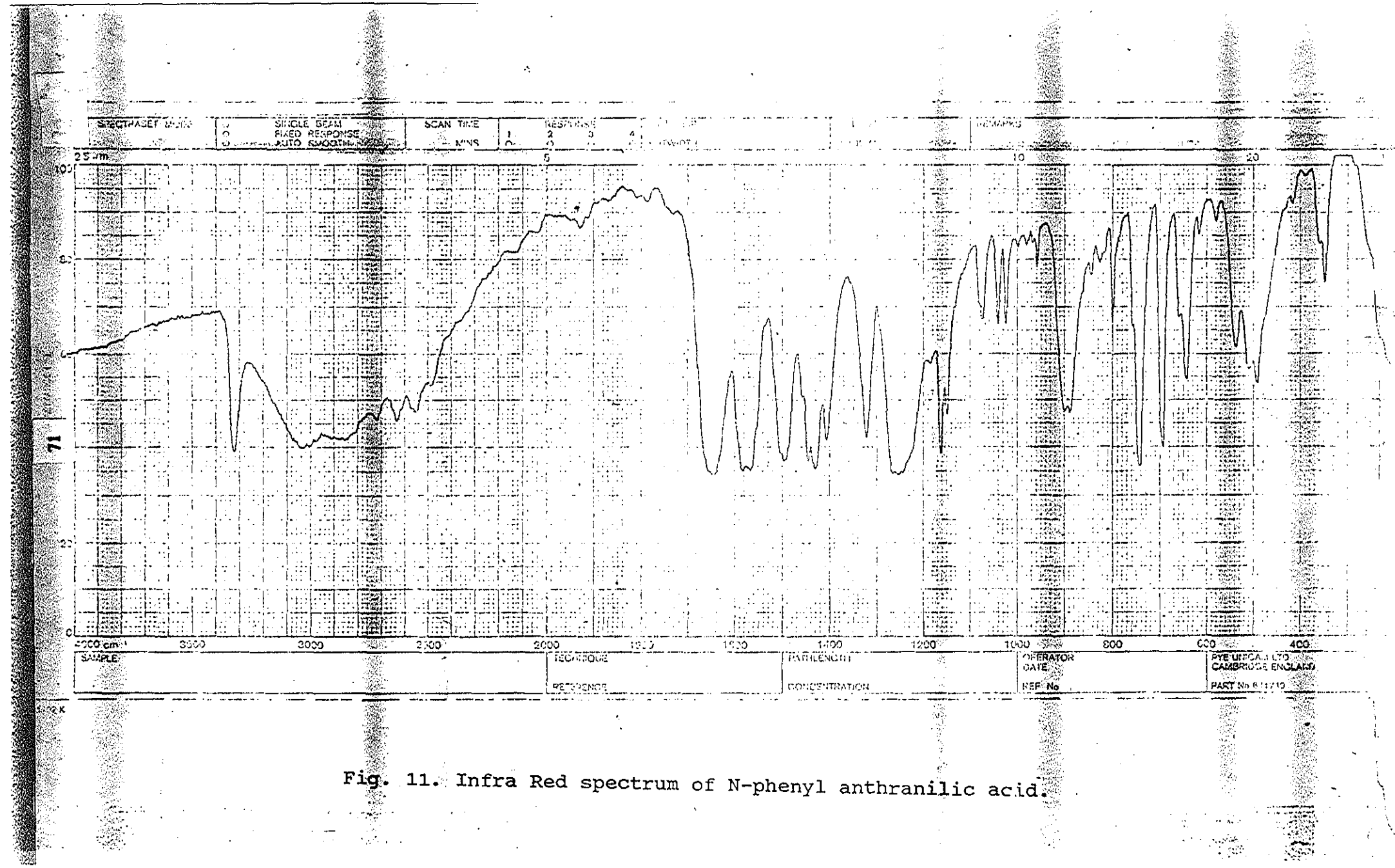


Fig. 11. Infra Red spectrum of N-phenyl anthranilic acid.

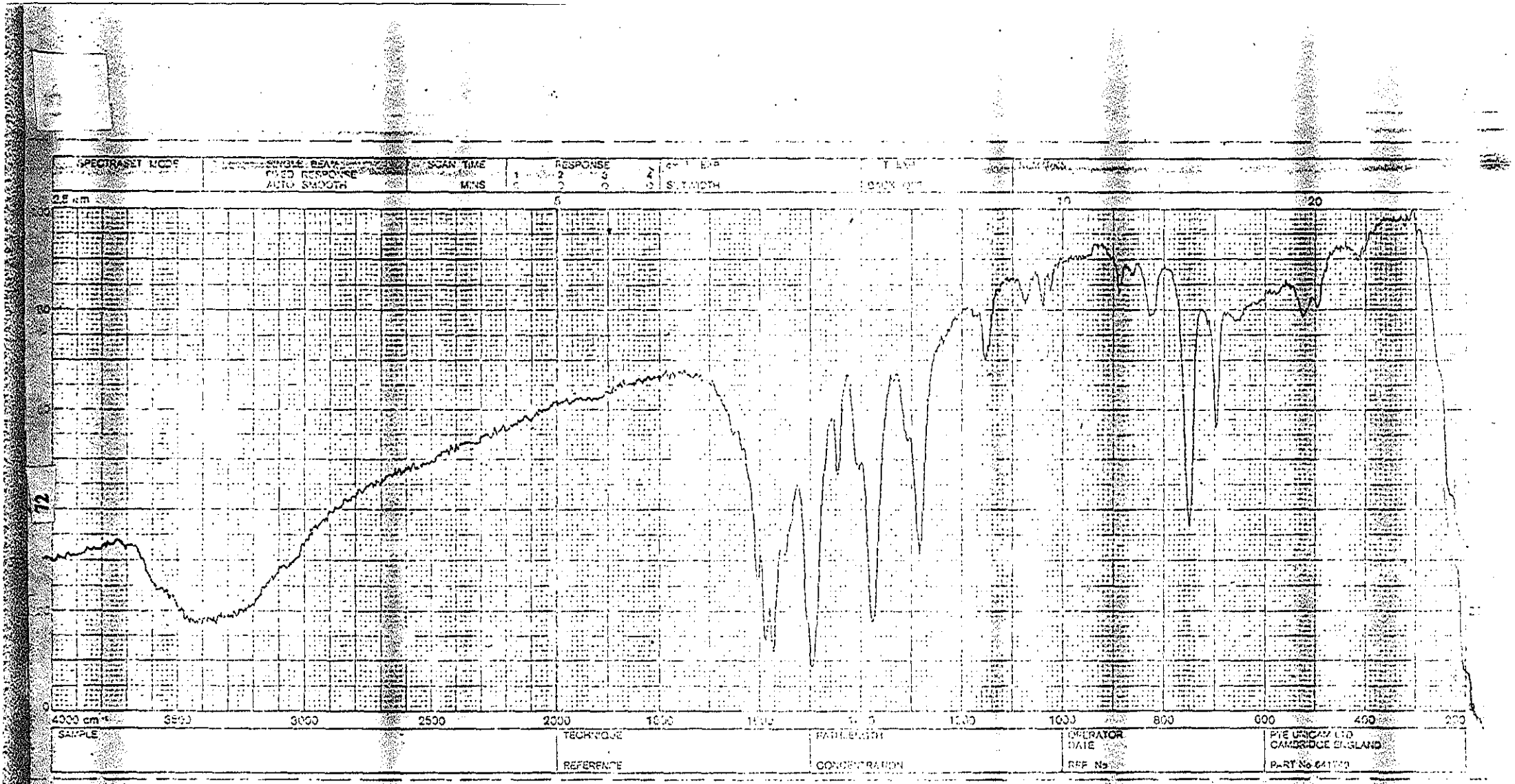


Fig. 12. Infra Red spectrum of silver(I) N-phenyl anthranilic acid.

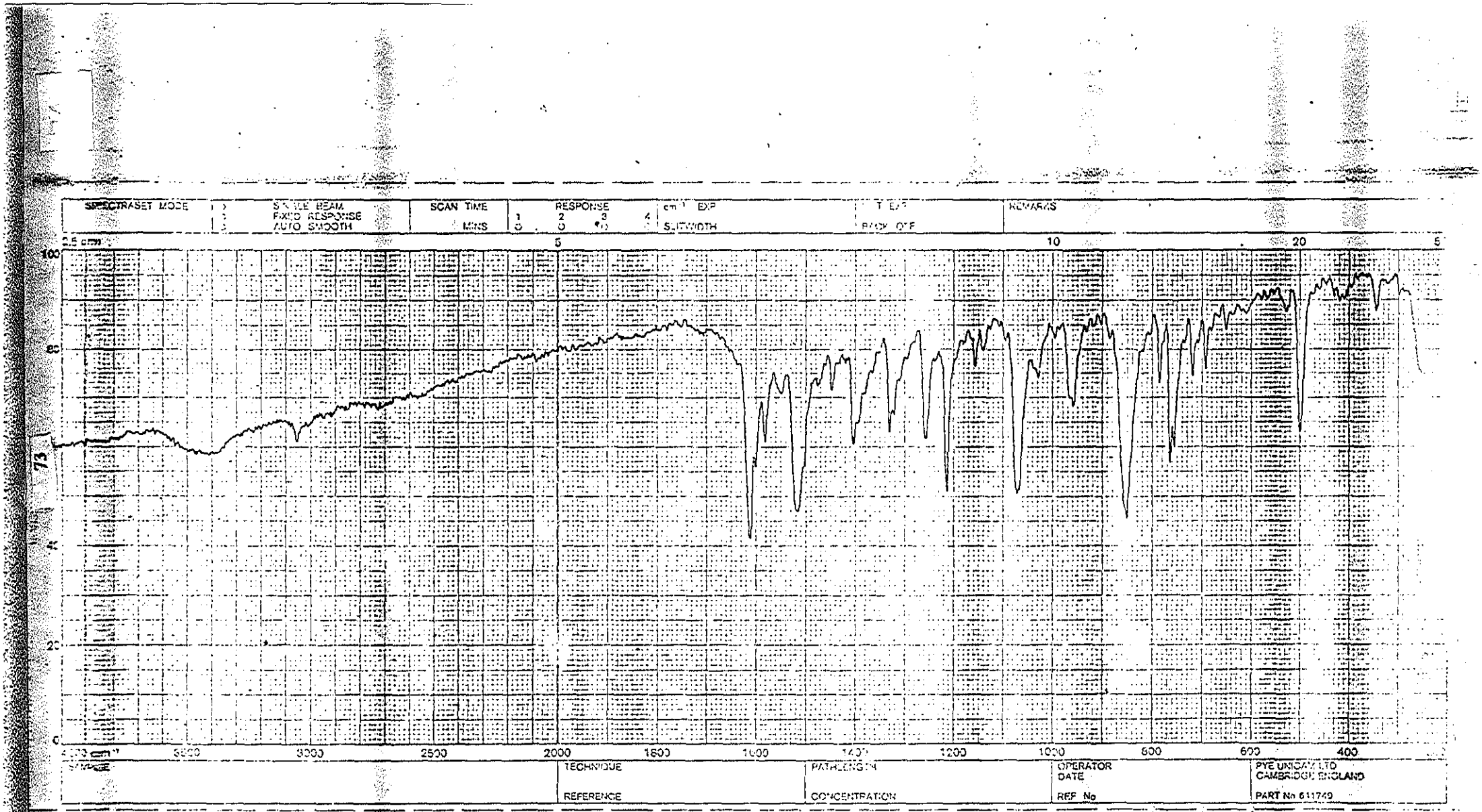


Fig. 13. Infra Red spectrum of 1-nitroso-2-naphthol.

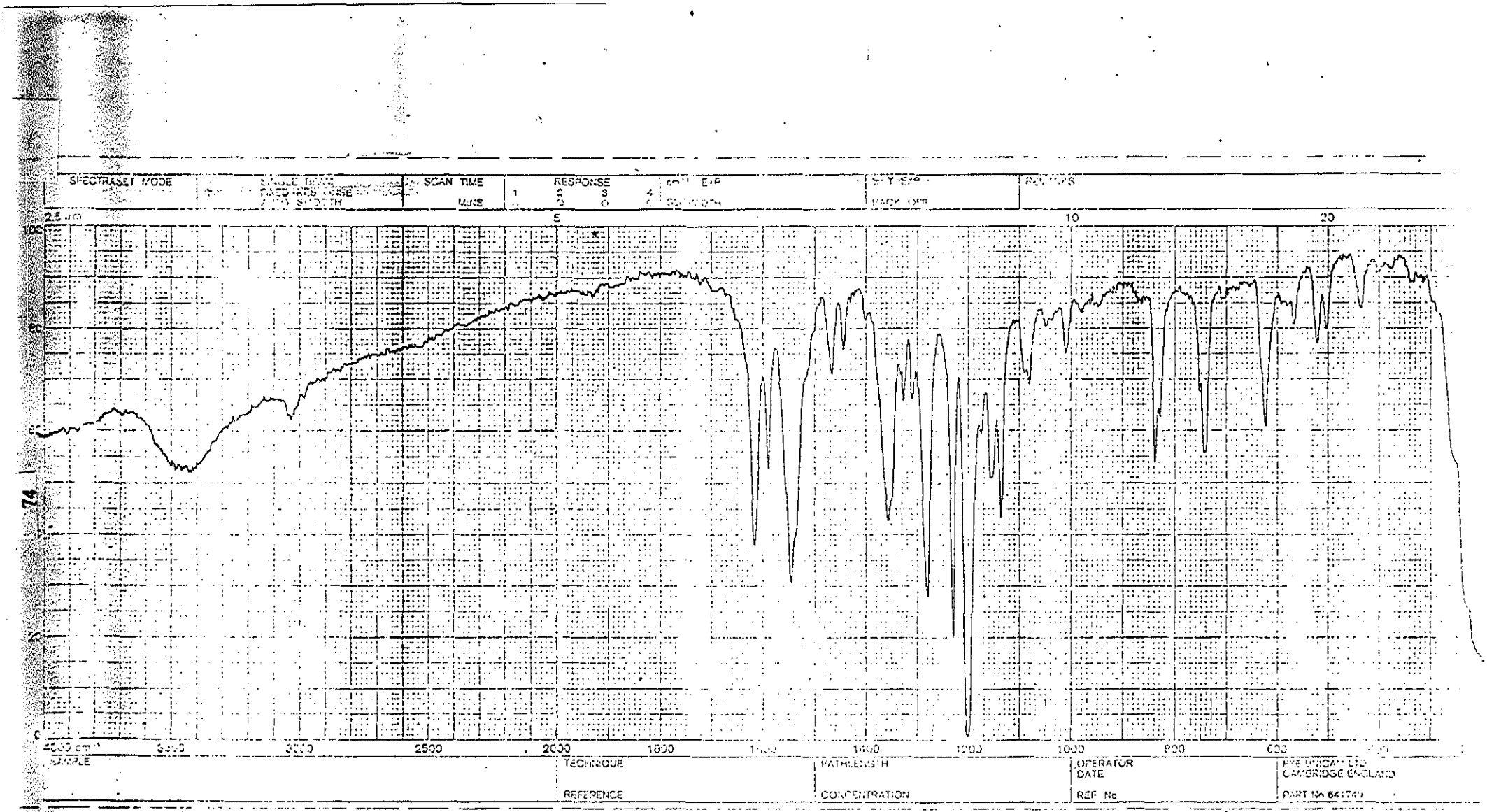


Fig. 14. Infra Red spectrum of silver(I)-1-nitroso-2-naphthol.

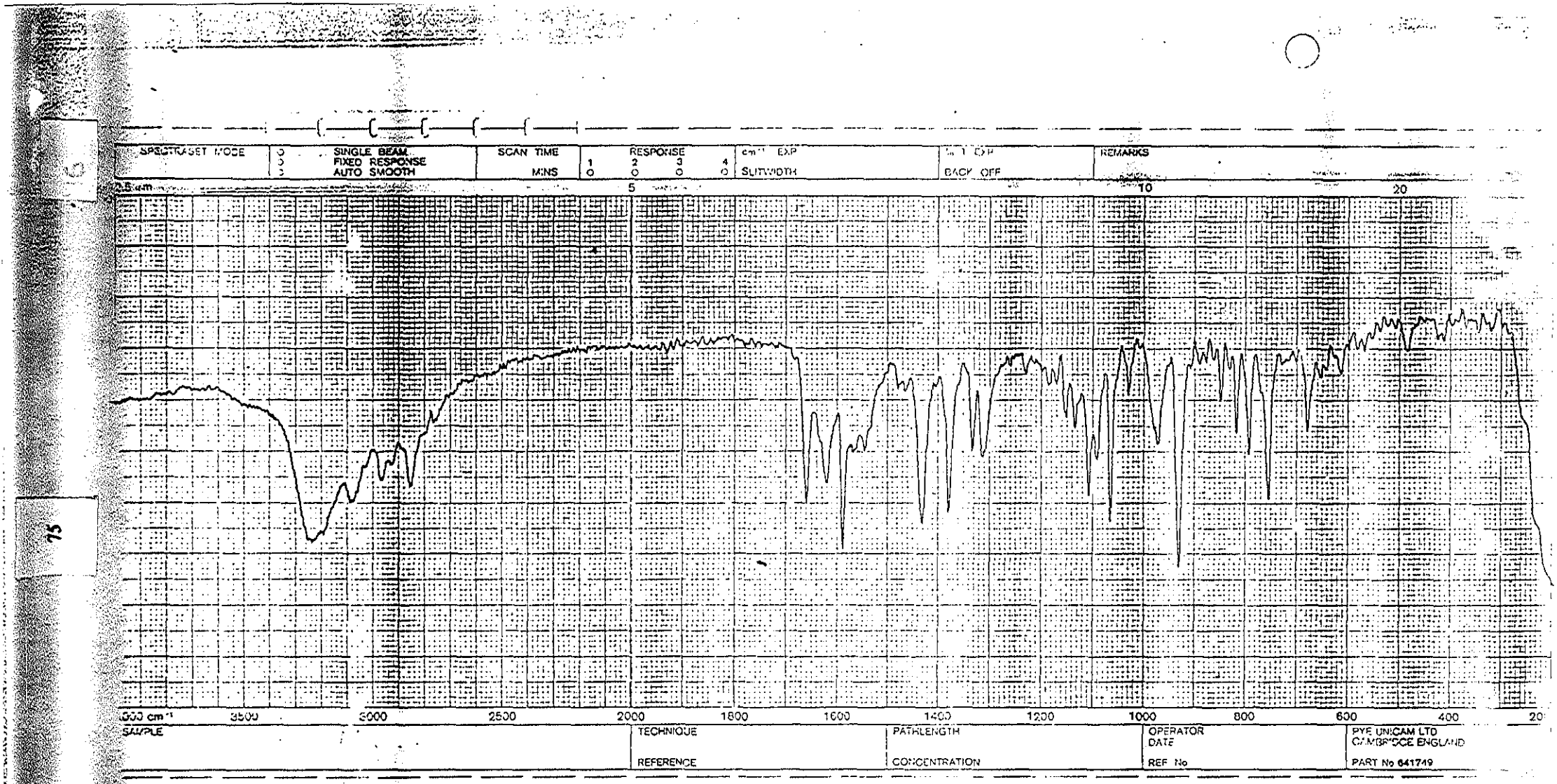


Fig. 15. Infra Red spectrum of 2-nitroso-1-naphthol.

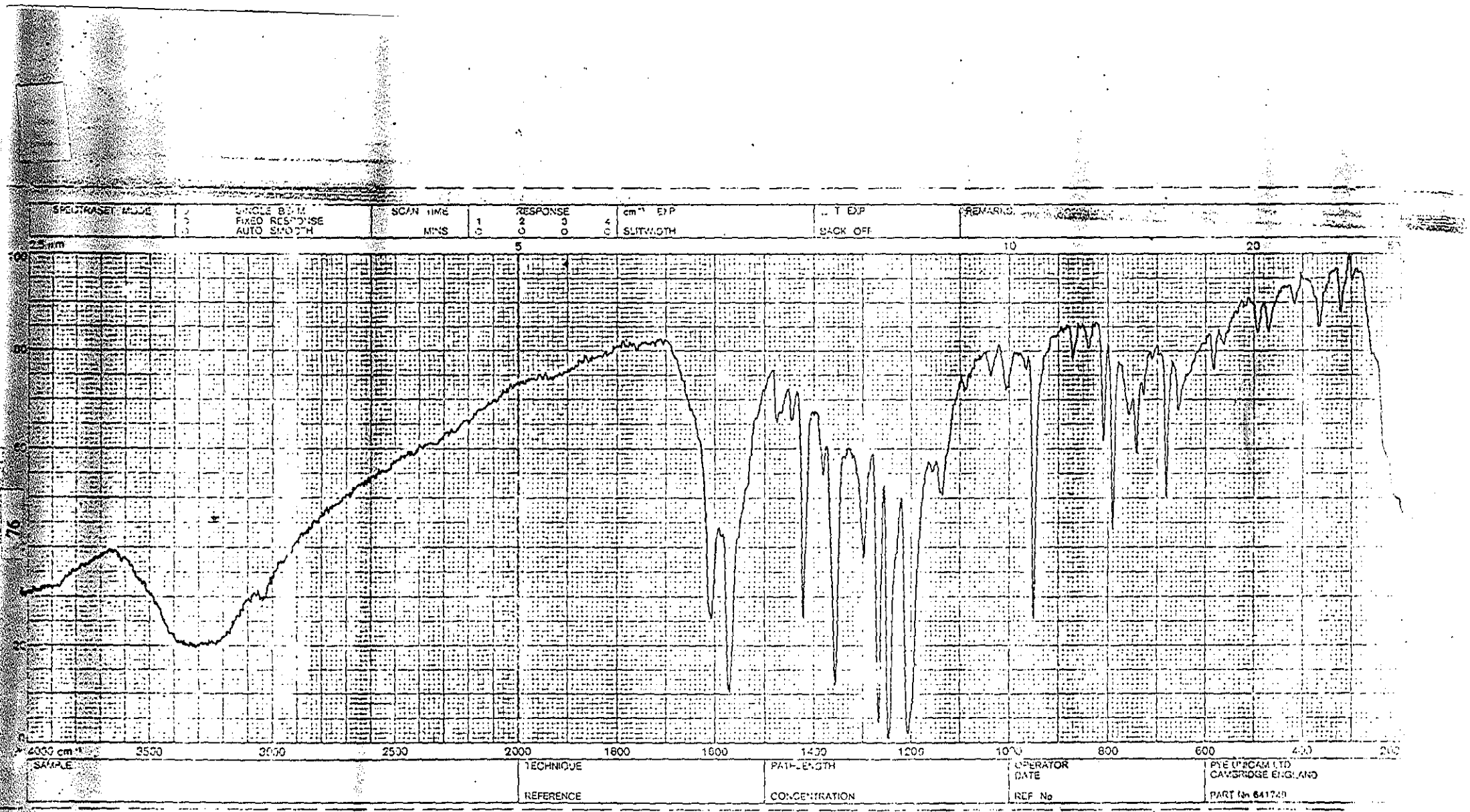
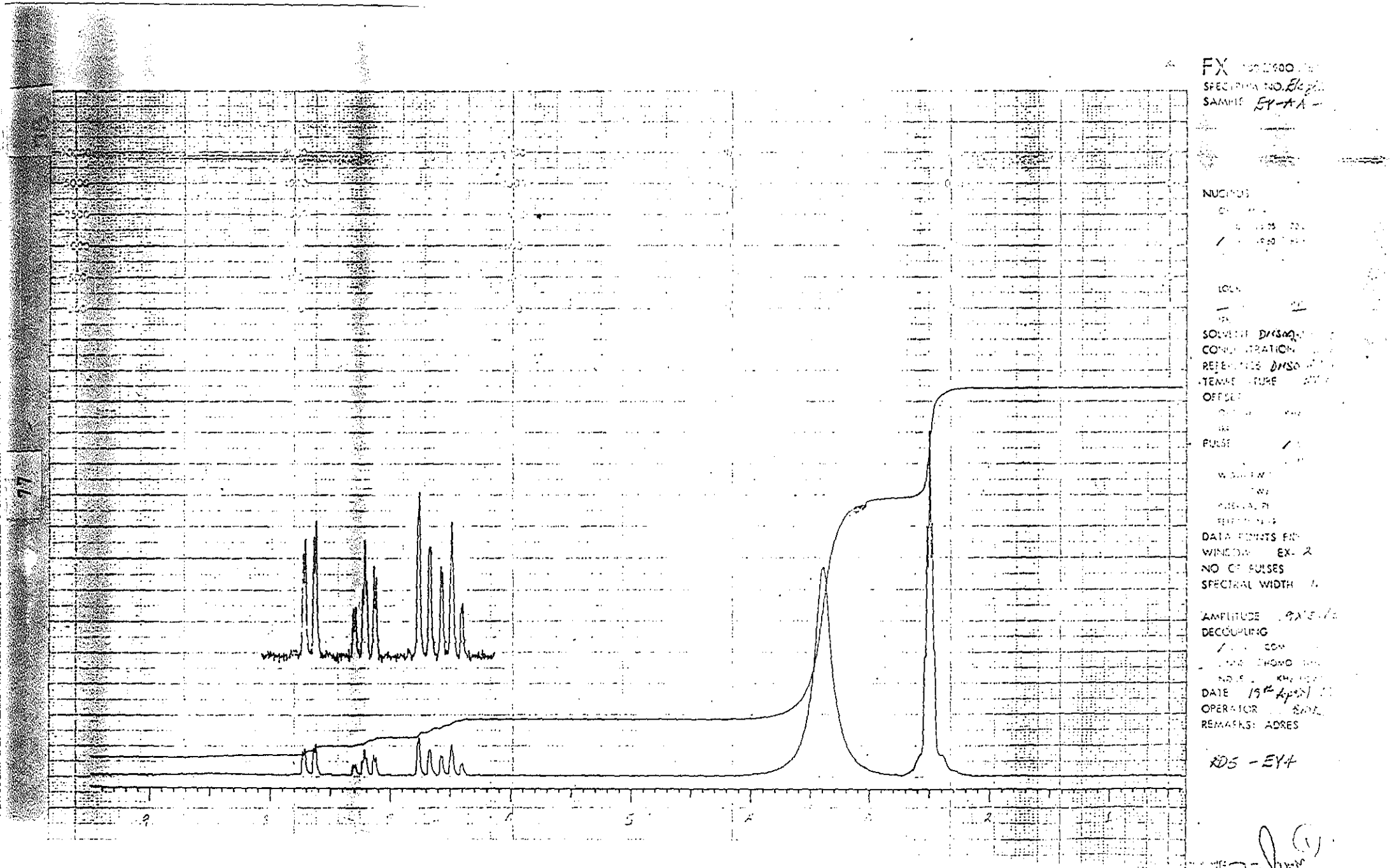


Fig. 16. Infra Red spectrum of silver(I)-2-nitroso-1-naphthol.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SOLVENT DMSO
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OFFSET
PULSE
DATA POINTS FID
WINDOW EX-2
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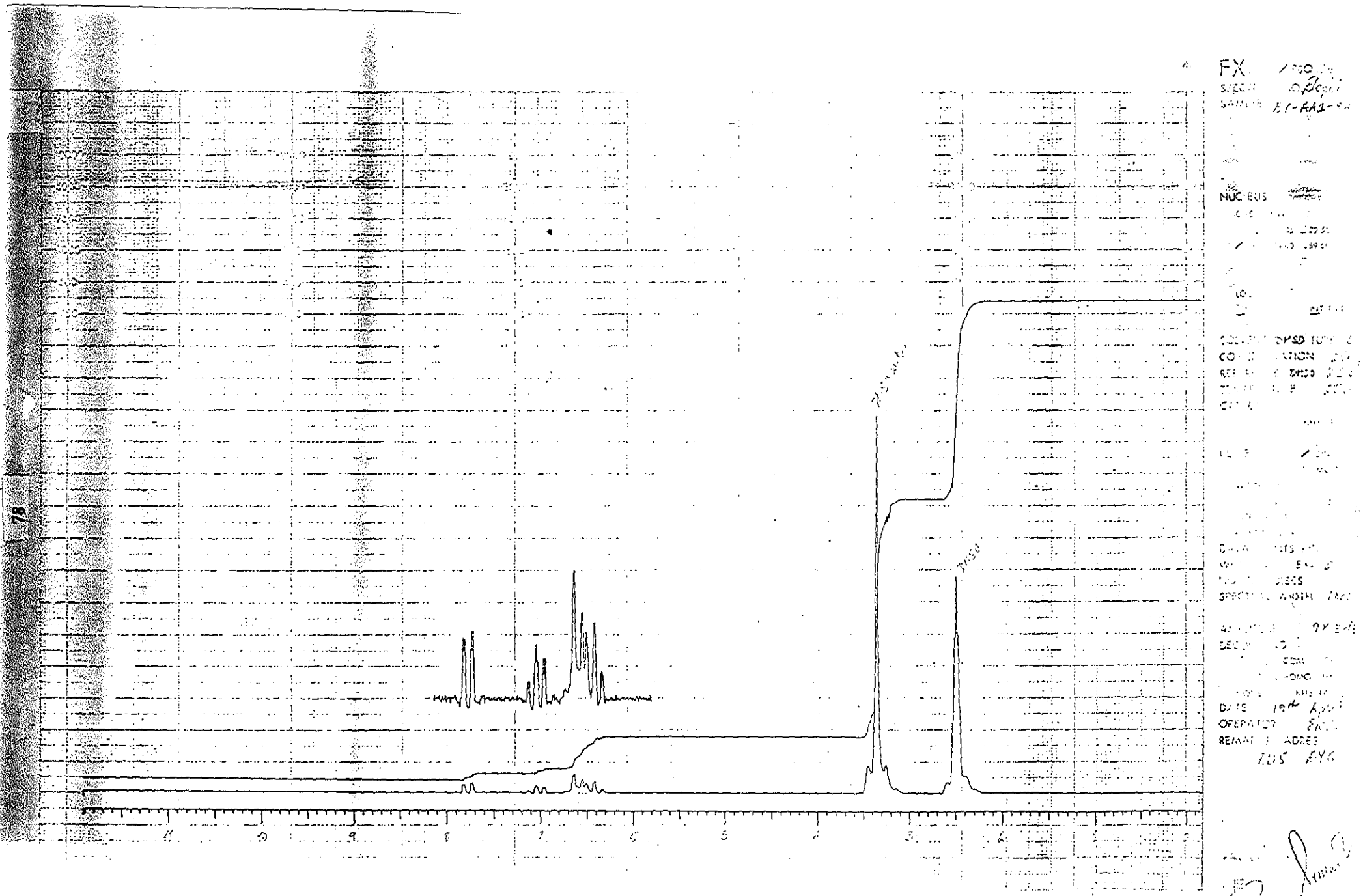
SPECTRAL WIDTH
AMPLITUDE
DECOUPLING
DATE 19th Apr
OPERATOR
REMARKS: ADRES
ADS - EY4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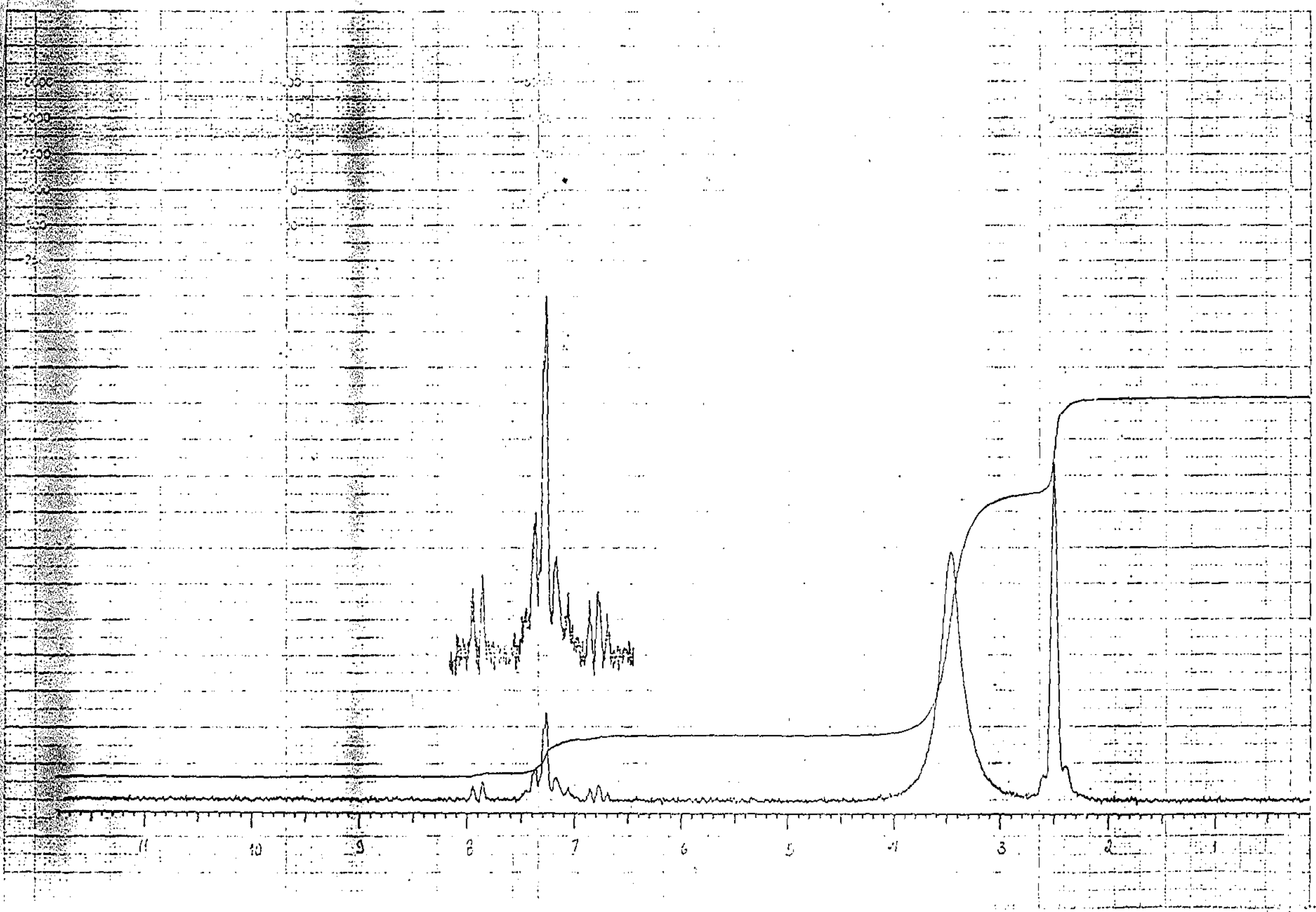


FX

SPECTRUM NO.

SAMPLE EY-NAA

NUCLEUS

LOCK

SOLVENT DMSO

CONCENTRATION

REFERENCE DMSO

TEMPERATURE

PULSE

DATA POINTS

WINDOW

NO. OF PULSES

SPECTRAL WIDTH

AMPLIFIER 7K3

DECOUPLING

DATE 15th April

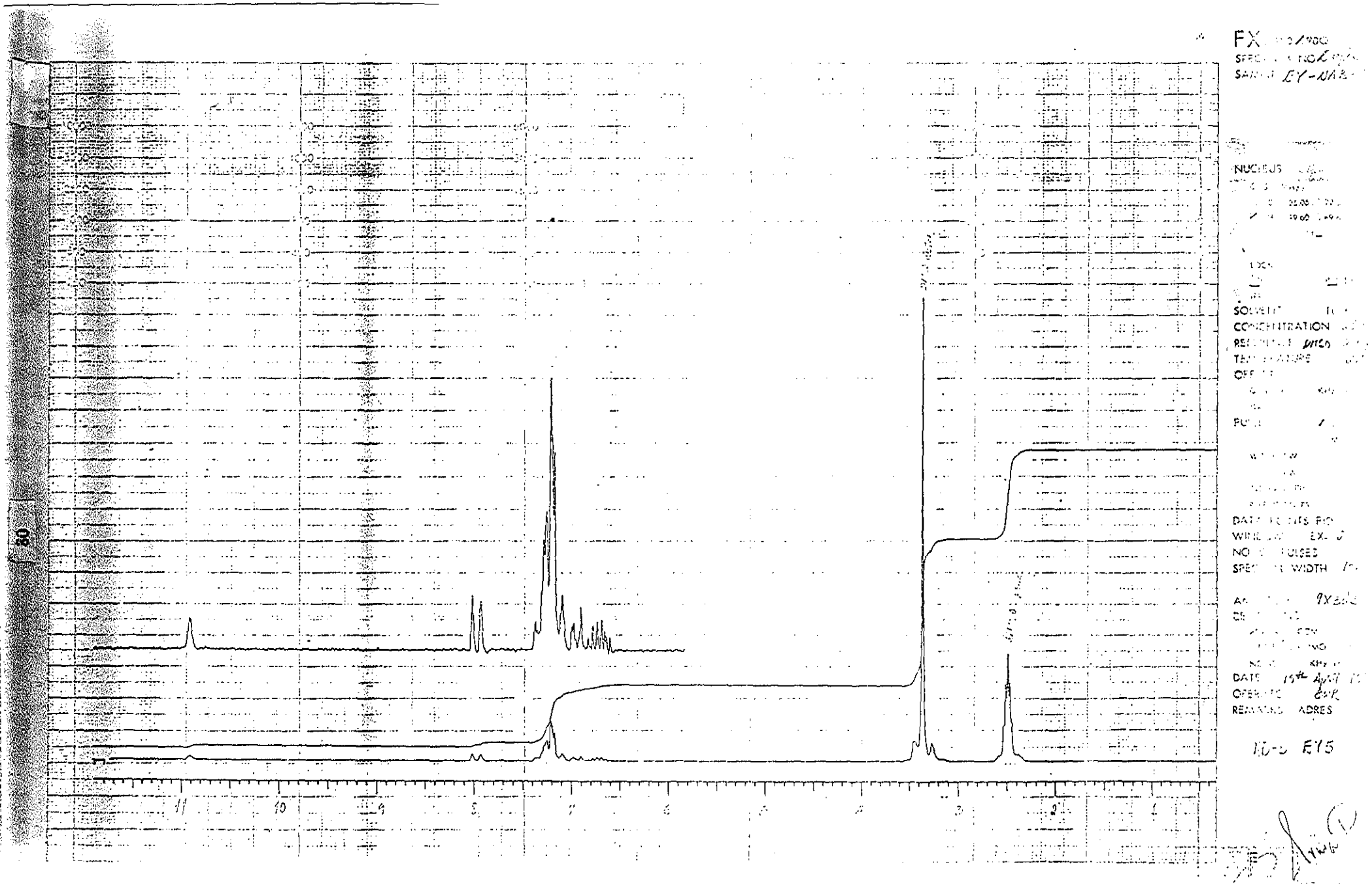
OPERATOR

REMARKS: ADREF

E05 EY-2

No signals for N-N' ~88 & bu-

so not present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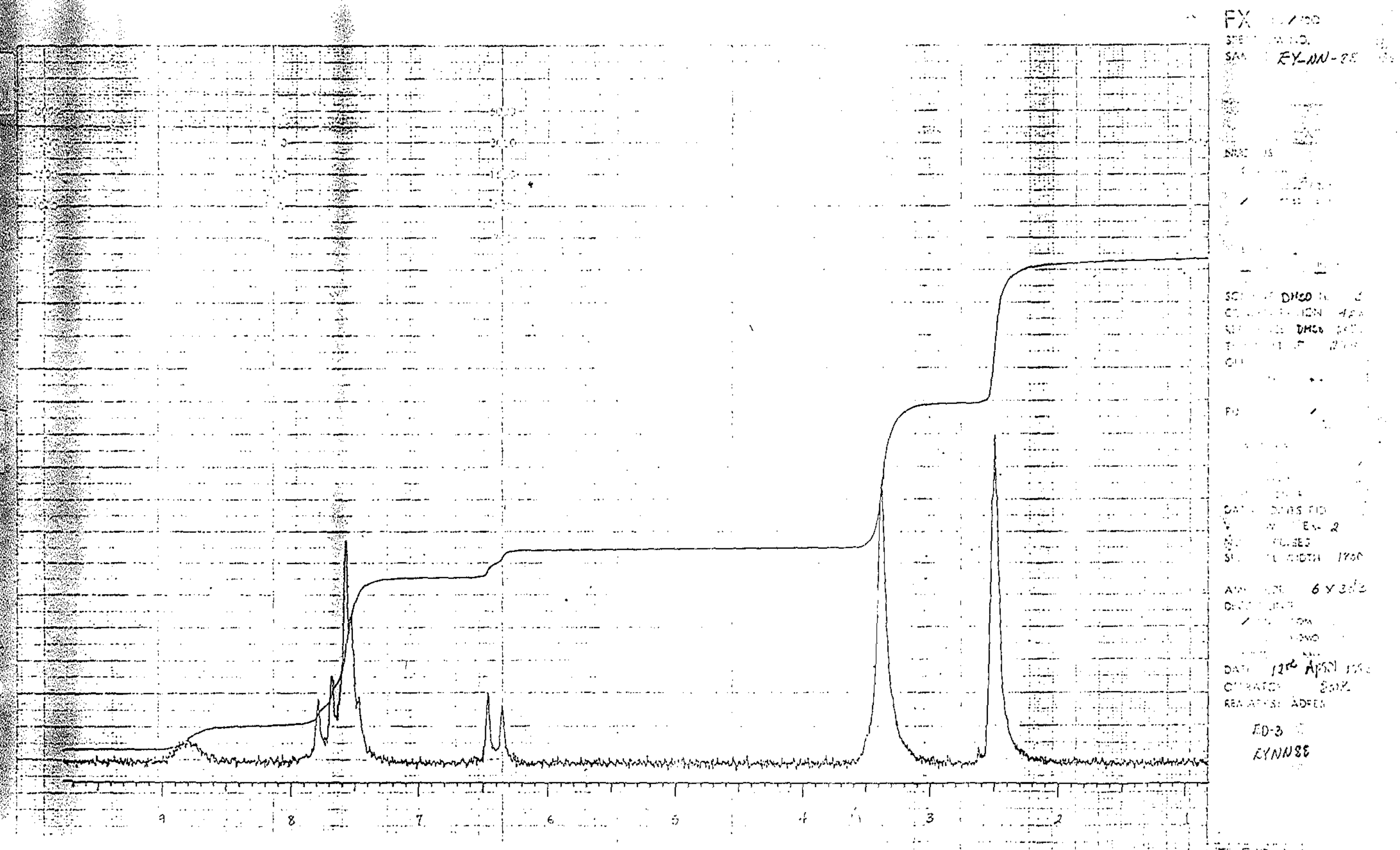
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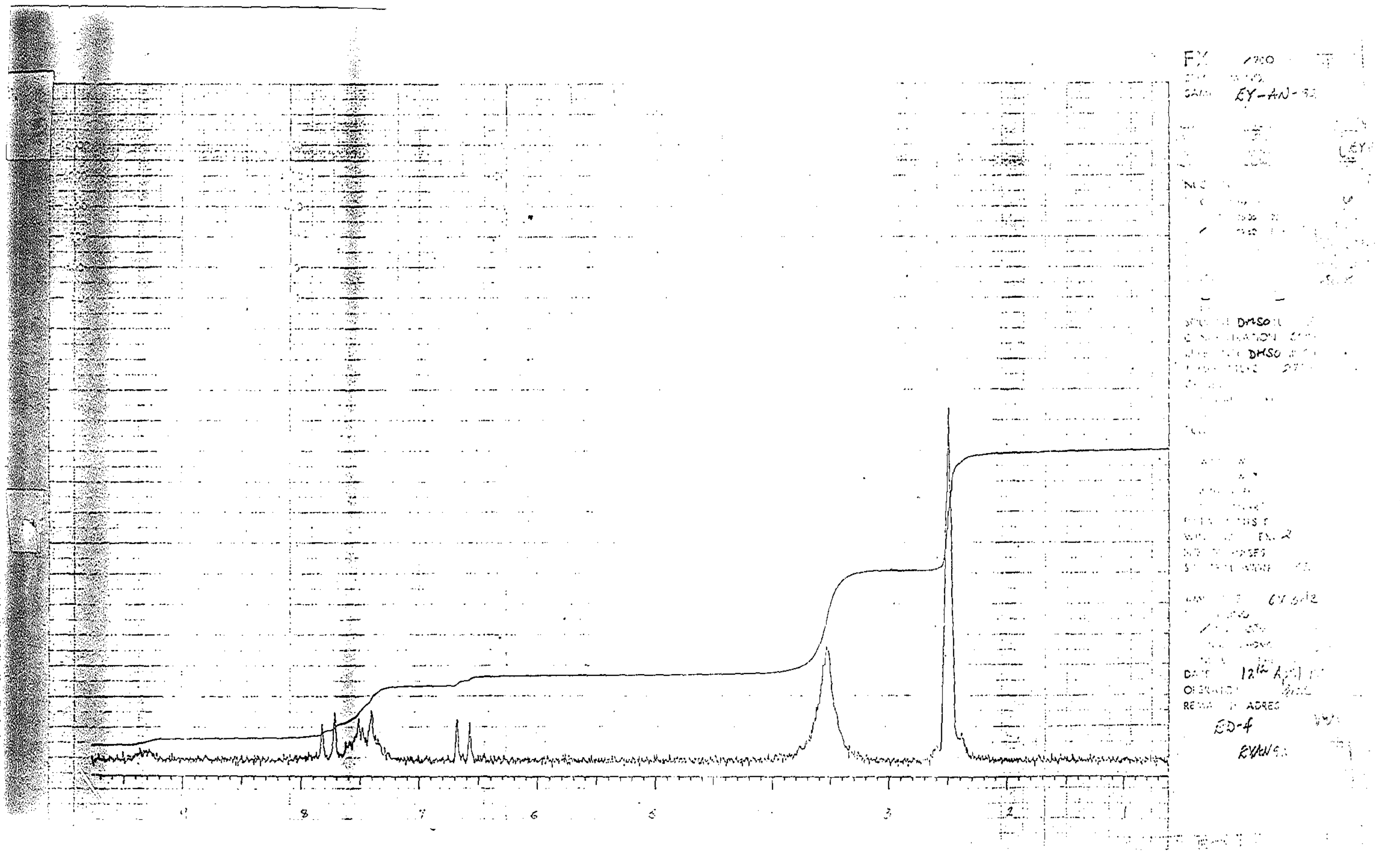
DMSO
6 X 3
12th April
ED-3
EYNN88



9
8
7
6
5
3
2
1
FX
EY-AN-
DMSO
DMSO
DATE 12th April
ED-4

EY-AA-93'

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EXPEF 39.5000PPM
OBS 1626.1466 MZ
NGAIN 12

NO	FREQ(HZ)	PPM	INT%
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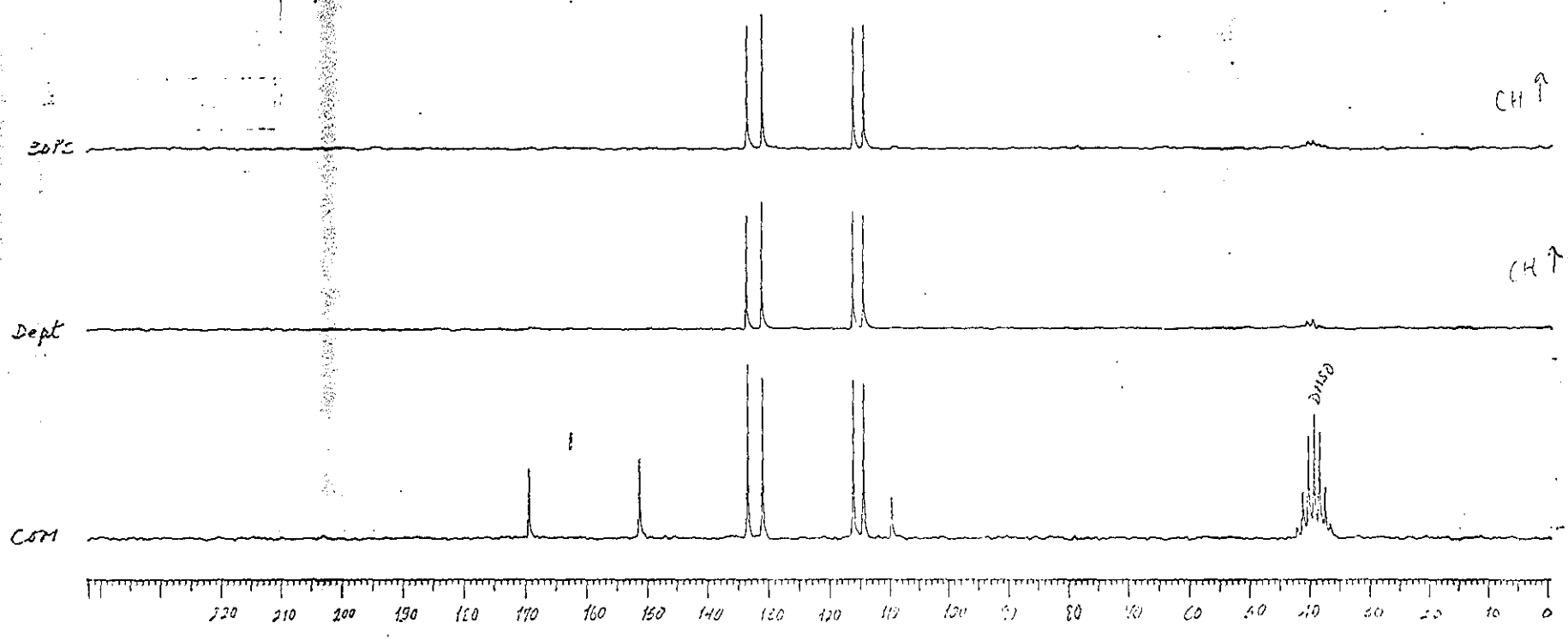
2	2418.67	151.350	3194
3	3018.22	133.592	6230
4	2954.59	131.119	6333
5	2621.59	116.741	6269
6	2623.32	114.642	6127
7	2476.57	109.985	1718
	972.78	41.327	1978
	918.09	40.423	4864
10	876.40	39.580	4859
11	869.69	39.546	4287
12	847.78	37.622	6858



83

TOTAL 13
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13	[illegible]	37.652	[illegible]

Elizabeth Y.
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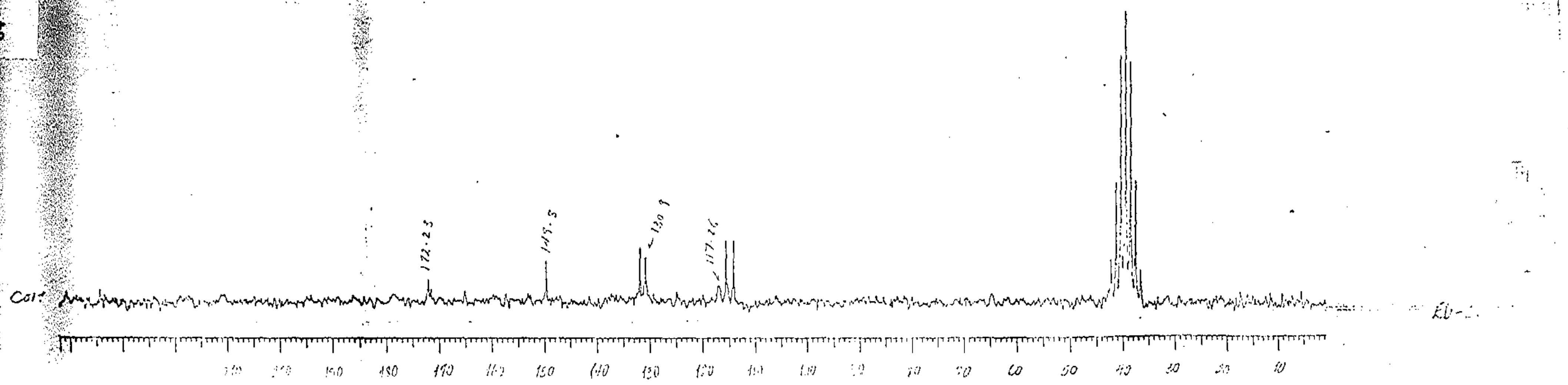
DMSO B.I. 39.5 ppm
^{13}C NMR
29th May 1993, [illegible]



DECLARATION

I, the undersigned, declare that this thesis is my work and that all sources of material used for this thesis have been duly acknowledged.

Name: Elizabeth Yohannes

Signature: Elizabeth Y.

Place and date of submission: Department of Chemistry

Addis Ababa University

June 10,1993.