COLLECTION, COMPILATION AND COMPUTER RETRIEVAL OF THE ANALYTICAL DATA OF COMPOUNDS LISTED IN THE MISUSE OF DRUGS ACT 1971.

By

David Watson

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Department of Pharmacy and the

Interdisciplinary Higher Degrees

Scheme,

University of Aston in Birmingham,

Gosta Green,

Birmingham, B4 7ET.

SUMMARY

The structure of the forensic science service and the functions of individual laboratories in England and Wales are briefly outlined.

The position in 1972 concerning the lack of forensic reference samples and analytical data on those compounds included in the Misuse of Drugs Act 1971 is described. As a result of these deficiencies a contract, which enabled the present work to be carried out was drawn up between the Interdisciplinary Higher Degrees Scheme and the Pharmacy Department at the University of Aston and the Home Office Central Research Establishment, Aldermaston. The requirements of this contract are given.

The methods adopted for creating a comprehensive reference sample and analytical data collection, based on the four methods of mass spectrometry, infra-red and ultra-violet spectrophotometry and thin layer chromatography included within the contract are illustrated. The commercial sources of 19 compounds are tabulated and the full synthetic methods for 18 compounds are listed in Appendix (1).

The application of "Chemical Ionisation" mass spectrometry to forensic analyses has been investigated and the conclusion formulated that the method was more specific than electron impact for potentially unstable compounds such as Methadone, Pethidine and Amphetamine.

The tabulated chemical ionisation mass spectra of 40 compounds are quoted.

The methods previously used to code analytical data for computer retrieval have been examined and a "major peaks" coding approach for mass and infra-red spectral data adopted. The development of computer programs to retrieve the coded analytical data in order to provide a fully comprehensive interactive retrieval system are described and the optimum conditions required when using this approach in terms of the quality of the analytical data and its future application to larger systems are proposed.

Flow diagrams, examples of the input required and the output produced by the program plus a detailed description of how the program operates fully illustrates the retrieval system in use. A full FORTRAN program listing is shown in Appendix (2).

The coded analytical details available for all the 117 compounds in the Misuse of Drugs Act are listed in Appendix (3).

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

A. The Forensic Science Service

Forensic Science has been defined as the application of scientific techniques to provide circumstantial evidence for the courts.

Traditionally forensic science was performed by a small number of pathologists who had developed interests in post-mortem investigation and chemical and physical analyses. They were usually consulted in all cases concerning offences against the person, rape assault, etc. and poisonings. This situation existed in England and Wales until the mid 1930's when the inventiveness of the modern criminal and the extent to which forensic examinations were becoming increasingly necessary exceeded the capabilities of the experts.

The first forensic science laboratory was opened by the Metropolitan Police in 1935 in order to provide an analytical service to the police in London and South East England.

Provincial laboratories followed, situated at Aldermaston, Birmingham, Bristol, Cardiff, Chorley, Harrogate, Newcastle and Nottingham. These laboratories are not administered by the police but are the responsibility of the Home Office Forensic Science Controller who in turn is directly responsible to a Secretary of State for Home

Affairs. Each laboratory provides an independent service to the police and, therefore, supplies a truly objective analysis on all case samples.

In 1966 a Central Research Establishment (C.R.E.), purely for research into forensic science was established alongside the Home Counties Regional Laboratory at Aldermaston. The Director of C.R.E. was also given responsibility for co-ordinating the research and development effort of the service as a whole.

Traditionally the forensic science laboratory in England and Wales was divided into 3 sections:-

(a) chemistry section, usually the largest and staffed mainly by chemists with a familiarity in the techniques of a wide variety of sciences and responsible for the analysis of any natural or manufactured product,

(b) a biology section dealing mainly but not exclusively with the investigation of offences against the person and being much involved with the identification and grouping of body fluid stains, the examination of hairs, fibres and the identification of plant material and

(c) a large important but somewhat ill defined section undertaking a wide range of work including document examination, firearms work, photography etc.

This organisational framework has evolved in the 40 years since the establishment of forensic science laboratories in this country. In recent years interdisciplinary boundaries have become blurred and the number of scientific

disciplines which might be involved in a single case has increased. The all round expert competent in a number of related fields and relying on his own knowledge and experience is disappearing giving way to groups of specialists supported by technicians. An example of this level of specialisation is seen in the field of chemical analysis where the traditionally large Chemistry section of forensic science laboratories is now divided into a smaller Chemistry section involved in the analysis of non-drug chemical samples, usually inorganic or metallic compounds, and a Toxicology section involved in the analysis of drugs and body fluids. All samples suspected of containing a drug, from white powders to the organs of poisoned patients are analysed in the Toxicology section of the laboratory.

The case work load of forensic science laboratories has greatly increased in the last 20 years mainly as a result of changing legislation. For example the Metropolitan Police laboratory dealt with a total of 1,325 cases in 1954 and with 40,007 in 1973. The cases in 1973 included 27,796 in connection with drink and driving offences and 6,940 involving drugs.

The investigation of cases involving drugs constitutes a large part of the case load of a forensic science laboratory. These samples can occur in varied form not all of which are commercially available. For example the hallucinogens L.S.D. and S.T.P., the doses of which are minute, may be absorbed on sugar lumps, blotting paper or "micro-dots". The principal and perhaps only concern of

the police and forensic scientists in all cases involving drugs (apart from poisoning) is to establish rapidly if possession of that drug is controlled by law. This is established after analysis of the samples by instrumental and non-instrumental methods and comparison of those results against authentic reference standards analysed in the same way. The identity of an unknown compound can only be established if its analytical data is very similar (within the limits of experimental error for each analytical technique) to that of a reference standard.

B. The Misuse of Drugs Act 1971 (M.D.A.)

The Misuse of Drugs Act 1971 replaced the Drugs (Prevention of Misuse) Act 1964 and the Dangerous Drugs Acts of 1957 and 1964. It provided statutory means for controlling the use of approximately 120 chemical compounds plus several biological samples such as coca leaf and raw opium.

C. The Contract

The attention of scientists at C.R.E. was focussed on to the fact that, although almost all the M.D.A. case samples encountered were easily identified the total number of chemical compounds controlled by the Act was far greater than the reference samples and analytical data available. It was considered that many of the obscure compounds in the Act could only be obtained by synthetic means. An external contract was drawn up to provide financial support for a project to be undertaken by the Author at the University of Aston, to synthesise the

compounds required and conduct an appraisal of the future use of computerised analytical data retrieval in forensic science.

A small 8K Hewlett Packard 2200 mini-computer had just been installed (1972) at C.R.E. and the initial development work started, also an electron impact mass spectrometer was on order from V.G. Micromass for which delivery was expected in January (1973). The contract was worded as follows, to include the use of both these advanced pieces of equipment,

"to study the problems associated with and to pursue,

(a) collection,

(b) compilation and retrieval of those substances controlled by the Misuse of Drugs Act 1971.

For the purposes of collection, controlled drugs shall be obtained from commercial sources, where available, but in the absence of such sources the drugs shall be synthesised and adequate confirmation of structure presented.

For compilation of the analytical data, emphasis shall be placed on ultra-violet and infra-red spectrophotometric techniques, mass spectrometry and thin layer chromatography using the modified Curry-Powell system."

CHAPTER 2

COLLECTION AND SYNTHESIS OF SAMPLES AND METHODS OF ANALYSIS

(I) Collection and Synthesis of Samples

A. Drug Samples Readily Available

The results of an initial survey on the drug collection at C.R.E. established that 73 compounds restricted by the Misuse of Drugs Act were available in quantities of 10 mgs or more. Three more compounds, N,N-Dimethyltryptamine, N,N-Diethyltryptamine and Bufotenine were purchased from R. Emmanuel to establish an initial collection of 76 compounds.

B. Sources of Additional Samples

The schedules to the M.D.A. restricted possession of some 117 named chemical bases plus any additional derivatives or salts of those bases. The 41 named compounds still required (33% of the total) had to be obtained in order to complete the collection.

Two approaches could have been followed with a view to completing the collection. One was to obtain the compounds from their original manufacturers or research chemists and the other to synthesise them by their previously published routes.

Analysis of the response to a standard letter sent to all British Drug Companies holding a Dangerous Drugs Licence (issued under the old Dangerous Drugs Act), had previously given scientists at C.R.E. valuable information as to possible sample sources. The letters had contained a request that the drug companies circulated should

indicate, from the full list of M.D.A. substances provided which drugs they had available. No overseas companies had been approached. The response to this circular had been disappointing. In the light of this information and after considerable discussion with scientists at C.R.E., it was decided that the best course of action would be to synthesise the compounds still required.

(1) Compounds Synthesised

The majority of the synthetic methods attempted followed previously published routes. An extensive literature search was undertaken to establish possible methods of synthesis for each of the compounds. Several of the compounds were covered by patents which contained only scant synthetic detail and often required complex multistage syntheses.

The following compounds were prepared over a period of 8 months:-

Acetyldihydrocodeine, Alphacetyl and Betacetylmethadol, Alpha and Betameprodine, Alpha and Betamethadol, Alpha and Betaprodine, Diampromide, Dioxaphetyl-butyrate, Morphine methobromide (and Methoiodide), Nicocodine, Nicodicodine, Normethadone, Norpipanone, Phenampromide & Prolintane.

Full synthetic methods are described in the Appendix(1) Syntheses of the 4 following compounds were attempted but proved unsuccessful:-

Allylprodine, Dimenoxadole, Metazocine & Myrophine.

A total of 18 compounds plus one derivative (Morphine methoidide) were prepared and included within the collection.

It was realised that it would not be possible to synthesise the compounds still required for the collection in the remaining time. During the course of this synthetic work, Burroughs Wellcome supplied four drug samples, in quantities of 100 mg or greater in each case.

A decision was made to approach manufacturers again because of the urgent need to complete the sample collection. It was felt that the major factor contributing to the lack of success of the previous letters was their lack of specificity and that a modified approach using a more specific and explanatory letter could well prove to have a greater positive response.

(2) Collection of Samples From Manufacturers

The previous literature search of synthetic methods was supplemented by additional searches on the location of drug companies and individual scientists. A letter was sent to each company whose name had been associated with a particular drug or drugs explaining the following:-

(i) the author's status at Aston and the exact nature of the project,

(ii) the potential legal problems if the samples requested were not made available for forensic identification,

(iii) the trivial name and full chemical name of the compound, plus the trade name and company code if available,

(iv) the names of the inventors and references to patents and publications,

(v) an offer to purchase the samples. All the samples received were obtained free of charge.

(vi) If the letter was sent to an overseas company a statement was included, to the effect that the appropriate M.D.A. Licence and import formalities would be handled by a senior scientist at C.R.E.

The responses to the letters were far beyond expectations. Details of the companies which supplied samples are listed below:-

Drug Company, Organisation or Scientist from whom Sample was Requested	Drug(s) Supplied	Quantity
Wellcome Foundation Ltd. London.	Dimethylthiambutene	100 mg
	Ethylmethylthiambutene	100 mg
	Isomethadone	100 mg
	Norpethidine	100 mg
Dr. E. May, N.I.H. Bethesda, Maryland, U.S.A.	Metazocine	200 mg
	Desomorphine	100 mg
	Myrophine	100 mg
	Racemoramide	100 mg
Hofmann La Roche, Basle, Switzerland.	Levomethorphan	100 mg
	Phenomorphan	100 mg
Dr. Casey, Liverpool Polytechnic, and Dr. Iorio, Rome.	Allylprodine	230 mg
Wyeth Research Labs. Pennsylvania, U.S.A.	Proheptazine	500 mg
Dr. Renk, Ciba-Geigy, Basle, Switzerland.	Etonitazene	100 mg
Winthrop Labs. New York, U.S.A.	Piminodine	1 g
Dr. Paul Janssen, Janssen Pharmaceutica, Belgium.	Phenoperidine	1 g
	Bezitramide	1 g

Drug Company, Organisation or Scientist from whom Sample was Requested	Drug(s) Supplied	Quantity
Carlo Erba, Milan, Italy.	Properidine	1 g
Mallinckrodt Inc. Missouri, U.S.A.	Metopon	1 g
Reckitt & Colman, Hull, Yorkshire.	Etorphine	500 mg

Several other drug companies were approached as possible sources, two of which perhaps require further mention.

A sample of Dihydrocodeinone-o-carboxy-methyloxime was requested from Merrell, Cincinnati, Ohio, U.S.A. In their reply, it was stated that the company did have a sample but they were not able to supply it because it was not their property.

For the second example, a request was made to Endo Laboratories, New York, for a sample of Hydromorphinol. The company gladly offered to supply a sample of Oxymorphone which they, the original manufacturers of this compound, felt was the equivalent of Hydromorphinol. No other confirmation of this could be obtained from the literature[1].

In all cases where drugs were imported the appropriate licence to import was granted by the Dangerous Drugs Branch of the Home Office. For substances which had not been included within the W.H.O. estimates of dangerous drugs allowed to be imported and exported in any one

year, special application was made to Geneva. For example, in order to obtain the drug Properidine as well as the M.D.A. licence and the request for addition to W.H.O. estimates a formal application also had to be made to the Italian Consulate signed personally by the Assistant Under Secretary of State.

(3) Final Position with Regard To Sample Collection

76 samples were initially available,

18 compounds were synthesised,

19 compounds were obtained from manufacturers,

and 4 compounds, Dimenoxadole
Clonitazene
Hydromorphinol
6-Methyldihydromorphine,

were discovered in very small quantities of about 1 mg each at C.R.E., sufficient for mass-spectral analysis only.

A total of 117 compounds were now available. Two compounds Acetorphine and Dihydrocodeine-o-carboxymethyl-oxime were not available. (The drug Acetorphine, one of the most powerful narcotic agents known is prepared by a simple acetylation of Etorphine. This reaction, however, was not performed because of the potential hazards involved.)

(II) Methods of Analysis

Analysis of the compounds in the collection by 4 analytical methods was required by the Home Office Contract. Each of the methods employed is briefly described below.

(1) Infra-Red Spectrophotometry (I.R.)

In the infra-red region of the electromagnetic spectrum lie the rotational and vibrational spectra of molecules, i.e. the manifestations of the changes in the molecular rotational and vibrational energy that can occur under certain conditions by the interaction of infra-red radiation with matter.

The rotational and vibrational frequencies which thus appear are directly dependent on certain molecular constants, for example, the force constants between atoms and the moments of inertia about certain axes. The molecular constants can thus be calculated on the basis of simple molecular models. Infra-red spectrophotometry (the optical and electronic instrumental arrangements which permits observation of the infra-red region) has become today an indespensable auxiliary technique for chemical structural analysis.

The physicist and technologist characterise infra-red radiation, just as that of other spectral regions by its wavelength. The micron (μ) is generally used as the unit. Chemists involved with the investigation of molecular structure prefer another convention. The radiation is characterised by stating the number of waves which are contained in a length of 1cm. This number, the

reciprocal of the wavelength in centimetre units is called the wavenumber; its unit is the reciprocal centimetre (cm^{-1}). Up to date no binding agreement over the exclusive use of one of these two systems has been concluded. Machines are available for recording spectra in terms of their wavelength (where the wavelength is on a linear scale, as on the Perkin Elmer 137 at C.R.E.) or in terms of their wavenumber (where the wavenumber is on a linear scale, as on the Unicam SP 200 at Aston). Examples of both are illustrated and compared in FIG:2.1

The most important area of the infra-red spectrum for comparative identification is the "fingerprint" region of 1333-667 cm^{-1} (7.5-15μ).

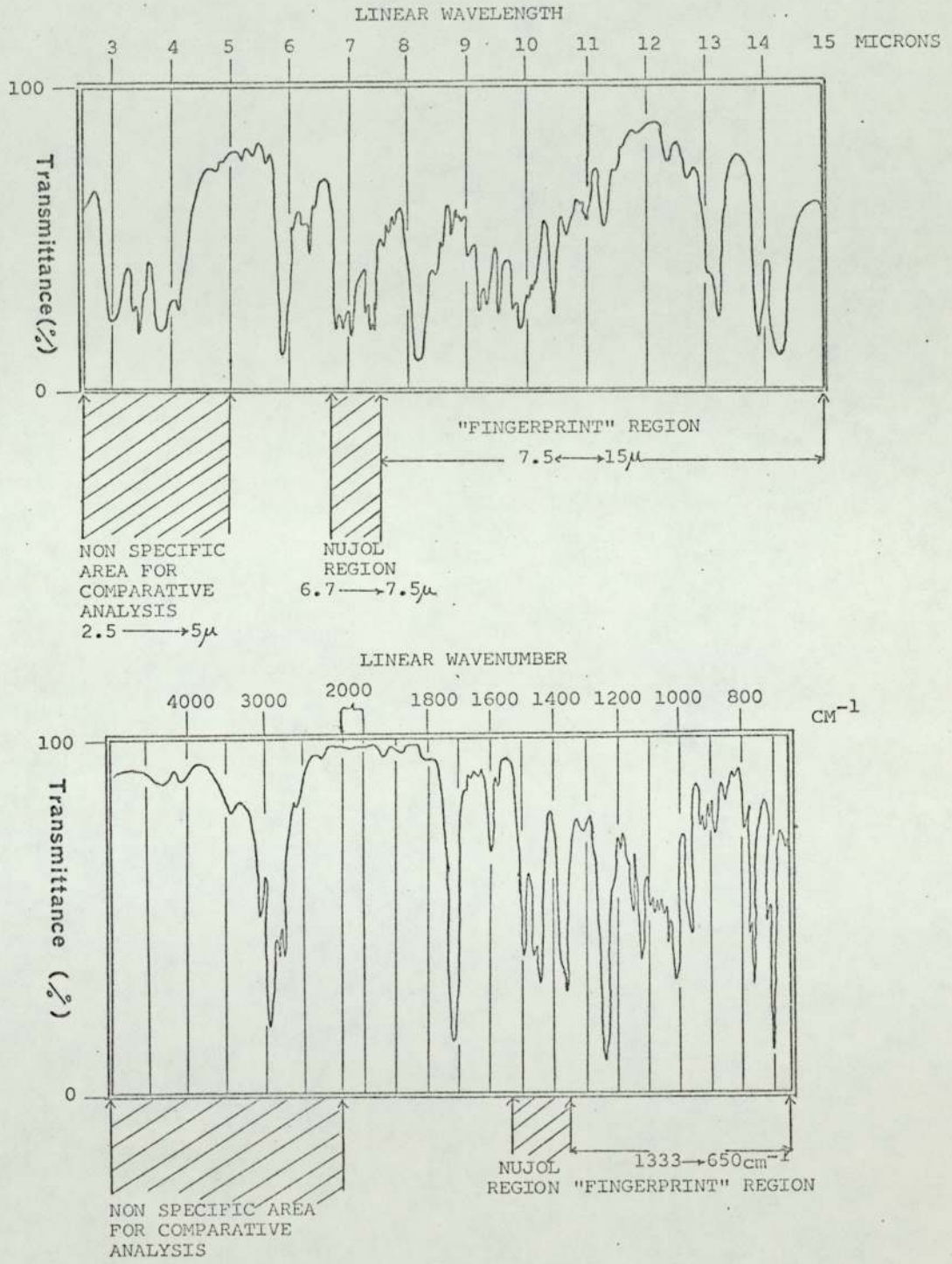
Spectra for forensic analyses are usually recorded in the solid state either as nujol mulls (suspensions in liquid paraffin) or potassium bromide discs. For this project potassium bromide discs were preferred since they permitted spectra to be recorded on samples of the order of 0.5mg and avoided producing interfering peaks in the nujol (hydrocarbon) regions, 2900, 1465 and 1380 cm^{-1}.

Infra-red spectrophotometry has the disadvantage of requiring relatively large amounts (0.5mg) of pure sample. Samples, however, can be purified by elution from a paper or thin-layer chromatogram. If micro potassium bromide discs are used on conventional instruments or, if high resolution instruments are used, then as little as 10μg can give a spectrum of practical use.

FIG: 2.1

INFRA-RED SPECTRA

α-Acetylmethadol



For this project spectra were recorded as potassium bromide discs on the Perkin Elmer 137 at C.R.E.

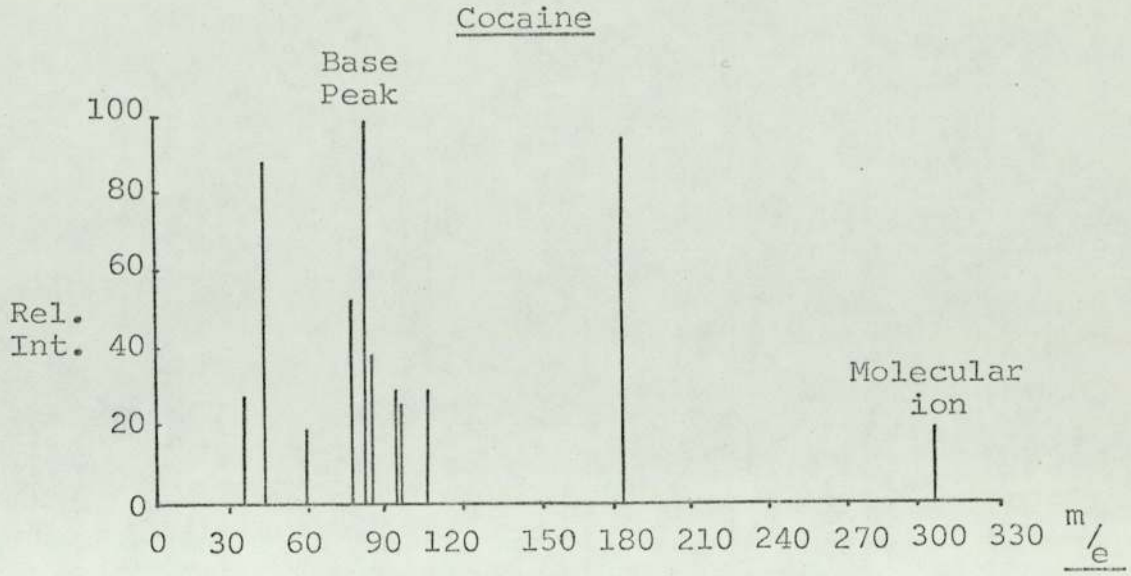
(2) Mass Spectrometry (M.S.)

Structural analysis by electron impact (E/I) mass spectrometry is accomplished by bombarding submicrogram quantities of a compound with an electron beam of 5-70 e.v. and recording the fragmentation pattern according to mass.

Sample vapour diffuses from the gas chromatograph, direct insertion probe or liquid inlet into the low pressure system of the mass spectrometer where it is ionised with sufficient energy to cause fragmentation of the chemical bonds of the original molecule. The positively charged ions produced by a series of unimolecular reactions are accelerated into a magnetic field which focusses the ions according to their mass-to-charge ratios ($^{m}/_{e}$ values) and permits relative abundance measurements. The resulting record, usually a photographic trace of ion abundance versus mass-to-charge ratio constitutes a fragmentation pattern. The peaks on the photographic trace are counted manually (or automatically in the case of M.S. - computer systems) from low to high mass to provide the $^{m}/_{e}$ values and since all the peak widths are constant the relative intensities of each $^{m}/_{e}$ value are usually presented as a bar diagram as shown in FIG:2.2

FIG: 2.2

ELECTRON IMPACT MASS SPECTRUM



The spectrum is normalised so that the most abundant ion equals 100% (termed the base peak) and the remainder are expressed as a fractional percentage of that ion. The ion which represents the molecular weight of the compound is termed the molecular ion (M^+). Isotopic contributions and ion-molecular reactions can produce ions at $^m/_e$ values greater than the M^+ and, therefore, for comparative analyses the highest $^m/_e$ value cannot be presumed to represent the molecular weight of the sample.

The quality of the spectrum obtained is determined by the samples' stability (Chapter 3), its purity and chemical form (Chapter 6 Section 1). Impure samples must be treated by a chromatographic procedure before they are examined by mass spectrometry. For this project the mass spectra were recorded initially on the A.E.I. MS 9 Spectrometer at Aston and later repeated on the Micromass 12B at Aldermaston.

(3) Ultra-Violet Spectrophotometry (U.V.)

Absorption spectra in the ultra-violet and visible regions of the spectrum arise from transitions induced in the outer electrons of molecules, and principally those electrons involved in bond formation. The spectra are of special interest in organic chemistry because they reveal double bond structure, more particularly conjugated double bonds, as in the benzene ring.

Two energy conditions operate. The first controls the frequency of radiation which causes transitions and is called the Quantum condition. Electrons may be induced to jump from a bonding valence shell to an unoccupied non-bonding site at another level. In order to facilitate this jump, one quantum of energy, equal to the difference between the two levels, is required to be imparted to it. The electron is thus excited from the ground state. The excited state is unstable and the electron returns to the ground state loosing surplus energy in the process. These electronic jumps can be induced by electrical or radiation energy. The highest separation of energy levels is found when σ bonds are excited

producing $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$ transitions and they give rise to absorptions in the 120-200 nm region. This region (termed the vacuum ultra-violet) is both difficult to measure and uninformative, however, at 200 nm and above excitations of electrons from p, d and π orbitals giving rise to $\pi \rightarrow \pi^*$ transitions and $n \longrightarrow \pi^*$ transitions particularly in π conjugated systems gives readily measured and informative spectra.

The second energy condition determines the intensity of absorption. The intensity of absorption is directly proportional to the concentration of the solution under examination (in gm moles per litre) the path length of the light passing through the solution (in centimetres) and a term ε (the molar extinction coefficient) which is the inherent amount of energy a chromophore absorbs at any particular wavelength. For analytical purposes, in order to provide a comparative means of identifying the relative intensities of molecules this is quoted as the $\underline{E^{1\%}_{1cm}}$, i.e. the extinction coefficient for a 1% solution in a cell of 1 cm path length calculated in the following way:-

$A = a, b, c$ (Beer-Lambert law)

A = absorbance value on spectrum

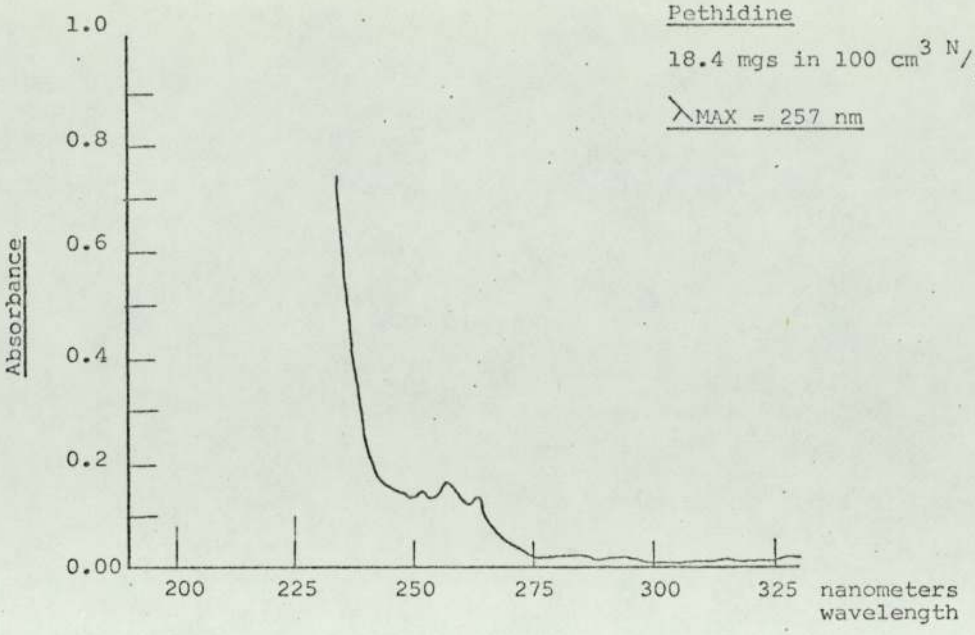
$a = \underline{E^{1\%}_{1cm}}$

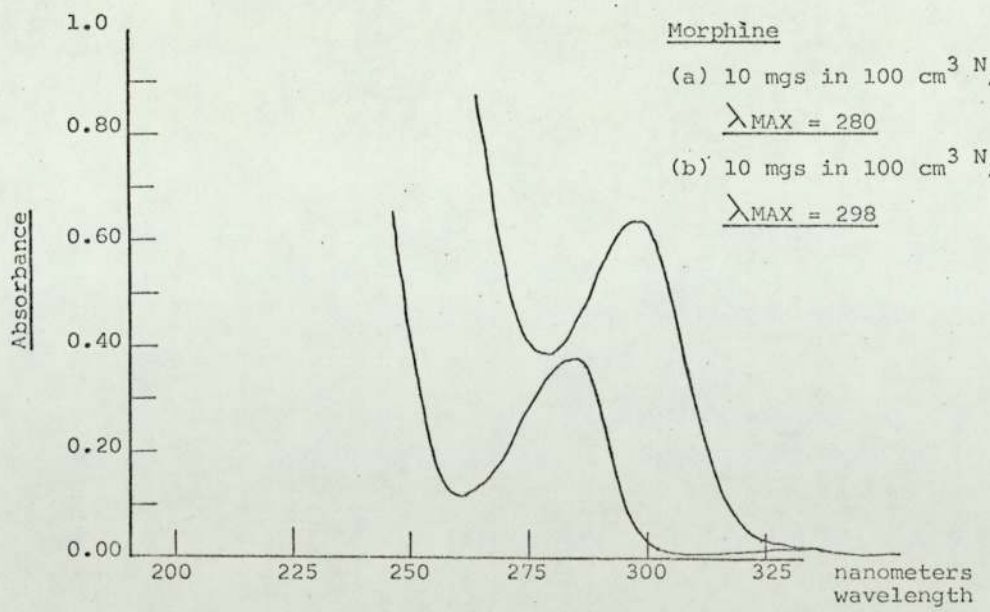
b = path length of 1 cm

c = concentration of 1% solution

Spectra can be obtained on microgram quantities of material depending on the value of the $E^{1\%}_{1cm}$ (the nature of the absorbing chromophore).

FIG: 2.3 ULTRA-VIOLET SPECTRA





The characteristic qualitative feature of a U.V. spectrum is the position (wavelength) at which the maximum absorbance value is recorded, termed the λ_{MAX}. The value of the λ_{MAX} provides valuable evidence on the nature of the molecule present. For example, pethidine which only contains the weak benzene chromophore has a λ_{MAX} = 257 nm, whereas morphine has an intense absorption of λ_{MAX} = 280 nm.

For the purpose of this project a file was established, recorded on the Unicam SP 800 Spectrophotometer at C.R.E. of the λ_{MAX} in $^{N}/_{10}$ sulphuric acid solution for all the compounds in the collection.

The spectra of the bases were also obtained and the acid-base shift was recorded, as well as the quantitative estimation of intensity $E^{1\%}_{1cm}$.

(4) Thin-Layer Chromatography (T.L.C.)

The separation of complex mixtures is carried out on a glass or plastic plate precoated with a mixture of binding agent (usually plaster of Paris) and static phase. This plate after treatment with a drop or smear of the mixture is usually held vertically in a tank containing a liquid solvent phase which absorbs up the plate and separates the mixture into its respective components. The mechanism of separation involves partition, adsorption, or ion-exchange, individually or in combination.

The distance on the plate travelled by the sample divided by the distance on the plate travelled by the solvent front is termed the Rf value. This is universally

accepted as the qualitative feature of thin-layer chromatography.

An enormous variety of static phases and solvent systems have been utilised and certain methods have been preferred for the analyses of particular classes of compound. For this project the Curry-Powell[2] system was chosen for its wide applicability to the separation of bases.

Thin-layer chromatography is a valuable supporting technique to the other three methods chosen because of its ability to separate microgram quantities of material which can then be utilised for I.R., U.V., or M.S. analyses. It is unfortunately perhaps the most difficult to reproduce and work is currently being undertaken at C.R.E. to improve and identify sources of error in all chromatographic techniques.

A file of the Rf values for all the compounds in the collection was established.

CHAPTER 3

CHEMICAL IONISATION MASS SPECTROMETRY

(I) Initial Observations on the Electron Impact Mass Spectral Data

A. Introduction

For the purpose of this study the drugs controlled by the Misuse of Drugs Act were divided into 4 major chemical groupings:-

(1) Morphine-type

(2) Pethidine-type

(3) Methadone-type

(4) Amphetamine-type

The remainder of the drugs were a miscellaneous collection of hallucinogens and appetite suppressants which were not classified or examined at this stage.

The drugs in groups 2, 3 and 4 had proved to be particularly difficult to identify by conventional electron impact mass spectrometry.

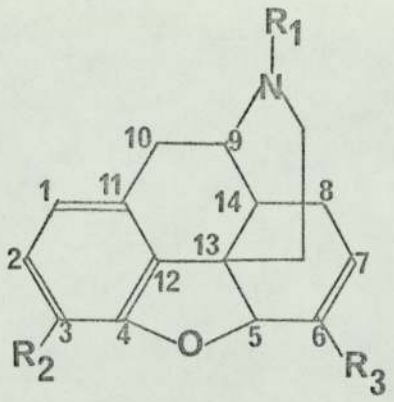
B. Results and Discussion

1. Morphine and Related Compounds

Structures - FIG: 3.1 (a), (b) & (c)

The results in tables 3.1 (a), (b) & (c) illustrate the diagnostic peaks which occurred in the electron impact spectra of a series of drugs related to morphine. All of the materials except nicodicodine showed a molecular ion as a significant peak in the spectrum. This permitted ready identification of these materials except in the case of the isomeric compounds morphine and norcodeine.

FIG: 3.1(a)
Drugs Based on the Morphine Structure

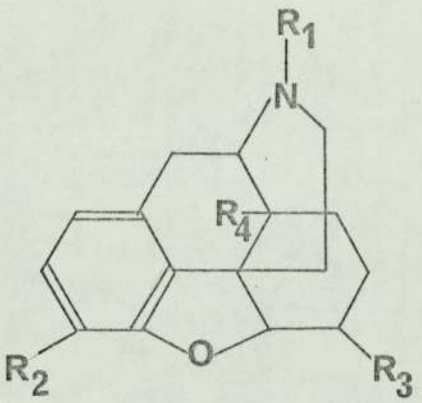


Name	R_1	R_2	R_3
Normorphine	H	OH	OH
Norcodeine	H	OCH_3	OH
Codeine	CH_3	OCH_3	OH
Ethylmorphine	CH_3	OCH_2CH_3	OH
Benzylmorphine	CH_3	OCH_2–C$_6$H$_5$	OH
Pholcodine	CH_3	OCH_2CH_2–N(CH$_2$CH$_2$)$_2$O	OH
Nicocodine	CH_3	CH_3	$OC(=O)$–C$_5$H$_4$N
Nicomorphine	CH_3	$OC(=O)$–C$_5$H$_4$N	$OC(=O)$–C$_5$H$_4$N
Diacetylmorphine	CH_3	$OCCH_3$	$OCCH_3$

TABLE 3.1(a)
Electron Impact Results for Morphine and Related Compounds

Name	Formula	Mol.Wt.	Highest $^{m}/_{e}$ and the 4 Major Peaks (Rel. Int.)
Normorphine	$C_{16}H_{17}NO_3$	271	271(100),271(100), 81(77),150(64),148(55)
Norcodeine	$C_{17}H_{19}NO_3$	285	286(19), 285(100), 81(32),262(32),148(20)
Morphine	$C_{17}H_{19}NO_3$	285	286(14), 285(100), 42(43), 70(41),162(25)
Codeine	$C_{18}H_{21}NO_3$	299	300(20), 299(100), 81(33), 42(26),229(24)
Ethylmorphine	$C_{19}H_{23}NO_3$	313	313(100),313(100),243(76),162(54),124(49)
Benzylmorphine	$C_{24}H_{25}NO_3$	375	376(13), 284(100), 91(62),375(50), 81(38)
Pholcodine	$C_{23}H_{30}N_2O4$	398	398(3), 100(100),114(96), 42(16), 56(12)
Nicocodine	$C_{24}H_{22}N_2O4$	404	404(100),282(90), 106(59), 78(42),229(39)
Nicomorphine	$C_{29}H_{25}N_3O5$	495	495(10), 172(100),106(80), 42(56), 57(47)
Diacetylmorphine (Heroin)	$C_{21}H_{23}N$ 05	369	370(16), 327(100),369(66), 43(51),268(42)

FIG: 3.1(b)
Structures of the Compounds Related to Dihydromorphine



$R_1 = CH_3$

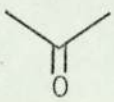
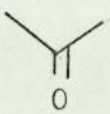
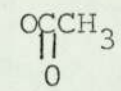
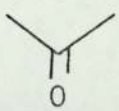
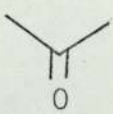
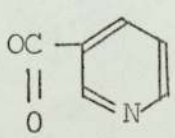
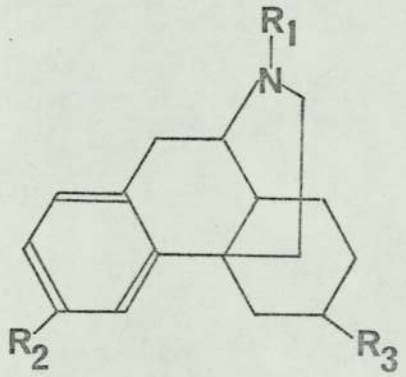
Name	R_2	R_3	R_4
Dihydromorphine	OH	OH	H
Dihydrocodeine	OCH_3	OH	H
Hydromorphone (Dihydromorphinone)	OH		H
Hydrocodone	OCH_3		H
Acetyldihydrocodeine	OCH_3		H
Oxymorphone	OH		OH
Oxycodone	OCH_3		OH
Nicodicodine	OCH_3		H

TABLE 3.1(b)
Electron Impact Results for Dihydromorphine Compounds

Name	Formula	Mol.Wt.	Highest $^{m}/_{e}$ and the 4 Major Peaks (Rel. Int.)
Dihydromorphine	$C_{17}H_{21}NO_3$	287	288(16), 287(100), 70(44), 44(27), 42(25)
Dihydrocodeine	$C_{18}H_{23}NO_3$	301	302(19), 301(100), 44(88), 70(70),164(32)
Hydromorphone	$C_{17}H_{19}NO_3$	285	286(22), 277(100),214(58),229(45),228(44)
Hydrocodone	$C_{18}H_{21}NO_3$	299	300(19), 299(100), 44(71),242(49), 59(48)
Acetyldihydro-codeine	$C_{20}H_{25}NO_4$	343	344(21), 343(100),284(22),344(21),300(21)
Oxymorphone	$C_{17}H_{19}NO_4$	301	302(16), 44(100), 42(91),301(83),115(48)
Oxycodone	$C_{18}H_{21}NO_4$	315	316(19), 315(100),230(35), 70(25), 44(23)
Nicodicodine	$C_{24}H_{26}N_2O4$	406	348(12), 106(100), 78(81), 70(65), 59(45)

TABLE 3.1(c)
Structures of Compounds Based on Modified Morphine



Name	R_1	R_2	R_3
Norlevorphanol	H	OH	H
Levorphanol (Racemorphan)		OH	H
Racemethorphan (Dextrorphan)		OCH_3	H

Table of E/I Results for Compounds Based on the Modified Morphine Structure

Name	Formula	Mol.Wt.	Highest $^m/_e$ and the 4 Major Peaks (Rel. Int.)
Levorphanol	$C_{17}H_{23}NO$	257	257(75), 59(100),257(75),256(60),150(34)
Racemethorphan	$C_{18}H_{25}NO$	271	272(13), 59(100),271(69), 58(65),150(40)

2. Amphetamine and Related Compounds

Structures - FIG: 3.2

Within table 2 are listed the results of a similar investigation on the electron impact spectra of a series of amphetamine and related materials. In these spectra there were a large number of compounds which showed no molecular ion peaks and the strongest peaks in the spectrum were at low mass. Peaks such as $^{m}/_{e}$ 44, 58 and 91 are simply due to the basic aromatic structure and cannot give conclusive identification of an individual drug.

3. Pethidine and Related Compounds

Structures - FIG: 3.3

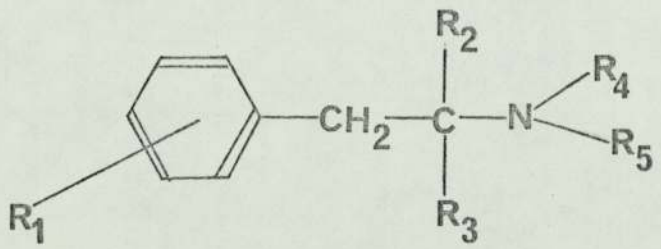
The results within table 3.3 present the principal features of the electron impact spectra of a series of drugs related to pethidine. The spectra of these materials as for the drugs related to amphetamine showed no significant molecular ion peak and the base peaks of the spectra were only indicative of the basic pethidine type structure. On substitution at R_1 fragmentation was almost independent of the nature of R_1 and led to the cleavage at the R_1-N bond producing non-specific mass spectra.

4. Methadone and Related Compounds

Structures - FIG: 3.4

The spectra recorded in table 3.4 analyse the electron impact data of methadone and a series of closely related derivatives. Molecular ion peaks were small and base peaks were often at non-diagnostic low masses. Substitution on the amine grouping in R_2 led to substantial fragmentation, making specific identification on the basis of electron

FIG: 3.2
Structure of Amphetamine and Related Compounds

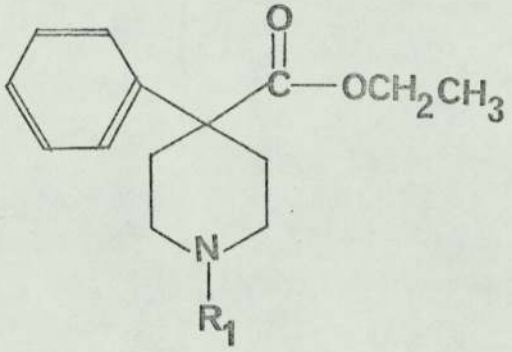


Name	R_1	R_2	R_3	R_4	R_5
2-Phenylethylamine	H	H	H	H	H
Amphetamine	H	H	CH_3	H	H
Phentermine	H	CH_3	CH_3	H	H
Methylamphetamine	H	H	CH_3	H	CH_3
Benzylamphetamine	H	H	CH_3	CH_3	$-CH_2-C_6H_5$
Mescaline	3,4,5 Tri-OCH_3	H	H	H	H
Mephentermine	H	CH_3	CH_3	CH_3	H
S.T.P.	4-CH_3 2,5 Di-OCH_3	CH_3	H	H	H

TABLE 3.2
Electron Impact Results for Compounds Related to Amphetamine

Name	Formula	Mol.Wt.	Highest $^{m}/_{e}$ and the 4 Major Peaks (Rel. Int.)
2-Phenylethylamine	$C_8H_{11}N$	121	
Amphetamine	$C_9H_{13}N$	135	120(2), 44(100), 103(8), 91(6), 65(3)
Phentermine	$C_{10}H_{15}N$	149	134(5), 58(100), 91(9), 59(8), 44(8)
Methylamphetamine	$C_{10}H_{15}N$	149	134(2), 58(100), 91(6), 56(4), 59(3)
Benzylamphetamine	$C_{17}H_{21}N$	239	165(2), 91(100), 148(84), 149(9), 92(8)
Mescaline	$C_{11}H_{17}NO_3$	211	211(32), 182(100), 181(69), 149(57), 44(52)
Chlorphentermine	$C_{10}H_{14}ClN$	184	168(2), 58(100), 42(5), 125(3), 59(3)
Mephentermine	$C_{11}H_{17}N$	163	148(5) 72(100), 91(9), 73(7), 56(6)
S.T.P.	$C_{12}H_{19}NO_2$	209	209(1), 44(100), 163(9), 42(7), 71(5)

FIG: 3.3
Structures of Pethidine and Related Compounds



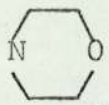
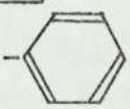
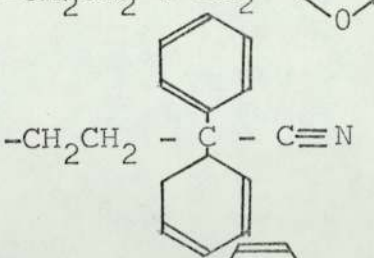
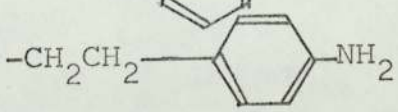
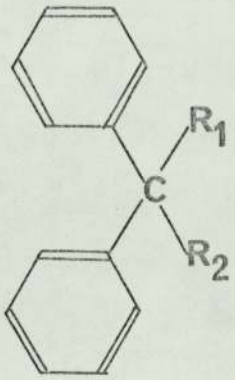
Name	R_1
Norpethidine	H
Pethidine	CH_3
Morpheridine	$-CH_2CH_2-$ 
Benzethidine	$-CH_2CH_2-O-CH_2-$ 
Furethidine	$-CH_2CH_2-O-CH_2-$ 
Diphenoxylate	
Anileridine	
Etoxeridine	$-CH_2CH_2-O-CH_2CH_2OH$

TABLE 3.3
Electron Impact Results for Compounds Related to Pethidine

Name	Formula	Mol.Wt.	Highest $^{m}/_{e}$ and the 4 Major Peaks (Rel. Int.)
Norpethidine	$C_{14}H_{19}NO_2$	233	234(4), 57(100),233(31),131(15),100(13)
Pethidine	$C_{15}H_{21}NO_2$	247	247(16), 71(100), 70(50), 57(31), 42(27)
Morpheridine	$C_{20}H_{30}N_2O_3$	346	246(100),246(100),100(29), 42(27), 82(10)
Benzethidine	$C_{23}H_{29}NO_3$	367	246(100),246(100), 91(18), 42(17),233(12)
Furethidine	$C_{21}H_3NO_4$	361	247(16), 246(100), 42(14), 71(10), 43(10)
Diphenoxylate	$C_{30}H_{32}N_2O_2$	452	452(4), 246(100),372(34), 42(26),247(20)
Anileridine	$C_{22}H_{28}N_2O_2$	352	246(100),246(100), 42(16),247(16),120(8)
Etoxeridine	$C_{18}H_{27}NO_4$	321	247(16), 246(100),247(16), 42(15), 45(5)

FIG: 3.4
Structures of Methadone and Related Compounds



Name	R_1	R_2
Normethadone	$-\overset{O}{\overset{\|}{C}}CH_2CH_3$	$-CH_2CH_2-N(CH_3)_2$
Methadone	$-\overset{O}{\overset{\|}{C}}CH_2CH_3$	$-CH_2-\underset{CH_3}{CH}-N(CH_3)_2$
Dipipanone	$-\overset{O}{\overset{\|}{C}}CH_2CH_3$	$-CH_2-\underset{CH_3}{CH}-N$ (piperidine)
Phenadoxone	$-\overset{O}{\overset{\|}{C}}CH_2CH_3$	$-CH_2-\underset{CH_3}{CH}-N$ (morpholine)
Dextromoramide	$-\overset{O}{\overset{\|}{C}}-N$ (pyrrolidine)	$-\underset{CH_3}{CH}-CH_2-N$ (morpholine)

FIG: 3.4 (Cont.)
Structures of Methadone and Related Compounds
(Continued)

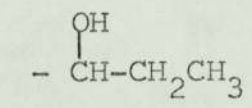
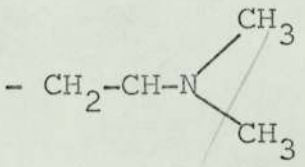
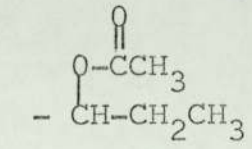
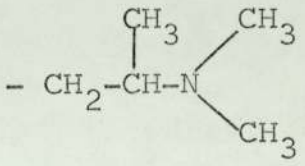
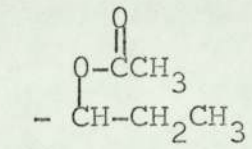
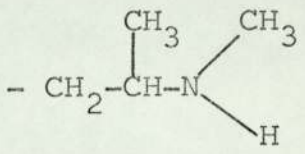
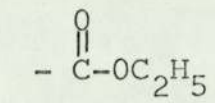
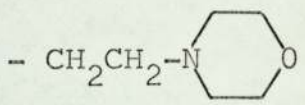
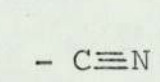
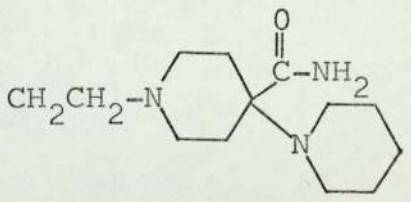
Name	R_1	R_2
Alphamethadol		
Alphacetylmethadol		
Noracymethadol		
Dioxaphetylbutyrate		
Pirintramide		

TABLE 3.4
Electron Impact Results for Methadone and Related Compounds

Name	Formula	Mol.Wt.	Highest $^{m}/_{e}$ and the 4 Major Peaks (Rel. Int.)
Normethadone	$C_{20}H_{25}NO$	295	295(5), 58(100), 72(50), 71(31), 42(25)
Methadone	$C_{21}H_{27}NO$	309	293(3), 72(100), 73(5), 58(5), 57(4)
Dipipanone	$C_{24}H_{31}NO$	349	334(3), 112(100),113(9), 41(8), 56(5)
Phenadoxone	$C_{23}H_{29}NO_2$	351	190(11),162(100),105(33), 57(15),163(14)
Dextromoramide	$C_{25}H_{32}N_2O_2$	392	266(6), 100(100),265(34),128(32), 56(11)
Alphamethadol	$C_{21}H_{29}NO$	311	225(3), 72(100), 56(9), 91(8), 129(8)
Alphacetylmethadol	$C_{23}H_{31}NO_2$	353	225(2), 72(100), 43(8), 73(4), 46(3)
Noracymethadol	$C_{21}H_{29}NO_2$	339	250(5), 58(100),134(17), 43(15), 99(12)
Dioxaphetylbutyrate	$C_{22}H_{27}NO_2$	354	353(4), 100(100), 42(7), 56(7), 101(5)
Pirintramide	$C_{27}H_{34}N_4O$	430	387(28),386(100),138(37), 42(29),387(28)

impact alone very difficult indeed.

C. Methods of Ionisation

It was concluded from the previous results that the more unstable molecules were being fragmented by the combined thermal and energetic processes within the ion source of the mass spectrometer. In order to obtain more specific mass spectra (i.e. intense peaks in the molecular ion region) techniques were sought which had a less destructive effect on the compounds.

There are principally three methods available for the production of ions within the mass-spectrometer:-

(1) electron impact (E/I),

(2) chemical ionisation (C/I) and

(3) field ionisation/field desorption (F.D.)

The thermal and energetic processes involved in each of these methods were examined and compared.

(1) Electron Impact (E/I)

There are three sources of sample degradation:-

(a) high energy electron beam 70ev - 5ev,

(b) hot source 200°C+,

(c) hot probe 25° - 100°C.

(2) Chemical Ionisation (C/I)

Here again there are three possible sources of sample breakdown:-

(a) high energy electrons 70ev.(This in fact proved to be a minor source of breakdown, because the excess of reactant gas permitted little or no electron impact on the sample at sample concentrations of $< 0.1\%$.),

(b) hot source 200°C,

(c) hot probe.

(3) Field Ionisation/Field Desorption (F.D.)

Low temperature source and warm probe. The sources of possible breakdown were minimal since the heated probe wire provided the only means of ionisation. The extent of sample fragmentation reduces from electron impact, the most energetic process, to chemical ionisation and finally, the least energetic process, field desorption.

D. Joint Project with V.G. Micromass

At the time when the above work was in progress V.G. Micromass made it known that they were interested in demonstrating the analytical capabilities of their new chemical ionisation mass spectrometer (12F).

This was the major reason for choosing chemical ionisation mass spectrometry as the less energetic alternative to E/I although objectively it did have two other major advantages for forensic applications.

Firstly C/I instruments are easy to operate in both the E/I and C/I modes of operation. (This is a time consuming and difficult procedure in field desorption), and secondly field desorption is expensive, requiring a sophisticated computer package to record and peak count the spectra obtained. The virtual lack of F.D. fragmentation produces a spectrum which has little or no background and is, therefore, impossible to peak count by conventional means.

(II) Chemical Ionisation Mass Spectrometry

A. Introduction

The extent to which chemical ionisation mass

spectrometry, first described by Field and Munson in 1966, has been utilised for the analysis of drugs and chemical compounds has been more than adequately reviewed by several authors[4,5,6,7,8] . The first published report of the identification of Dangerous Drugs[9] by C/I M.S. provided spectroscopic data for a number (48) of unrelated drugs of varied chemical composition ranging from the widely used aspirin to the anti-depressant chlordiazepoxide and finally to cocaine. During the course of this work the total number of C/I spectra available in the literature on compounds of forensic and biological importance has increased rapidly[10,11,12] . Most of the previously published reports have concentrated on either the identification of individual compounds from mixtures[11] or on large compilations of data for comparative forensic identification[12]. None of the examples cited have described a study of closely related compounds. The compiled data collections have included only a very small number of the chemical ionisation spectra of drugs listed in the Misuse of Drugs Act. The sample collection (Chapter 2) contained 4 series of closely related compounds for which chemical ionisation mass spectrometry could prove to be more specific than electron impact.

B. "Chemical Ionisation" - has been defined as a means of ion production which consists of reacting the sample under investigation with a known pre-selected set of ionising ions.

Chemical ionisation requires the following criteria:-

(1) Relatively high pressure (1 TORR) within the source. This was achieved by means of a large differential pumping system and also by increasing the repeller potential at the interface of the ionisation chamber and the analyser. The increase in repeller potential had the effect of prolonging the residence time of the ions within the source thereby increasing their chances of reaction.

(2) The reactant ions had to be formed by a combination of electron impact and ion molecule reactions.

(3) The concentration of sample was required to be of the order of 0.1% of that of the reactant in order to prevent sample - sample ion molecule reactions.

(4) Finally, The reactant had to be gaseous at the temperature of the source. Several compounds have been used as the reactant for C/I spectrometry. Strongly basic compounds have been shown to react with weak proton donors such as H_2O, C_2H_5OH, CH_3OH and NH_3. Stronger proton donors such as H_3^+, CH_5^+ and <u>tert</u> - $C_4H_9^+$ have been used for weaker bases, the most common gases being methane and isobutane.

(5) <u>Sequence of Events</u>

The sequence of events which usually takes place within the mass spectrometer is presumed to be:-

(a) the reactant gas is ionised by electron impact

(b) this undergoes ion-molecule reactions to provide the reactant ions,

(c) these then are involved in further ion-molecule reactions with the sample to produce the C/I spectrum.

(6) The Reactions

The reactions which take place within the mass spectrometer have been described as proton transfer - with possible elimination and cleavage and /or addition reactions.

(a) Proton Transfer

For example methane used as the carrier gas produces 3 major addition ions:-

(i) CH_5^+ (ii) $C_2H_5^+$ (iii) $C_3H_5^+$

produced in the following way:-

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \quad (CH_5^+ (48\%))$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \quad (C_2H_5^+ (41\%))$$

$$CH_2^+ + CH_4 \longrightarrow C_3H_5^+ + 2H_2 + H \quad (C_3H_5^+ (6\%))$$

of which (i) and (ii) have an 89% contribution. These ions are extremely powerful electrophiles and react either by proton transfer or by hydride abstraction. Therefore methane on reaction with a hypothetical compound BH would produce the following reactions:-

$$CH_5^+ + BH \longrightarrow CH_4 + BH_2^+$$

$$C_2H_5^+ + BH \longrightarrow C_2H_4 + BH_2^+$$

$$C_2H_5^+ + BH \longrightarrow B^+ + C_2H_6$$

BH_2 can now decompose to produce daughter ions of lower molecular weights.

The ion H_3^+ was the most exothermic for both hydride abstraction and proton transfer and therefore produced the most fragmentation. The tert - $C_4H_9^+$ ion from isobutane produced a much smaller exothermic reaction and therefore

produced less fragmentation. For the purposes of this study isobutane was utilised because of its proven mild reagent properties.

(b) Addition Reactions

If stable addition ions can be formed then addition products are observed:-

$$M + C_2H_5^+ \longrightarrow MC_2H_5^+$$

and $$M + C_4H_9^+ \longrightarrow MC_4H_9^+$$

Fragmentation reactions can also be observed of the appropriate addition reactions.

C. Results and Discussion

1. Morphine and Related Compounds

The results of a study on the isobutane C/I mass spectra of a series of compounds based on the morphine structure are shown in Table 3.5(a),(b)& (c). In the compounds which were unsaturated in an α position to the 6-hydroxy function the most intense peak corresponded to a loss of the 6-hydroxy from the P + 1 ion as H_2O which led to a stabilised allylic carbonium ion. The parent (P) and (P + 1) peaks were still apparent, however with approximately 30% intensity to that of the base peak. The remaining peaks in the spectrum generally at higher mass than P + 1 were accounted for as products of ion-molecule reactions between the drugs and isobutane fragments giving the peaks at P + 15, P + 29, P + 41, P + 57. On occasion these addition ions lost water to yield significant fragment peaks.

In FIGS:3.5(a) & (b) the electron impact and chemical ionisation spectra of morphine and dihydromorphine are compared.

TABLE 3.5(a)
Chemical Ionisation Results for Morphine and Related Compounds

Name	Base Peak Origin	4 Major Peaks 1. Origin	2. Origin	3. Origin	4. Origin
Normorphine	254(100)P+1-H_2O	255(20)	272(19)P+1	271(5)P	310(4)P+57-H_2O
Norcodeine	268(100)P+1-H_2O	285(37)P	286(29)P+1	269(20)	328(6)P+43
Morphine	268(100)P+1-H_2O	285(22)P	286(22)P+1	269(20)	328(7)P+43
Codeine	282(100)P+1-H_2O	300(26)P+1	299(21)P	342(5)P+43	340(2)
Ethylmorphine	296(100)P+1-H_2O	313(36)P	314(26)P+1	297(21)	356(6)P+43
Benzylmorphine	358(100)	376(78)P+1	375(40)P	359(28)	268(24)
Pholcodine	399(100)P+1	400(28)	104(24)	100(7)	441(6)P+43
Nicocodine	282(100)	405(32)P+1	300(11)	406(9)	342(8)

TABLE 3.5(b)
Chemical Ionisation Results for Morphine and Related Compounds (Continued)

		4 Major Peaks			
Name	Base Peak Origin	1. Origin	2. Origin	3. Origin	4. Origin
Nicomorphine	496(100)P+1	497(34)	124(25)	391(16)	373(8)
Diacetylmorphine (Heroin)	370(100)P+1	371(22)	430(14)	429(12)	431(3)
Dihydromorphine	288(100)P+1	287(30)	289(19)	330(9)P+43	270(5)P+1-H_2O
Dihydrocodeine	302(100)P+1	301(29)P	303(21)	284(15)P+1-H_2O	344(5)P+43
Hydromorphone	286(100)P+1	287(19)	285(14)P	284(9)	288(7)
Hydrocodone	300(100)P+1	299(20)P	301(20)	257(4)	340(4)P+41
Acetyldihydrocodeine	344(100)P+1	284(32)	302(22)	343(33)P	345(22)
Oxymorphone	302(100)P+1	303(19)	342(3)P+41	344(2)P+43	

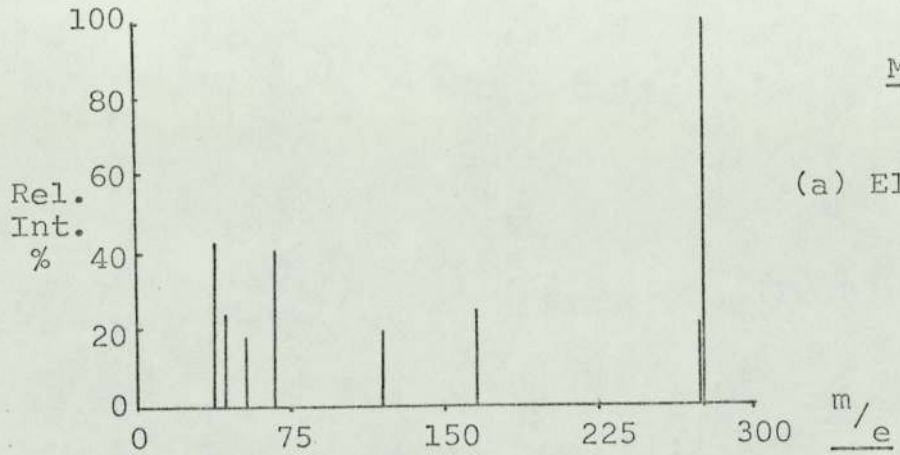
TABLE 3.5(c)
Chemical Ionisation Results for Morphine and Related Compounds (Continued)

Name	Base Peak Origin	4 Major Peaks			
		1. Origin	2. Origin	3. Origin	4. Origin
Oxycodone	316(100)P+1	315(22)P	317(20)	356(4)P+41	298(3)P+1-H_2O
Nicodicodine	407(100)P+1	408(27)	406(14)P	302(11)	284(4)
Levorphanol	258(100)P+1	257(40)P	256(31)	259(19)	300(15)P+29
Racemethorphan	272(100)P+1	271(59)P	270(29)	273(17)	314(10)P+43

FIG: 3.5

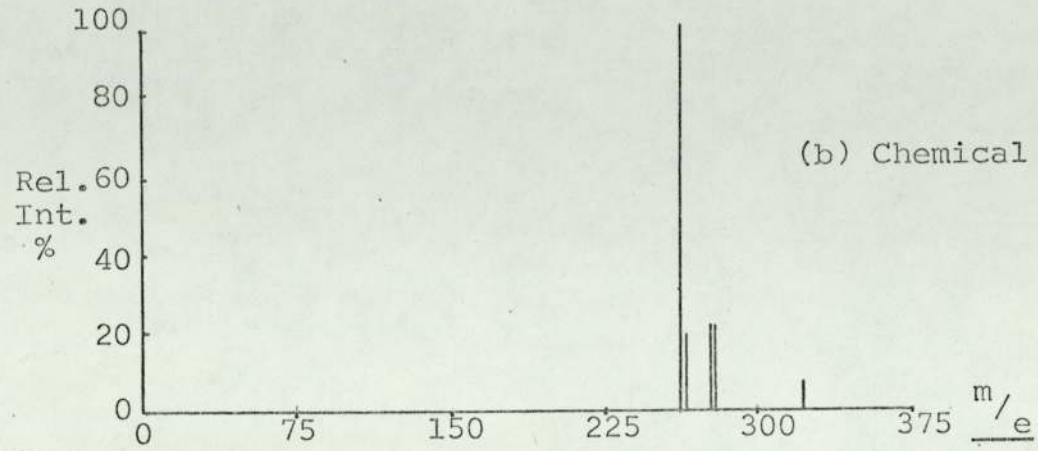
MASS SPECTRA

A



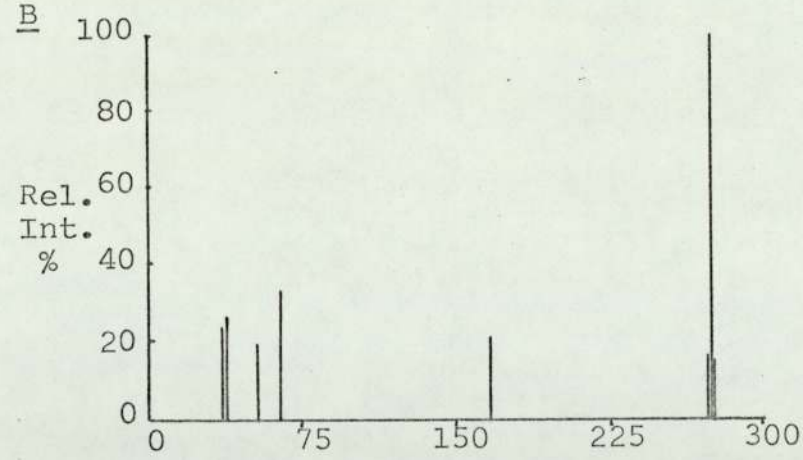
Morphine

(a) Electron Impact



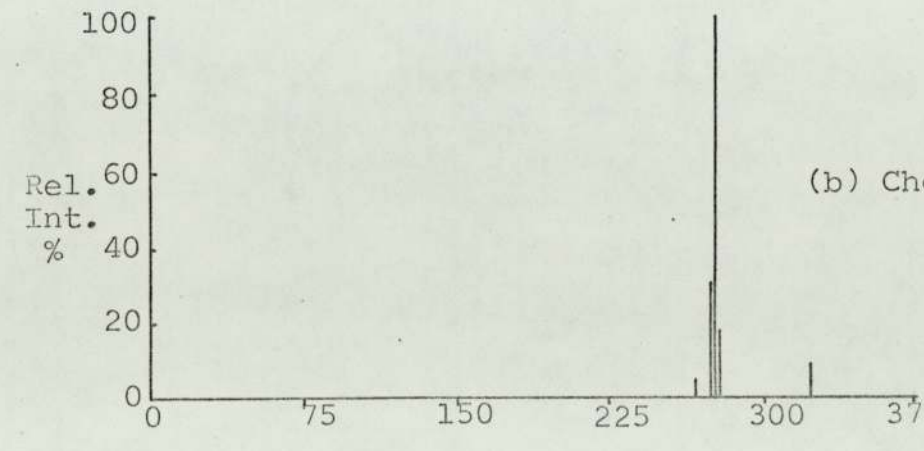
(b) Chemical Ionisation

B



Dihydromorphine

(a) Electron Impact



(b) Chemical Ionisation

These observations on the C/I mass spectra immediately indicated a specific diagnostic test for morphine and closely related analogues with an unsaturated bond in the C-ring and a 6-hydroxy function.

Furthermore the isomeric morphine and norcodeine compounds were distinguished by comparison of minor fragment ions at $^{m}/_{e}$ 148 and $^{m}/_{e}$ 164 (both 2% intensity of 268) which were observed in the spectrum of norcodeine but not in that of morphine.

2. Amphetamine and Related Compounds

The results obtained from the isobutane C/I spectra of a series of amphetamines are shown in table 3.6. The general feature apparent here, in contrast to the E/I spectra was the appearance of the (P + 1) peak as the base peak in almost every case. The only exception to this generalisation was benzylamphetamine where the base peak corresponded to a loss of $C_7H_7^+$ (peak at $^{m}/_{e}$ 91) giving a P + 1 peak of 43% intensity. In this case however the $C_7H_7^+$ ion reacted with the parent molecule to generate an ion at (P + 91) $^{m}/_{e}$ 330 which had 4% intensity. These observed fragments produced by collision induced ion-molecule reactions generated in the C/I source led to direct diagnostic structural peaks in the spectrum.

A comparison of the electron impact and chemical ionisation spectra of amphetamine is illustrated in FIG: 3.6(a)

3. Pethidine and Related Compounds

In the C/I spectra of pethidine and related compounds Table 3.7 a similar effect is observed to that for

TABLE 3.6

Chemical Ionisation Results of a Series of Compounds Based on Amphetamine

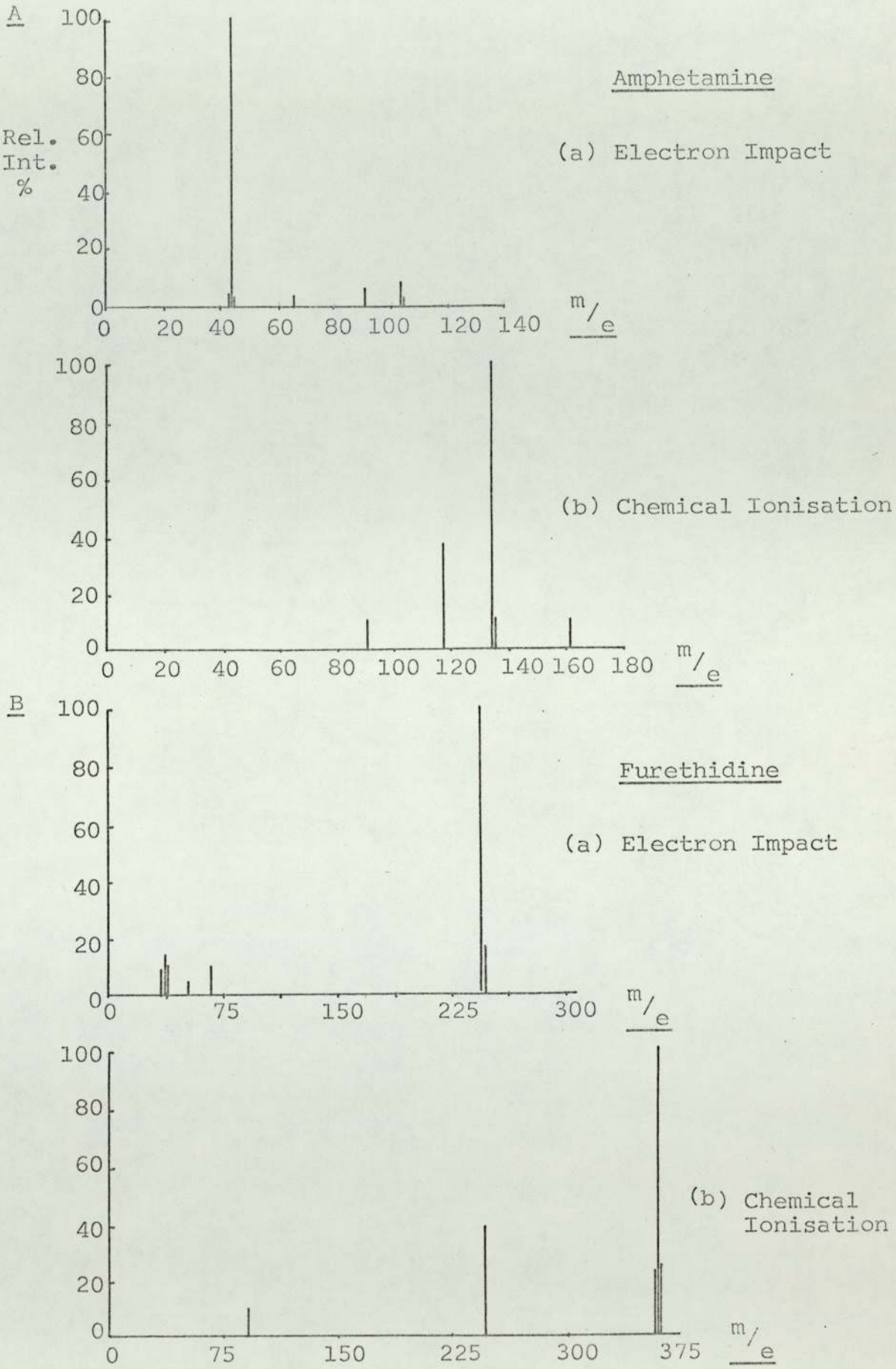
Name	Base Peak Origin	4 Major Peaks 1. Origin	2. Origin	3. Origin	4. Origin
2-Phenylethylamine	122(100)P+1	105(25)P+1-NH_3	147(17)P+43-NH_3	123(16)	164(10)P+43
Amphetamine	136(100)P+1	119(37)P+1-NH_3	91(10)	137(10)	161(10)P+43 -NH_3
Methylamphetamine	150(100)P+1	151(11)	148(7)	119(6)	192(5)P+43
Benzylamphetamine	148(100)	240(43)P+1	238(15)	91(13)	149(11)
Mescaline	212(100)P+1	182(33)P+1 -CH_2NH_2	195(19)P+1-NH_3	213(12)	211(11)P
Chlorphentermine	185(100)P+1	168(27)P+1-NH_3	186(22)	210(15)P+43-NH_3	169(10)
Mephentermine	164(100)P+1	73(75)P-91	165(12)	133(5)P+1 -CH_3NH_2	-
S.T.P.	212(100)P+1	193(59)P+1-NH_3	166(46) P-CH_3CHNH_2	211(8)	167(7)

TABLE 3.7
C/I Results of a Series of Compounds Related to Pethidine

Name	Base Peak Origin	4 Major Peaks			
		1. Origin	2. Origin	3. Origin	4. Origin
Norpethidine	234(100)P+1	235(15)	233(12)	276(6)P+43	232(4)
Pethidine	248(100)P+1	247(20)	249(17)	246(12)	72(7)
Morpheridine	347(100)P+1	246(41)	348(24)	345(8)	247(7)
Benzethidine	368(100)P+1	369(21)	246(19)	233(8)	260(5)
Furethidine	362(100)P+1	246(37)	363(24)	360(11)	85(9)
Diphenoxylate	453(100)P+1	454(34)	246(33)	248(11)	181(10)
Anileridine	353(100)P+1	354(27)	246(17)	395(5)	351(4)

FIG: 3.6

MASS SPECTRA



amphetamines. The spectra all show the presence of the (P + 1) ion as the base peak. In addition fragment ions were observed which were indicative of stepwise elimination of the component of R_1. In other words not only could evidence of identity be gained from molecular weight information but also structural identification of the side chain R_1. All spectra showed a peak at $^{m}/_{e}$ 246 indicative of the pethidine structure. Comparison of the E/I and C/I spectra of a pethidine analogue is illustrated in FIG: 3.6(b).

4. Methadone and Related Compounds

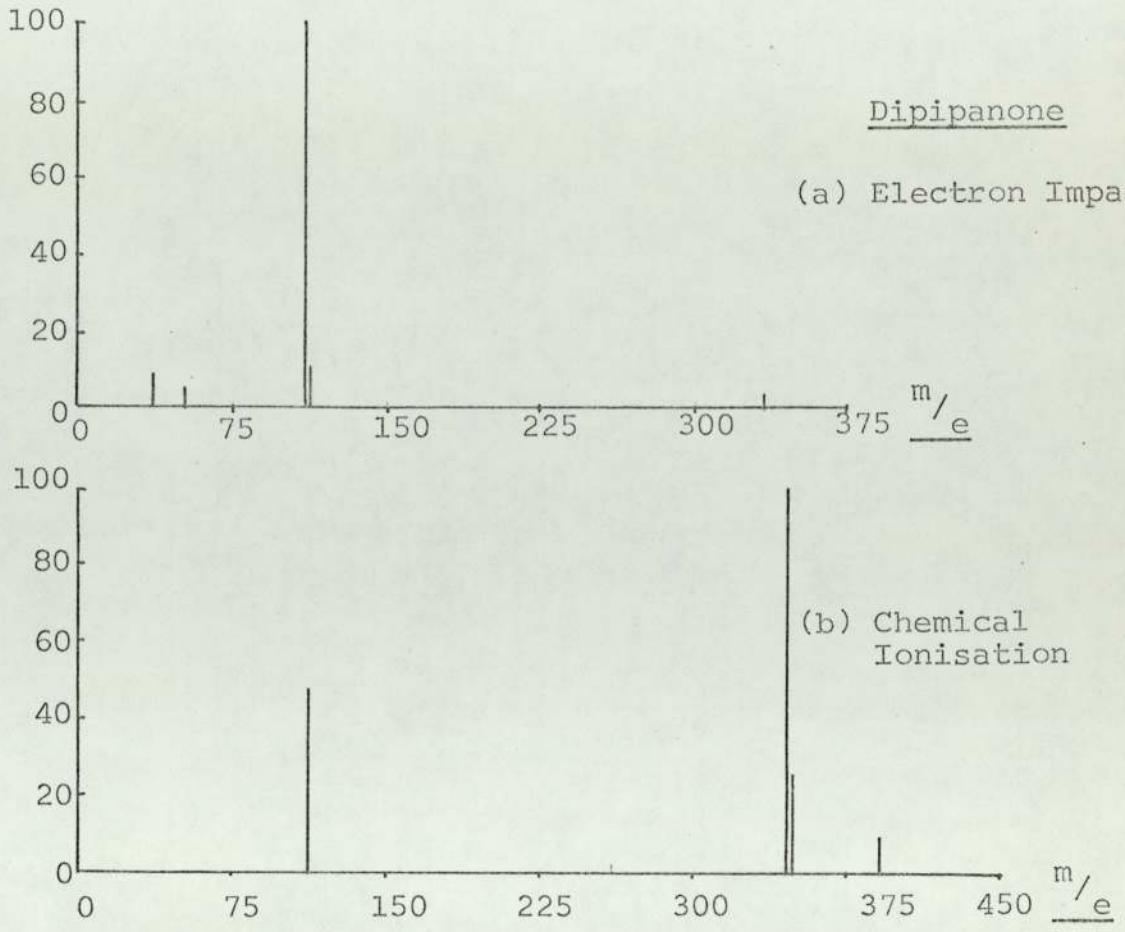
The isobutane C/I results of a series of compounds related to methadone are recorded in Table 3.8. In contrast to the E/I results almost all the compounds gave the (P + 1) ion as the base peak in the spectrum. The only exception was α-acetylmethadol in which (P + 1) was 73% of the base peak. The base peak in this case corresponded to loss of the acetyl group on R_1 leaving a secondary carbonium ion stabilised by the presence of the benzene ring structure. A comparison of the E/I and C/I of a methadone analogue is illustrated in FIG: 3.7.

TABLE 3.8
C/I Results of a Series of Compounds Related to Methadone

Name	Base Peak Origin	4 Major Peaks			
		1. Origin	2. Origin	3. Origin	4. Origin
Normethadone	296(100)P+1	297(22)	294(7)	72(6)	251(6)
Methadone	310(100)P+1	72(37)	311(25)	265(8)	303(6)
Dipipanone	350(100)P+1	112(48)	351(26)	392(9)P+43	265(2)
Phenadoxone	352(100)P+1	114(31)	353(27)	265(6)	394(5)P+43
Dextromoramide	393(100)P+1	394(27)	128(13)	265(11)	100(7)
Alphamethadol	312(100)P+1	72(50)	294(38)	313(15)	295(9)
Alphacetylmethadol	312(100)	354(73)P+1	312(26)	292(24)	355(20)
Noracymethadol	340(100)P+1	280(69)	341(29)	281(18)	134(10)
Dioxaphetylbutyrate	355(100)P+1	356(25)	100(19)	354(7)	397(5)P+42
Pirintramide	431(100)P+1	432(30)	386(20)	473(8)P+43	474(3)

FIG: 3.7

MASS SPECTRA



D. Conclusions from C/I Results

The previous results indicated three general conclusions which could be drawn from this work. First, in all cases without exception the isobutane C/I spectrum afforded molecular weight information. Second, in cases where fragmentation was significant, the technique was sufficiently mild as to generate easily identifiable fragment ions. This led, in many cases, not only to the identification of a spectral type but also to the nature of the substituents.

In general the identification of a compound from a C/I spectrum was carried out in the molecular ion region well removed from interfering peaks, which is particularly important when the identification of nanogram or subnanogram quantities is required.

CHAPTER 4

CODING OF THE ANALYTICAL DATA FOR COMPUTER RETRIEVAL

A. Introduction

The growing quantity of chemical and physical data available to the forensic analyst has necessitated the development of automatic methods for manipulating such data. It was felt that a retrieval method based on a combination of 4 non-correlated analytical techniques could evaluate within a short space of time all the possible analytical similarities of an unknown with a standard reference data file. It would provide a valuable aid in situations where the identification was not immediately obvious and also confirm previously obtained results by an alternative method. A major obstacle to this process was the conversion of the analytical data into digital form.

B. Coding of Ultra-Violet Spectral Data and Thin Layer Chromatography

U.V. and T.L.C., the nature of which have been described in Chapter 2 were by far the simplest data to code and essentially had the same sort of coding requirements. No computer retrieval systems utilising data from either technique had been described in the literature at the start of the project although one[13] based on the comparison of full ultra-violet spectra and the other[14] based on combinations of chromatographic techniques plus ultra-violet and infra-red spectral data were described during the work. The combined approach was developed by scientists at C.R.E. and used the two qualitative analytical parameters previously adopted for this project,

that is the acidic λ MAX of the base in $^{N}/_{10}$ sulphuric acid solution for U.V. and the Rf value of the compound in the Curry Powell system for T.L.C. Also during the project experiments were conducted at C.R.E. to determine the size of error "windows", i.e. the degree of flexibility to be allowed on numerical comparisons to compensate for experimental error. It was suggested that a window of $\pm$ 0.2 nm for U.V. would include all the results obtained from the 10 regional forensic laboratories as would a window of $\pm$ 0.1 Rf for T.L.C. Work is in progress at C.R.E. to isolate and identify the factors responsible for these errors.

C. Coding of Infra-Red and Mass Spectral Data

In qualitative infra-red and mass spectrometry the composition of a compound is normally proved unequivocally by matching its spectrum with that of an authentic standard.

Structural features and functional groups may be inferred from the positions and relative intensities of absorptions in the spectrum and these combined with information from other analytical techniques may be sufficient for a complete immediate identification. Sometimes, however, this approach fails and it is then vital to look for spectra from the library which either exactly correspond to the unknown or which bear such a close resemblance that the class of compound may be inferred. To perform such comparisons manually is impossible with large libraries of spectra and consequently, since this problem had been identified well before this project began, coding systems had been devised and published in the literature.

For any approach involving data previously represented for visual examination, it was required that every curve or trace be reduced to a series of parameters or codes and that the retrieval system be designed to compare these data and identify the spectrum which was identical to the unknown.

For the purpose of this work any coding system had to be carefully chosen so that the coded reference spectra were in a form which was compact for storage, easily utilised by simple programming techniques and flexible enough to allow continual updating and modification of the file.

(1) Review of Infra-Red Retrieval Systems

In the late 1940's and early 50's because of the wider availability of infra-red spectrophotometers there was a rapid increase in the amount of reference data compiled. Manual manipulation of data held in large collections (1,000-10,000 spectra) became impossible and necessitated the use of automatic sorting methods. These retrieval systems were all mechanical and utilised coded data stored on edge punched cards[15], body punch cards[16], absorption band indexing[17] and optical coincidence cards[18]. The number of spectra stored in the data collections continued to expand rapidly until mechanical methods for sorting files of 100,000 spectra were no longer feasible. (Computer retrieval was the only alternative.) The earliest computer retrieval systems based on the ASTM-Wyandotte collection of I.R. data were produced by commercial organisations[19,20].

Mechanical methods were still preferred for small laboratory collections until the early 1970's when low cost mini-computers made them almost obsolete.

The authors of two studies[21,22] undertaken in 1968, 1969 respectively, very adequately reviewed the mechanical sorting methods and in both cases they proposed modifications. In one[22] for a small laboratory collection of 2,000 spectra a modified optical coincidence card was suggested and in the other[21] a computerised system was developed to search a large collection of 100,000 spectra.

The computer and mechanical retrieval systems described in the literature fell into two categories, those based on "Absorption Band Indexing" and those on a "Major Peak" approach.

(i) Absorption Band Indexing

The most widely used example of this method is the "Sadtler Spec finder"[17]. Spectra are listed according to the strongest band (to the nearest 0.1μ) in each 1μ section of the spectrum 2 - 14.9μ. If there is ambiguity as to what comprises the strongest bands of a spectrum then all possibilities are included within the index. The spectra are listed in increasing order of size of the strongest band from 5 - 14.9μ and each spectrum is identified by an index number.

A computer system[23] was described which reduced the number of bands of the spectrum from the 12 of the "Spec finder" to 6 equal bands of 1.5μ in the area 5.5 - 15μ only. The reference data files contained 90,000 coded spectra and were searched in minutes. The facility to "wiggle" the data (place $\pm$ 0.1μ tolerance on the

comparison) was included in order to compensate for inaccuracies caused by minor variations in peak positions from spectrum to spectrum.

A very similar system[24] to the previous one was developed for the identification of pharmaceutical preparations. Each spectrum was divided into 10 sections by means of a pre-calibrated plastic overlay. The divisions were arranged so that the sections 2 - 9 inclusive coded the more important "fingerprint" region of the spectrum. Each of the 10 sections were again divided into a further 10 equal sized areas. The position of the largest peak in each section relative to the calibrations was indicated by a number 0 - 9. Zero indicated the absence of a peak within the section. This process was repeated for all the sections to produce a 10 digit number. The unknown was then compared against a file of data compiled in the same way and the sum of the difference of each element of the number indicated the degree of match. The smaller the value the better the match.

Another approach[25] not involving the use of a plastic overlay divided only the "fingerprint" region of the spectrum into 12 equal sections and the peaks were coded to provide a 12 digit number. This number was then compared against a file compiled in the same way.

All of the above methods were developed to ensure an even distribution of peaks across the coded area of the spectrum and to standardise the method of choosing peaks. There were, however, 3 disadvantages to this approach. The first was that the intensity threshold at which a peak was considered to be present or absent was difficult to

establish. Secondly the weakest and most intense peaks were given the same degree of importance and, therefore, all relative intensity information was lost. Finally the systems, particularly that involving a plastic overlay, produced coded data which was difficult to translate for use as a combined computer/manual retrieval method.

(ii) Major Peaks

In order to improve a system of I.R. retrieval at C.R.E.[22] based on optical coincidence cards, a 5 range method of coding, dividing the spectrum into 5 equal ranges and a 6 major peak approach were evaluated and compared. It was found that a 6 peak method was superior and that the average distribution of peaks across the spectrum from 5 - 15μ (ignoring the nujol region 6.7 - 7.5μ) was as good if not better than the 5 range method. Files of the order of 2,000 spectra were utilised for the study.

Two other computer systems[21,26] have been described based on a major peaks approach. The size of the data files utilised by each required that more than 6 peaks be coded. In the first facilities were provided to search for a maximum of 12 peaks at each of 4 levels of confidence, defined by the peaks relative intensities. Additional facilities were also included for combined molecular formula searching and the absence of specified peaks.

The second[26] described an interactive retrieval system operated from teletype terminals. The option of a "WINDOW" of 0 to $\pm$ 0.2μ on the peak comparisons was provided to compensate for minor positional variations in the spectra.

(iii) Coding Method Chosen For I.R. Data

It was decided to adopt the 6 major peak coding system for the following reasons:-

(a) It was the easiest to use.

(b) It has been shown to be as effective as an absorption banding system.

(c) Coding and storing the peaks in decreasing order of intensity retained valuable relative intensity information.

(d) Experience had already been gained in the routine use of this method at C.R.E.

(iv) Coding Rules for I.R. Spectra

The following coding rules were adopted from those first outlined by Curry[22]:-

(a) Only the peaks in the region 5 - 15μ were coded to the nearest 0.1μ. If peaks fell between two calibration lines they were coded as the next lowest 0.1μ interval.

(b) Any bands in the region 6.7 - 7.5μ were ignored to avoid complications with spectra obtained as nujol mulls.

(c) The strongest bands were defined as those bands nearest to 0% transmittance irrespective of the shape or background. Shoulders were only counted as bands if they were completely resolved and the point of maximum absorption easily determined. In cases where two or more peaks tied for the final coding the spectrum was recoded to include them both. If the major

peak was a hump rather than a sharp band and the point of maximum absorbance not easily determined, or the band was too intense as a result of the sample being too concentrated, the wavelength of the peak mid-point was taken for coding.

(V) "WINDOW" Error

A window of ± 0.2μ was to be included within the comparison program in order to compensate for minor positional variations from spectrum to spectrum. A survey conducted[27] during the course of this work which examined spectra from 10 regional forensic laboratories established that an error factor of ± 0.1μ was adequate, however, for the developmental stages of this work the window ± 0.2μ was retained.

(2) Review of Mass Spectral Data Retrieval Systems

The first method[28] which utilised automatic punched card methods to sort M.S. data was described in 1950. The first[29a,b,c,d] computer system was reported in 1964. Excellent selectivity was claimed when only 5 combined $^{m}/_{e}$ and intensity values were compared against a file. Only file compounds within selected molecular weight ranges were examined in order to reduce the time and expense involved in searching the full file.

In 1967 a G.C. - M.S.[30] was successfully coupled directly to a computer to provide automatic normalisation and plotting facilities. This development provided the means whereby reference data collections could be compiled rapidly. Automatic computer methods for manipulating these

files of data were subsequently developed.

From the literature 4 approaches to the retrieval of M.S. data were evident. These were:-

(i) Comparison of full spectra.

(ii) Division of the spectrum into consecutive equal regions from which the largest one or two peaks in each area were coded.

(iii) One bit encoding - where the value of 1 or 0 was used to indicate whether a peak was present or absent in the spectrum (above a threshold value) and subsequently compared against a file compiled in the same manner.

(iv) Major peak approach - the spectra were coded as the 5, 6, 8 or 10 largest peaks and compared against the unknown coded in the same way.

All four of these coding methods have been comprehensively reviewed[31] and only brief details of each method will be given here.

(i) Comparison of Full Spectra

This method involved[32] the comparison of each peak, $^{m}/_{e}$ and intensity value in the unknown against those stored in the file. The spectra were normalised so that the sum of all the peak intensities was equal to 1 and the intensity of each individual peak a fraction of 1. A discrepancy value D was devised to indicate empirically the quality of the match obtained. The maximum value of D (i.e. when all the peaks in the unknown were completely different to those in the file) was 2 and the minimum value (for a complete match) was zero.

This method although very precise did suffer from the twin disadvantages of requiring both a large amount of computer space to store all the data and also a long time to perform all the numerical comparisons.

Later methods selectively reduced the amount of data stored by coding only a limited number of features for each spectrum.

(ii) Division of the Spectrum into Consecutive Equal Regions

This approach was adopted[33] because it was realised that when an analyst examined a mass spectrum the most abundant peaks within peak clusters were considered first rather than the absolutely most abundant which were often at low non-specific mass.

The spectrum was divided in regions of 14 amu's and the largest two peaks in each region from $^{m}/_{e}$ 6 to the highest $^{m}/_{e}$ value were selected. The 14 amu region was chosen because it assured that homologous series of ions would be selected. The principle advantage in the use of this technique was that it was certain to include the molecular ion if present, or, if not, the ion of highest mass.

This coding method has had considerable success and two other operational systems have been developed from it; one used for forensic[34] analysis in California and the other in a hospital toxicology laboratory[35].

A modification of this method was proposed[36] which reduced the coding regions from 14 amu to 7 amu but has received no further support.

(iii) One Bit Encoding

This approach[37a-d] was developed as an extension of work on the pyrolysis - G.C. - M.S. designed for the Mars lander, project Viking. In this project a sample of Martian soil was to be analysed and the mass spectral results sent back to earth. Transmission of data over planetary distances required it to be coded so that the maximum amount of information could be packed into as small a space as possible. The mass range 12 - 200 amu was chosen and every peak above a predetermined threshold was coded (= 1) or absent (= 0). This process created a binary number 188 digits long. This "encoded" spectrum was then compared against a data file previously coded in the same way.

The major disadvantages of this method were that the data was difficult to translate for manual use and the binary comparisons required a large amount of computer time and sophisticated computer methods to perform them. This method was considered to be inappropriate to the requirements of this project.

(iv) Major Peaks

Mass spectroscopists had found printed indexes[38,39] to mass spectra, ordered on the 6 - 10 most intense peaks valuable for manual compound identification. A computer[40] retrieval system was directly developed from this approach which operated on the comparison of coded mass spectra against an 8 or 10 peak file. Considerable success was achieved with this method when peaks of the unknown ($^{m}/_{e}$ values only) were compared against the file in either their order of decreasing relative intensity or in any order. As a

result of this work an 8 peak index was compiled and marketed for manual retrieval[41].

The use of the "major peaks" coding method had three principal advantages. Firstly it was very easy to use and understand. Secondly it was economical in its use of both computer space and comparison time and finally the coded data was directly applicable to both computer and manual retrieval. For electron impact mass spectrometry it did have the disadvantage that for the more unstable compounds there was the possibility that no peaks would be coded in the molecular ion region of the spectrum. Compilation of files of chemical ionisation mass spectral data could alleviate this problem (C/I - M.S. was not included within this system although the coding methods adopted could apply equally well to data from C/I or E/I mass spectra).

A multinational interactive[42] system developed at N.I.H. and available over telephone lines in the U.K. through M.S.D.C. (Aldermaston) includes facilities for searching in both the 8 peak and 14 amu systems.

The experience of scientists at C.R.E. gained in using the 6 peak retrieval of infra-red data and the satisfactory observations of other workers in the use of 5 major M.S. peaks[43,44] influenced the decision towards the use of files compiled on the 8 largest peaks ($^{m}/_{e}$ values only), greater than or equal to $^{m}/_{e}$ 28. The 8 peak values were stored in a file from low to high $^{m}/_{e}$ value irrespective of their relative intensity. (This was later found to be a waste of valuable "rank order"

information (Chapter 6 Section 1) and for the final retrieval system the file of mass spectra was modified and coded so that the peaks were in their order of decreasing relative intensity.)

D. Conclusion

The computer retrieval system was to be based on 4 data files containing:-

8 mass spectral peaks, 6 infra-red peaks with a window of ($\pm$ 0.2μ), acidic λmax for ultra-violet spectroscopy with a window of ($\pm$ 2 nm) and Curry Powell Rf for thin layer chromatography with a window of ($\pm$ 0.1 Rf).

Chapter 5 Development of the Retrieval System

The program development is described in 4 sections:-

(i) the initial programs,

(ii) DW7 - the first combined system,

(iii) DWSORT - the second combined system,

(iv) DWSYST4 - the final system (Chapter 6).

The initial objectives of the work were to develop a retrieval system which would:-

(a) provide accurate results,

(b) produce a fast response,

(b) include interpretive facilities equivalent to those of an experienced analyst, and to

(d) write programs that were as small as possible. This latter requirement was in order to allow easy transfer to the Hewlett Packard mini computer which had recently been installed at Aldermaston.

Fortunately within a short time of starting this project the core availability on the Aldermaston system was expanded from 8 to 16K. Further expansion is envisaged in the near future which may facilitate the operation of remote terminals in all the regional forensic science laboratories.

(i) The Initial Programs

Four programs, one for each analytical technique, were developed. The programs FIG: 5.1, using the four data files FILEMS, FILEIR, FILEUV, FILESP, FIG: 5.2, were operated on the batch system, i.e. cards used as the only source of input information and all the output was produced on the line printer.

FIG: 5.1

FIRST INDIVIDUAL PROGRAMS

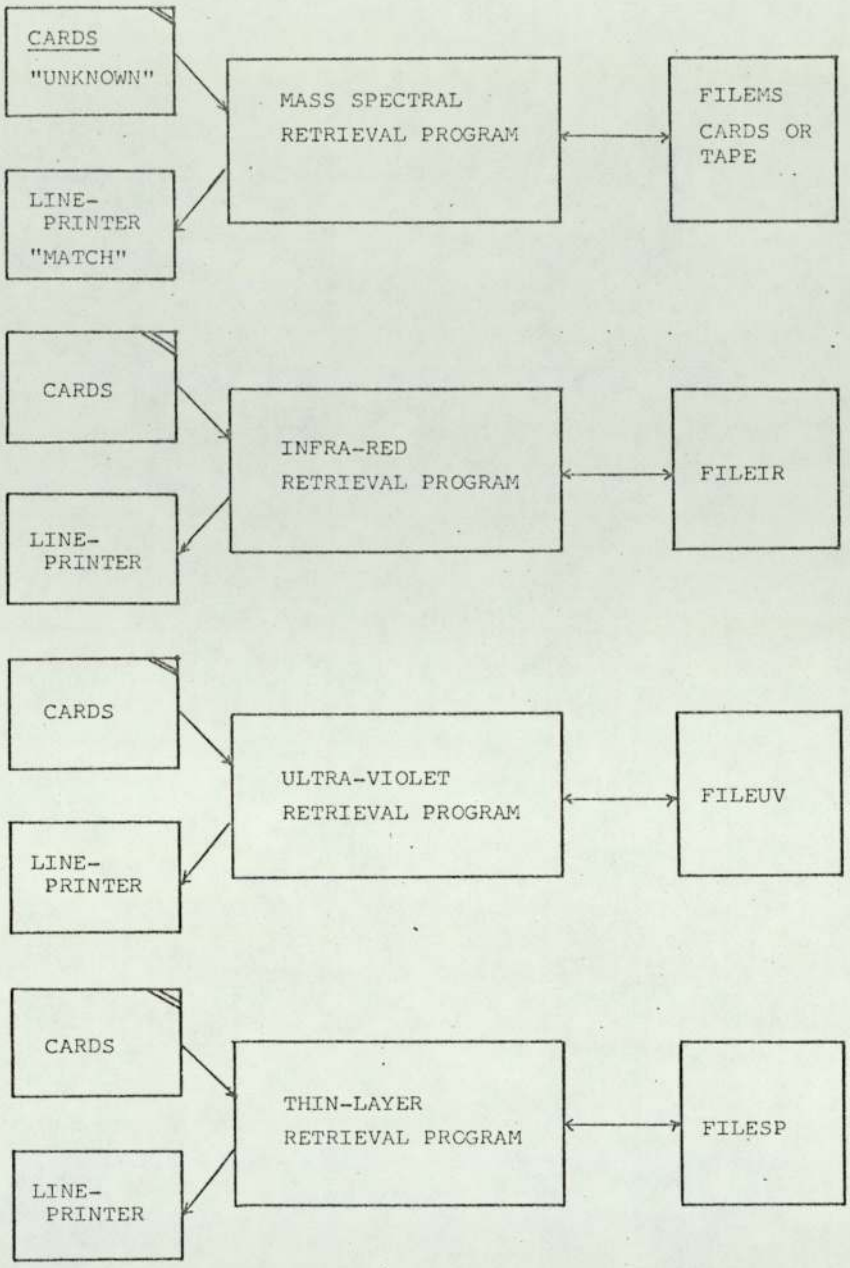


FIG: 3.2

THE ORIGINAL DATA FILES

DOCUMENT FILEMS

0	42	45	56	71	91	232	245	246FURETHIDINE
1	28	42	44	59	70	163	286	287DIHYDROMORPHINEHCL
2	36	42	56	100	114	232	246	247MORPHERIDINEHCL
3	28	36	38	42	91	233	246	247BENZETHIDINEHCL
4	28	36	42	44	70	115	229	229OXYCODONE
5	28	36	42	44	59	124	162	313ETHYLMORPHINEHCL
6	28	42	44	255	295	310	311	312THEBAINE
7	28	42	59	70	163	245	301	302DIHYDROCODEINETARTRATE
8	28	36	42	44	58	162	289	341THEBACON

DOCUMENT FILEIR

0	5.7	8.0	7.9	8.1	7.8	9.6ACETYLDIHYDROCODEINE
1	5.7	8.5	8.4	14.3	13.3	8.2PROHEPTAZINE
2	5.7	8.5	8.6	8.7	8.4	9.6ALPHAMEPRODINE
3	5.7	8.7	8.5	14.4	9.5	9.3BETAMEPRODINE
4	5.8	5.7	7.8	9.0	14.1	9.6COCAINE
5	5.8	6.6	9.7	7.9	10.7	10.20XYCODONE HCL
6	5.8	7.8	8.7	8.2	8.4	6.2HYDROXYPETHIDINE
7	5.8	7.8	9.0	8.8	9.3	9.8NICOMORPHINE HCL
8	5.8	7.8	9.8	9.2	8.8	8.2METOPON

DOCUMENT FILEUV

0	263FURETHIDINE
1	283DIHYDROMORPHINE
2	257BENZETHIDINE
3	281OXYCODONE
4	284ETHYLMORPHINE HCL
5	284THEBAINE
6	283DIHYDROCODEINE TARTRATE
7	280THEBACON HCL
8	280HYDROCODONE ACID TARTRATE

DOCUMENT FILESP

0	0.70FURETHIDINE
1	0.12DIHYDROMORPHINE
2	0.37MORPHERIDINE
3	0.87BENZETHIDINE
4	0.140XYCODONE
5	0.38BETHYLMORPHINE HCL
6	0.35THEBAINE
7	0.20DIHYDROCODEINE TARTRATE
8	0.35THEBACON HCL

The initial bases for the infra-red and subsequently the mass-spectral comparison routines were adopted from that already partially developed at Aldermaston for infra-red retrieval. Substantial modifications were required in order to permit the IR program to be used on the ICL computer. Essentially the program was completely re-written retaining only the basic comparison methodology. For each of the programs the "unknown" was compared repetitively against each file record stored on disk or tape FIG: 5.3. For files of this length this approach was adequate but for longer files it would have proved to be very slow. The programs within each comparison routine compensated for possible coding errors by including "windows", for IR, UV and TLC data and by comparing every peak within the unknown against every peak within the file for MS and IR data. (See FIG: 5.4 for MS as the example). Only the values of the peaks ($^{m}/_{e}$) were compared for equality and no importance was placed on the rank order within the group. A "full match" was obtained if the required number of peaks within the unknown matched within the file. For UV and TLC the values were compared directly ($\pm$ window error). The programs had two major disadvantages; they only permitted one search per run and there were no loops within them to enable repetitive scanning. For effective use the programs required considerable operator knowledge of the system.

(ii) DW7 - First Combined System

The objectives for this system were to:-

(a) Design an "interactive" system which was easy to use.

FIG: 5.3

FILE SEARCHING APPROACH ADOPTED FOR THE INITIAL PROGS, DW7, DWSORT.

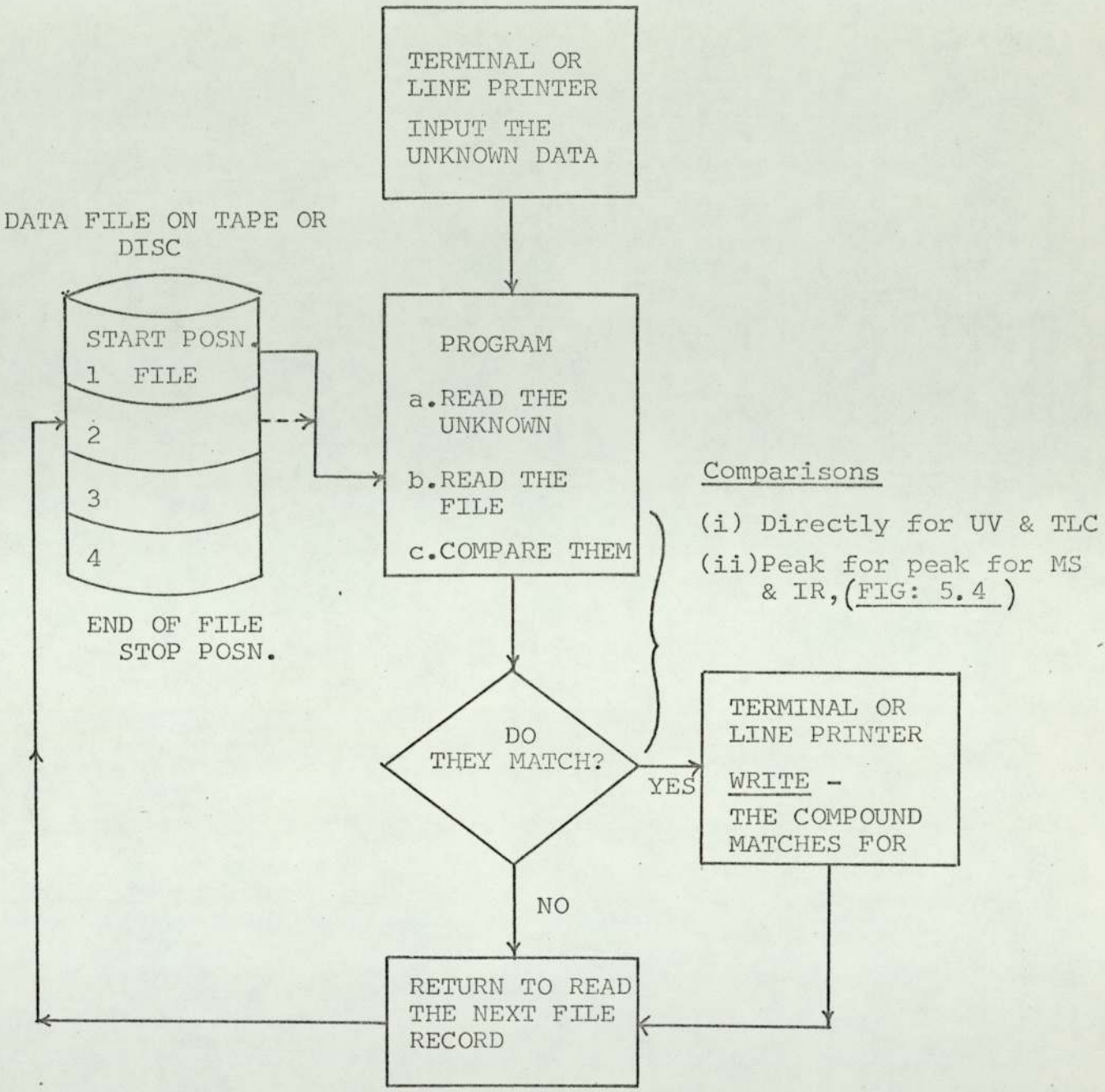
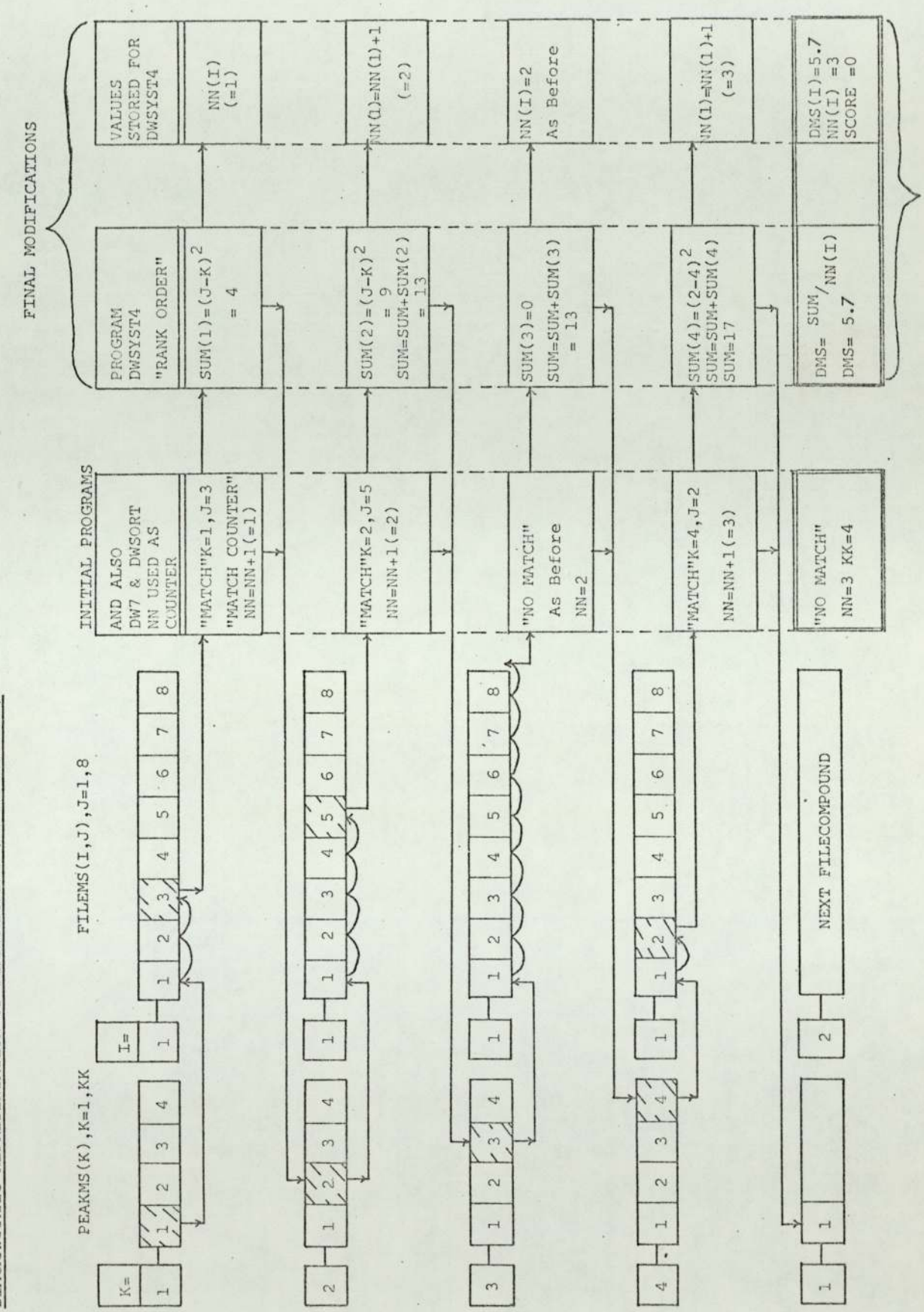


FIG: 5.4

DIAGRAMMATIC REPRESENTATION OF PEAKMATCHING (MS AS EXAMPLE)



DIAGRAMMATIC REPRESENTATION OF PEAKMATCHING (MS AS EXAMPLE)

(b) Produce a system capable of comparing several sets of data, at one session.

(c) Provide a degree of selectivity to the system by combining the matches produced from each analytical technique.

DW7, see FIG: 5.5, satisfied two of these objectives (a and b) with only minor modifications to the original four programs. The bases for the comparison routines (now named MS1DT, IR1DT, UV1DT and TLC1D were retained.

A new MASTER program was included which linked the four separate routines together. The input/output statements were modified to enable the program to operate from the terminal.

The "unknown" was compared repetitively against the file data held on magnetic tape or disk, FIG: 5.3, as for the previous programs. The modification to terminal operation, and the use of four tape files necessitated the use of a small MACRO program.

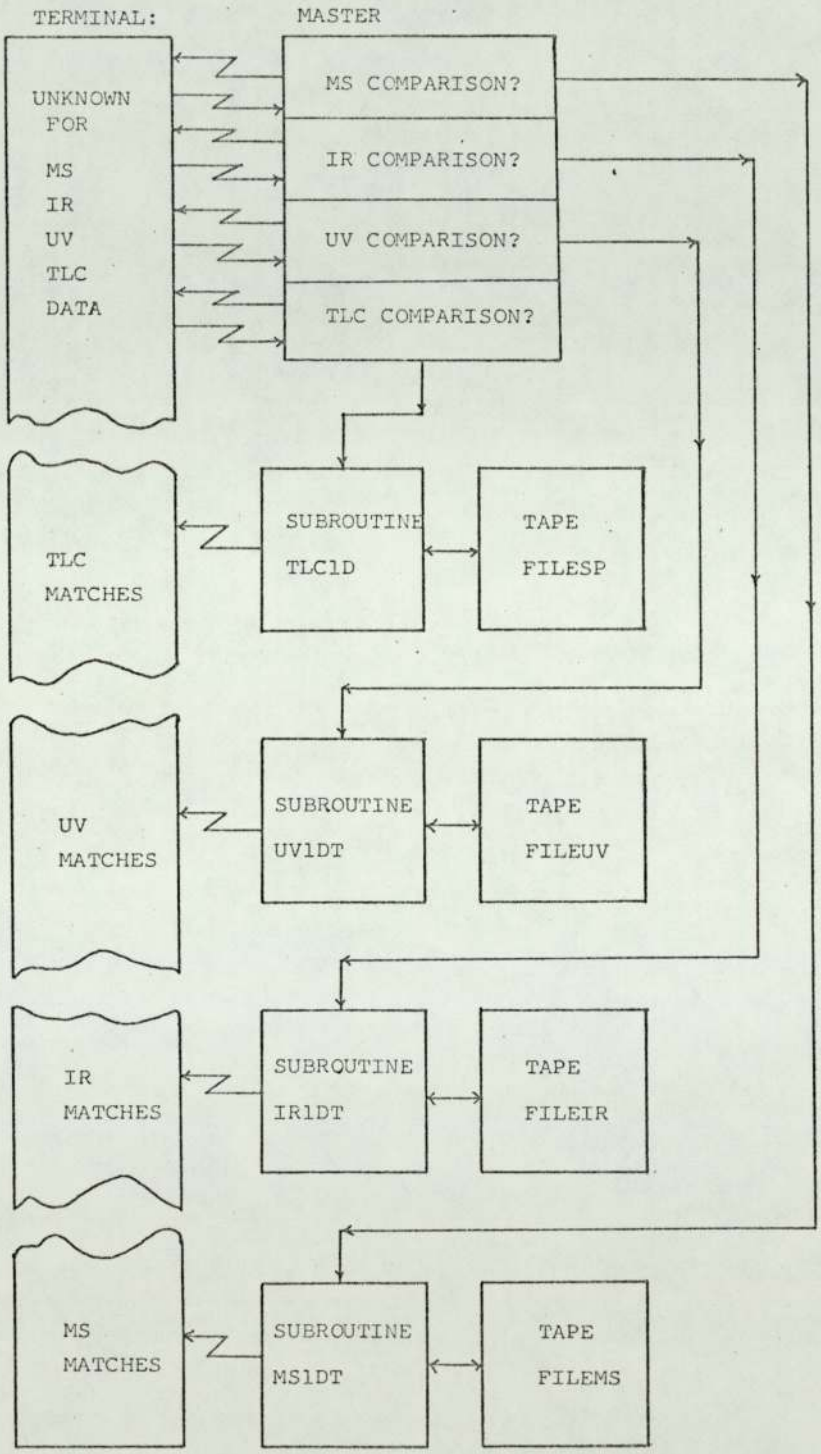
An ICL Macro COMMAND is defined as:-
A command statement which is expanded by the operating system into a series of basic commands. By this means a complex operation which requires many commands to be obeyed, can be initiated by a single statement. This series of basic commands written in the language of the operating system was termed the "MACRO PROGRAM" and was utilised by typing the single MACRO COMMAND, MACDW7 on the terminal.

This supporting program was responsible for file rewinds and the attachment of input/output devices to the main FORTRAN program.

FIG: 5.5

STRUCTURE OF PROGRAM DW7

FIRST COMBINED SYSTEM



Four individual sets of output were produced to the terminal, in the order MS, IR, UV, TLC. The order in which matches (for each technique) were output to the terminal, particularly for mass spectra and infra-red data, was not dependent on the quality of the match (in terms of rank order), but only on the compounds respective positions within the file.

This program offered the practical advantage of being "interactive", and was thus capable of being utilised from a computer terminal. The "interactive" approach adopted for DW7 created the fundamental basis for all further developments on the system.

Objective (c), the function of which was to introduce a degree of selectivity to the output produced by the system was not fulfilled; satisfaction of this requirement was the major objective for the next development, DWSORT.

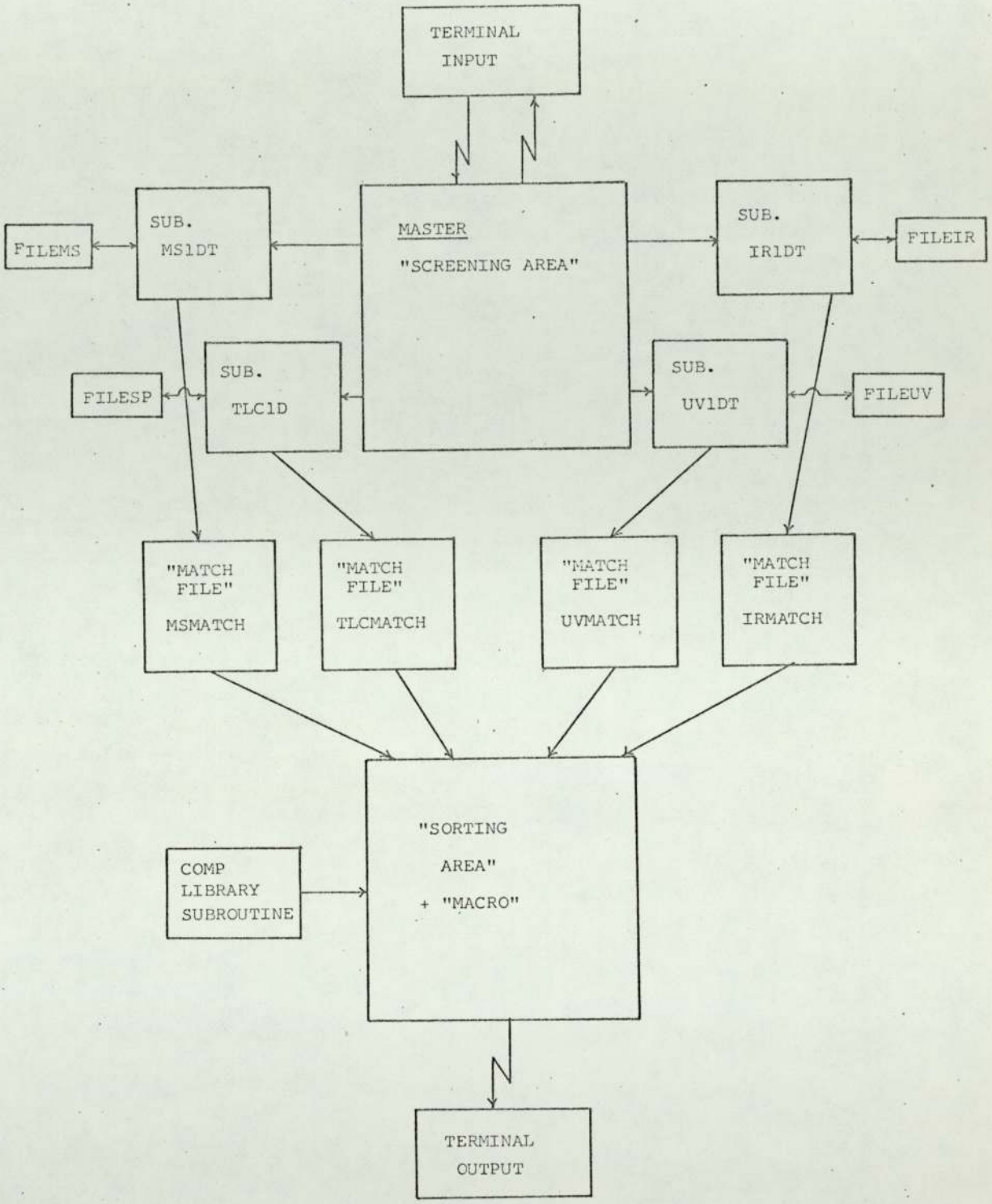
(iii) DWSORT - Second Combined System

Extension in the use and scope of the MACRO program together with considerable modifications to the Fortran retrieval program enabled facilities for sorting the possible match combinations to be included within the system. The structure of DWSORT is shown in FIG: 5.6. The MACRO program had been expanded, from the 40 lines required for the four files of DW7 to 95 lines for the 8 input/output files of DWSORT. The basic unit (the screening area FIG: 5.6) was almost identical to DW7. For this program the match output was directed, not to the terminal, but to four secondary "match" files, MSMATCH, IRMATCH, UVMATCH, TLCMATCH. When all the

FIG: 5.6

STRUCTURE OF DWSORT

SECOND COMBINED SYSTEM



compounds within the data files had been successfully screened the match files were released and re-attached (with the aid of the Macro) as input files to the second sorting area of the program. Using Macro/program interactions the match files were sorted into their possible match combinations.

The sorting process involved the comparison of the names in one "match" file against all those in the others using the ICL library subroutine COMP. COMP was the FORTRAN library subroutine available in the 1905E system for the comparison of character strings.

For sorting purposes, the major emphasis was placed on mass-spectrometry, secondary importance on infra-red, with TLC being least important. The sorting routine is illustrated in FIGS: 5.7 (a) (b) (c) (d). The terminal output produced by the program was considerably different from that of the previous program. Information was produced from DWSORT in the format required from a data retrieval system. Unfortunately the program/Macro interactions proved to be very slow. The method chosen also proved to be inadequate for sorting all the possible combinations of match. From four analytical methods a total of 15 combinations were theoretically possible. This program was capable of identifying only nine of the major combinations. Further modifications were still required and these are discussed in the following Chapter.

FIG: 5.7a

FIGURE: BROAD OUTLINE OF SORTING ROUTINE USED FOR DWSORT

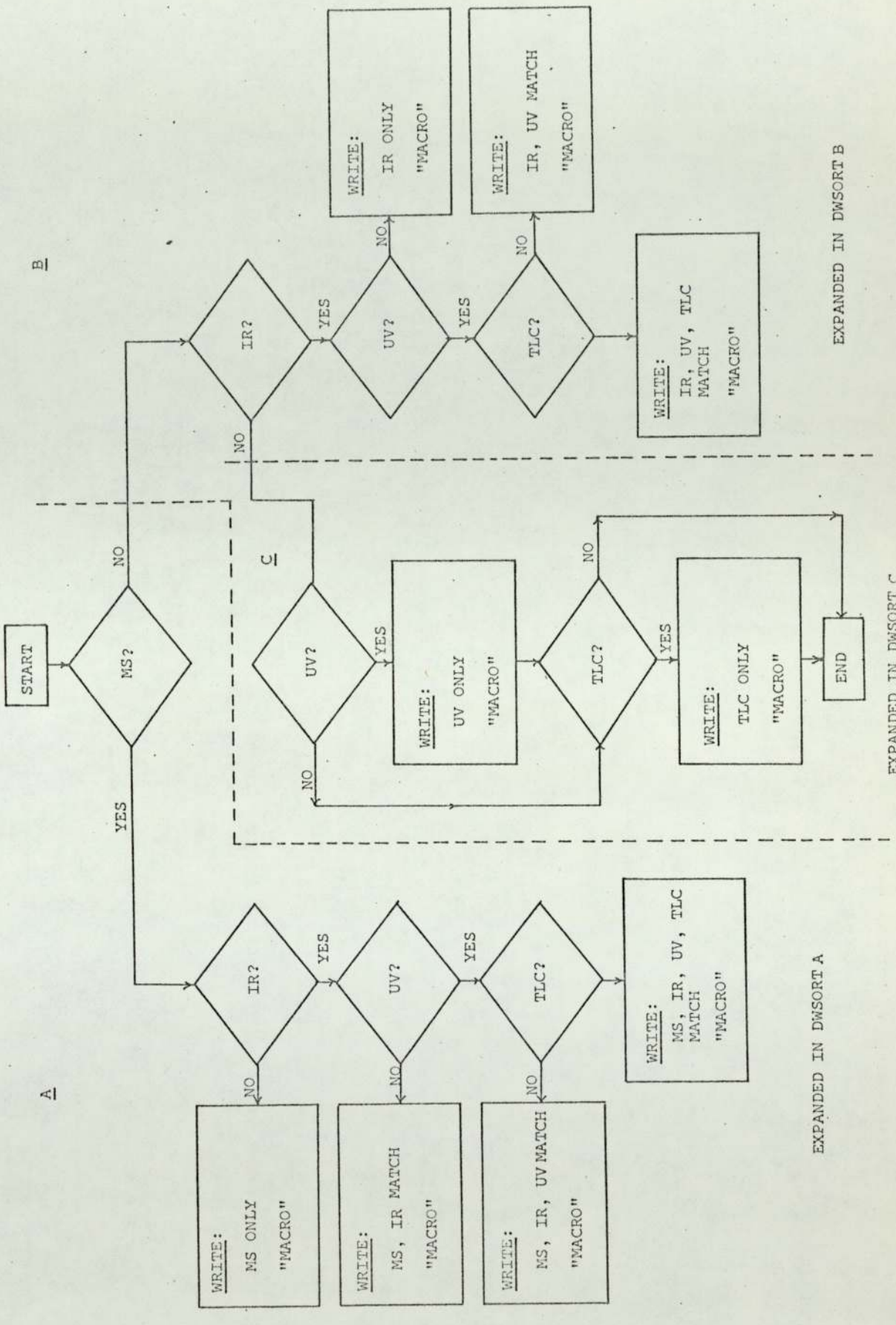


FIGURE: BROAD OUTLINE OF SORTING ROUTINE USED FOR DWSORT

FIG: 5.7 b

DWSORT A

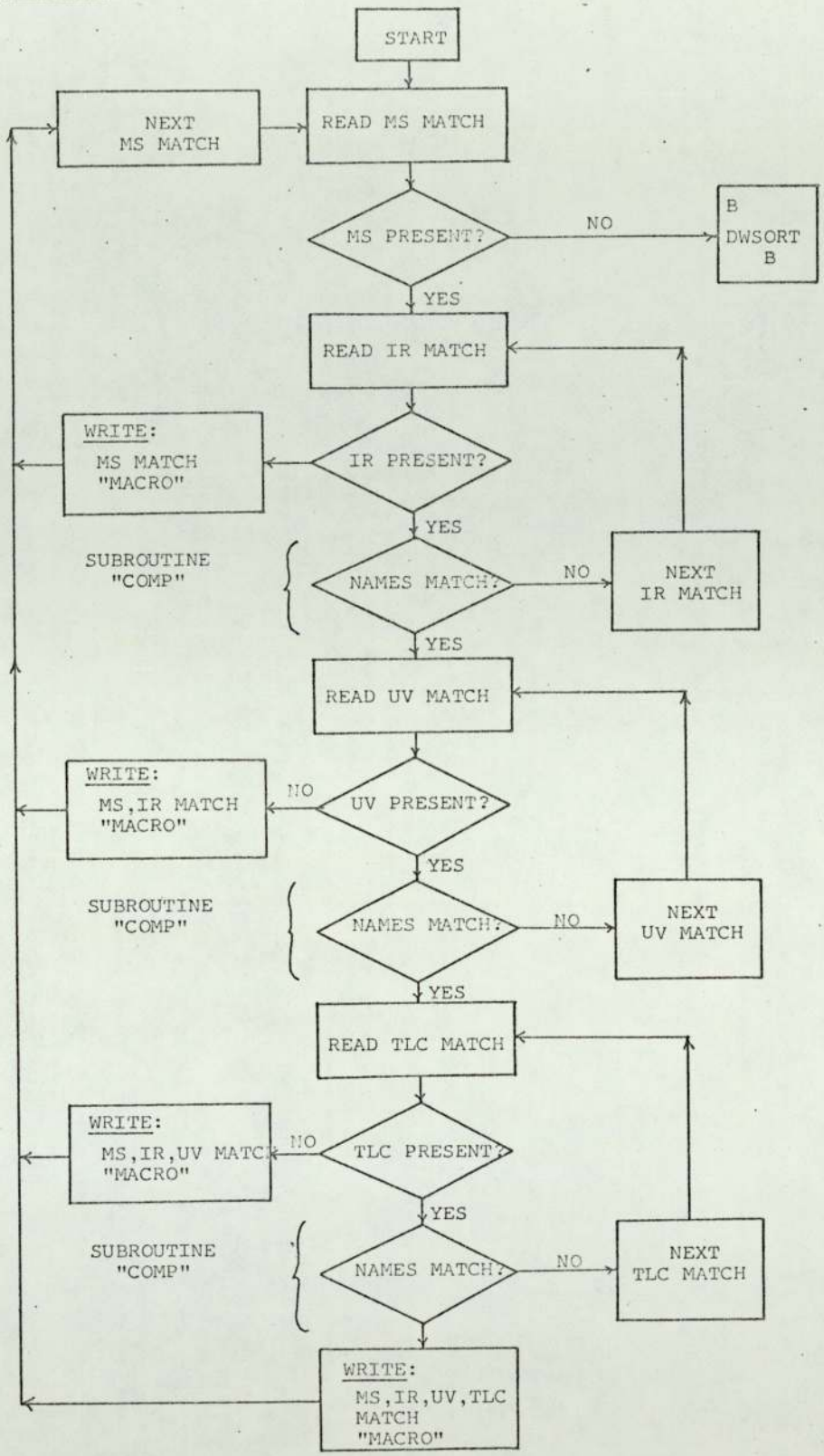


FIG: 5,7c

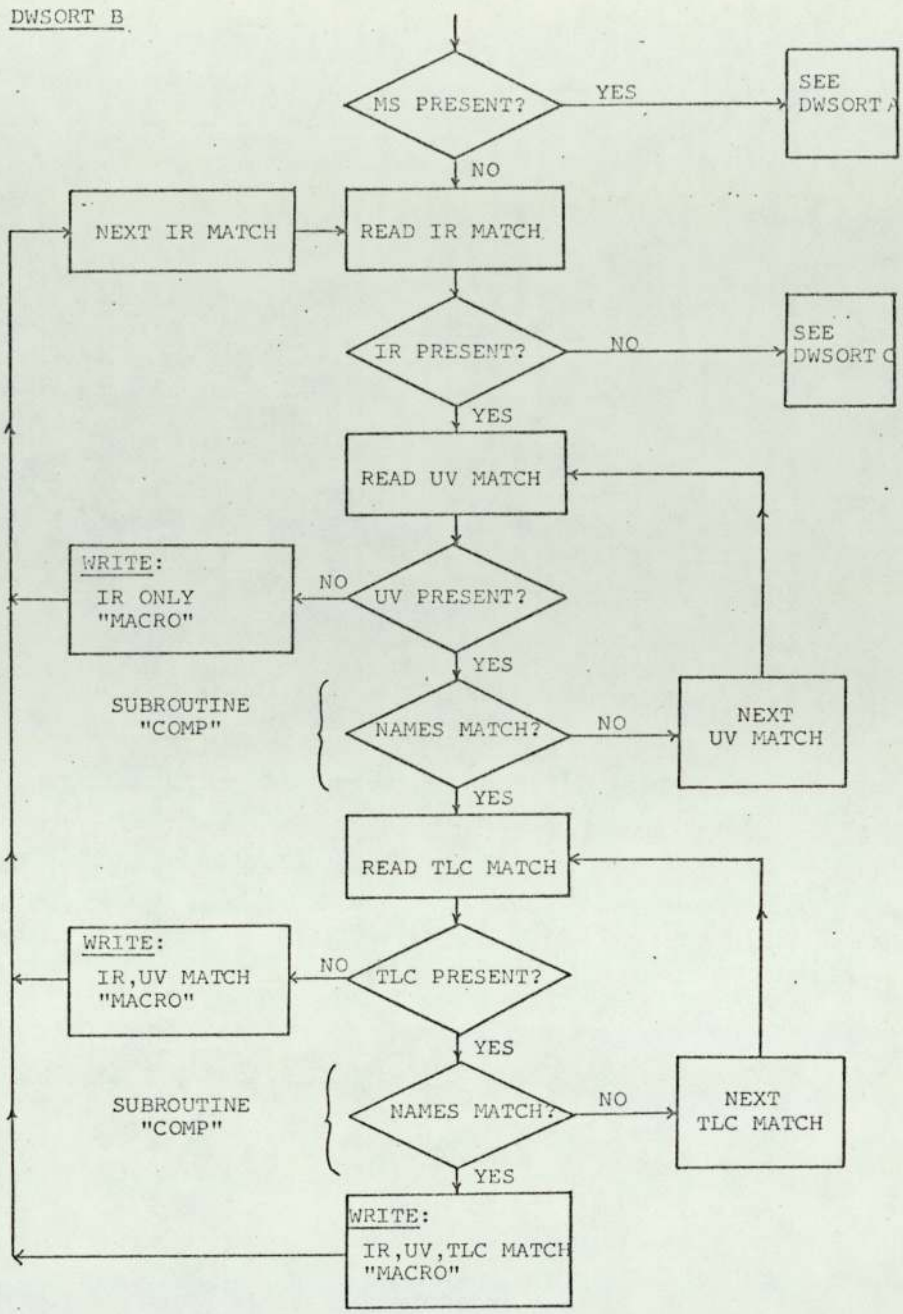
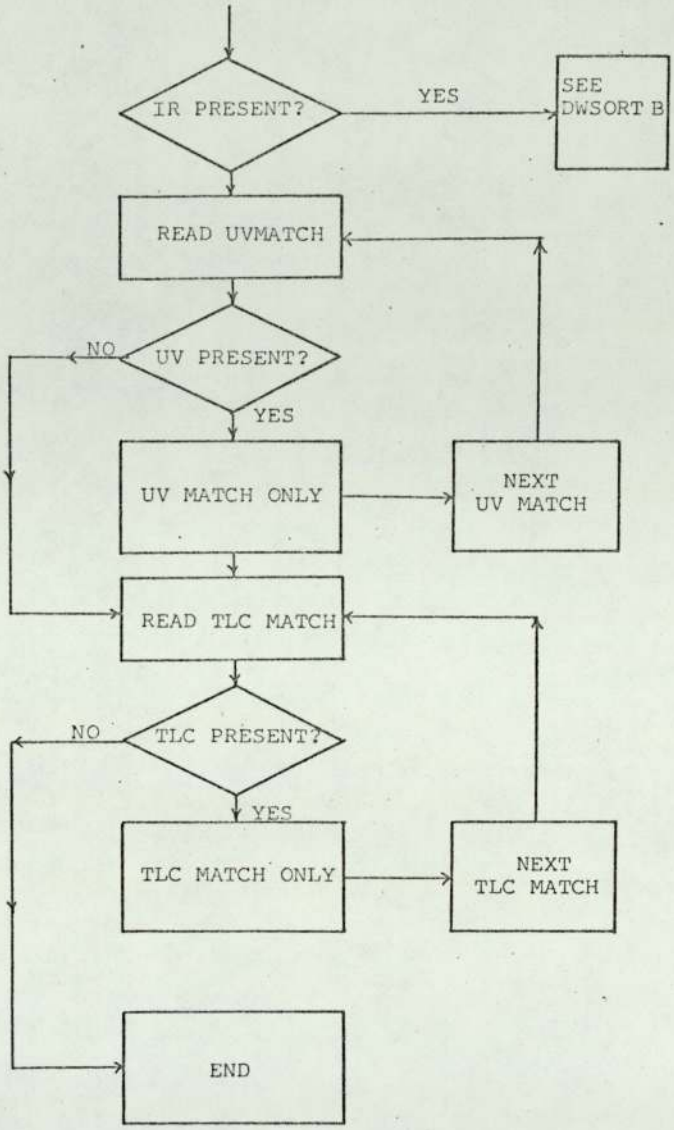

DWSORT B
MS PRESENT?
YES
SEE DWSORT A
NO
NEXT IR MATCH
READ IR MATCH
IR PRESENT?
NO
SEE DWSORT C
YES
READ UV MATCH
WRITE:
IR ONLY
"MACRO"
NO
UV PRESENT?
YES
SUBROUTINE "COMP"
NAMES MATCH?
NO
NEXT UV MATCH
YES
READ TLC MATCH
WRITE:
IR,UV MATCH
"MACRO"
NO
TLC PRESENT?
YES
SUBROUTINE "COMP"
NAMES MATCH?
NO
NEXT TLC MATCH
YES
WRITE:
IR,UV,TLC MATCH
"MACRO"

FIG: 5.7d

DWSORT C



Chapter Six Section 1

DATA RETRIEVAL SYSTEM DWSYST4

Within Chapter 5 it was concluded that program DWSORT was inadequate for operational use and that a new approach to the screening and sorting of the analytical data was required. A new set of objectives was formulated, to:-

A. Modify the structure of the data files in order to permit easier sorting of combined matches.

B. Decrease the time required for a search.

C. Maintain the style of the interactive approach but increase the flexibility and user acceptability of the system.

D. Restyle the sorting system so that it was more flexible and efficient.

A. Modification of the Data Files

The previous programs had utilised the analytical data stored on four separate files FIG:5.2. The analytical data for any one compound was frequently on different lines within each file. For example the mass spectral, infra-red, ultra-violet and thin layer data for thebaine were on lines 6, greater than 8, 5 and 6 respectively. This made cross-referencing of information from file to file almost impossible and the design of any sorting system difficult and cumbersome (as for DWSORT).

Uniting the four data files to produce a file of five line monographs each containing the name and the coded data from the four analytical techniques solved the problem. The initial file FILECOMB

FIG:6,1 contained only six full monographs but once the success of the approach had been demonstrated it was rapidly expanded to contain all of the analytical data from the 117 drugs listed in the Act. This combined file enabled automatic cross-referencing of information and facilitated a new approach to the screening and sorting of analytical data.

B. Increase in Speed of the System

For the previous programs the file searching approach had been to:-

1. Read one record from the file.
2. Compare it against the unknown.
3. Determine if it was a satisfactory match.
4. If so make a suitable indication on the terminal and then
5. Progress to compare the next record on file (See FIG:5,3).

For large files the average search time proved to be of the order of several minutes. To overcome this problem the modified file FILECOMB was read straight into the program by means of a small additional subroutine, SUBROUTINE READ, and stored within arrays in the core area of the computer. By this means objective C. was also fulfilled. All the numerical comparisons were now performed very rapidly which resulted in the reduction of the total time spent at the terminal and also improved the acceptability of the system to potential users.

D. Restyle of the Screening and Sorting Processes

The modified data file FILECOMB enabled a complete

FIG: 6.1

DOCUMENT FILECOMB

```
 0  28  32  41  42  44 162 215 285  (MS)  }
 1  7.6  8.5  8.7  9.0  9.4 12.7    (IR)  }
 2 285                               (UV)  } one
 3 0.12                              (TLC) } monograph
 4 MORPHINE SULPHATE                 (NAME)}
 5  1
 6    28  36  42  44  70 115 229 315
 7    5.8  6.6  7.8  9.0  9.7 10.5
 8   281
 9  0.14
10 OXYCODONE
11  1
12    42  43  56  71  91 232 245 246
13    5.8  8.2  8.4  8.9  9.4 14.3
14   258
15  0.70
16 FURETHIDINE
17  2
18    28  42  44  59  70 163 286 287
19    9.3 10.4 10.5 10.7 12.6 13.5
20   283
21  0.12
22 DIHYDROMORPHINE
23  1
24    28  36  42  44  59 124 162 313
25    7.9  8.4  8.9  9.4  9.6 12.5
26   284
27  0.38
28 ETHYLMORPHINE
29  1
30    28  42  44 255 295 310 311 312
31    6.2  7.8  8.1  8.7  9.7 11.0
32   284
33  0.35
34 THEBAINE
35  1
36   -1
37  ****
38
```

screen, comparing each of the full monographs on the coded analytical techniques against those of the unknown, to be performed on the whole file. A qualitative numerical "Scoring System" was developed for this purpose.

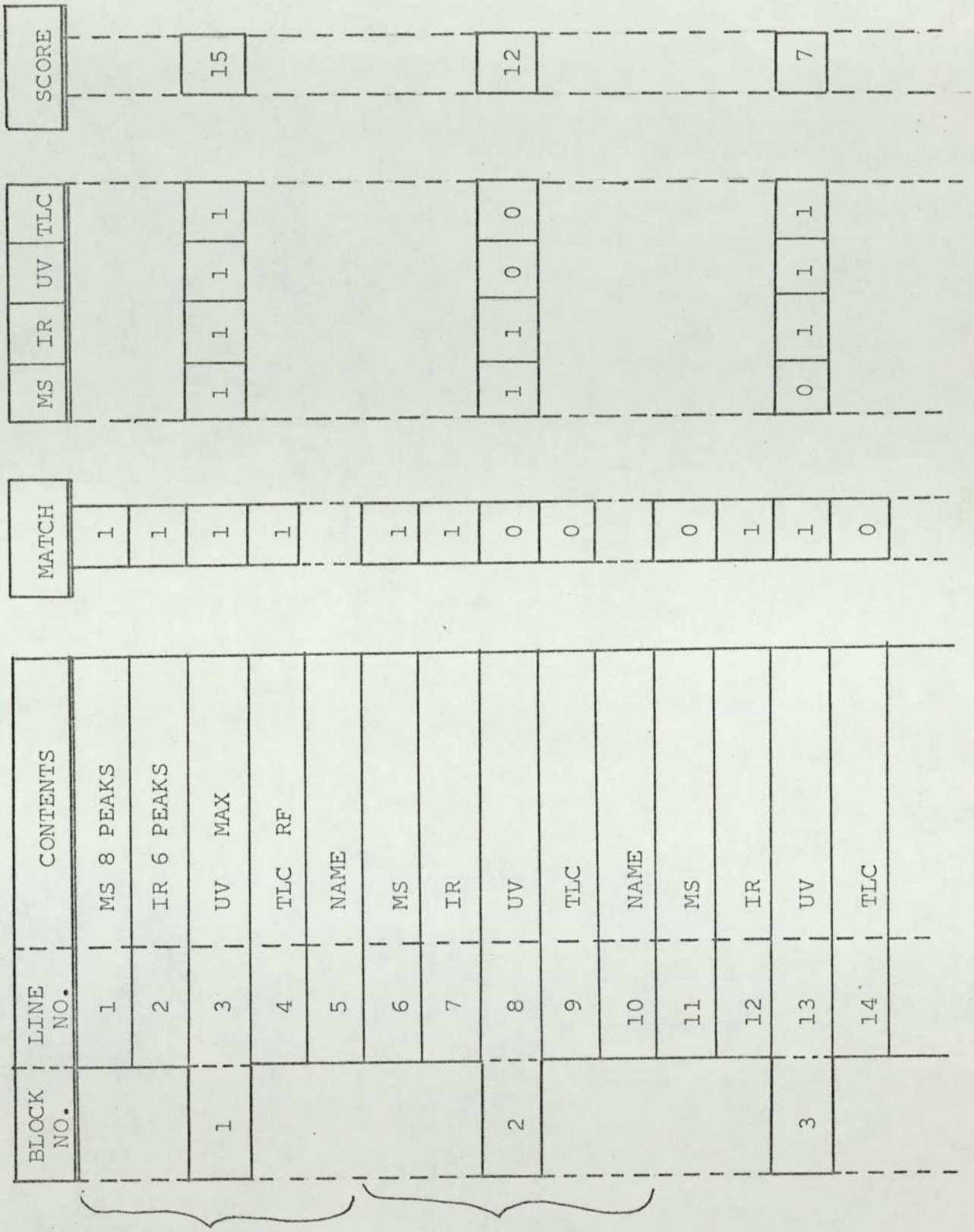
1. The SCORING SYSTEM - A combined method for screening all the analytical data held on the data file against those of the unknown.

The basic subroutines MS, IR, UV, TLC were retained for the comparisons which utilised the file data now stored within the core memory (arrays) instead of the repetitive approach used previously (FIG:5.3)

A SCORE which indicated the "total" match of all the analytical data on file (for each compound) was established as shown in FIG: 6.2. If the unknown data had produced a match against the mass-spectral data on file a 1 (YES) was inserted into the match column as shown (FIG:6.2). If no unknown data was compared or no match was obtained then a zero was inserted in the match column. Using the respective subroutines for each of the coded analytical techniques this process was repeated, monograph by monograph for all the data on file, in each case creating the appropriate match indicator. The match indicators for each monograph formed a binary four digit number. For the purposes of this program this was converted to base ten (integer) and stored within the array SCORE. Using more advanced computational methods these binary values could have been stored and used directly without conversion. For any combination of matches from the four analytical techniques, each SCORE value was unique, e.g. SCORE values

FIG: 6.2

DIAGRAMMATIC REPRESENTATION OF THE SCORING SYSTEM



of 15 and 12 would have indicated a match for MS, IR, UV, TLC(15) and MS and IR(12) respectively. All of the other possible combinations are illustrated in FIG:6.3. As for DWSORT the format of the analytical match combinations were ranked in the order MS ⟶ IR ⟶ UV ⟶ TLC. It was now possible to present match combinations to the terminal in their order of decreasing importance by sorting these SCORE values. The program was tested using the maximum amount of input information for the unknown, 8 MS peaks, 6 peaks IR, UV λ max and TLC Rf. for two chemically different compounds. The results are expressed below:-

Amphetamine Sulphate

SCORE:	0	1	2	3	15
Total Number Created by Program:	73	30	55	25	2

(Two "full" matches were obtained one for Amphetamine the other for the identical Dexamphetamine.)

Oxymorphone Base

SCORE:	0	1	2	3	4	11	15
Total Number Created by Program:	116	13	31	27	1	1	1

From these results it was concluded that the SCORE system based on the combination of analytical techniques was a specific and accurate means of cross-referencing the data from each.

2. <u>The Addition of Rank Order Correlation to the Peak Matching Routines for Mass-Spectral and Infra-Red Data</u>

The original data file (Chapter 3), for MS had stored the largest 8 peaks, in their order of increasing $^{m}/_{e}$, e.g. for MS $^{m}/_{e}$ 28 ⟶ 500, irrespective of their relative

FIG: 6.3

THE MATCH COMBINATIONS PRODUCED BY THE PROGRAM

QUALITY OF MATCH	SCORE VALUE	BINARY EQUIVALENT				FORMAT OF MATCH STATEMENT	
		MS	IR	UV	TLC		
1st	15	1	1	1	1	MS,IR,UV,TLC	15*
2nd	14	1	1	1	0	MS,IR,UV	14*
3rd	13	1	1	0	1	MS,IR,TLC	13*
4th	12	1	1	0	0	MS,IR	12*
5th	11	1	0	1	1	MS,UV,TLC	11*
6th	10	1	0	1	0	MS,UV	10*
7th	9	1	0	0	1	MS,TLC	9*
8th	8	1	0	0	0	MS ONLY	8*
9th	7	0	1	1	1	IR,UV,TLC	7*
10th	6	0	1	1	0	IR,UV	6*
11th	5	0	1	0	1	IR,TLC	5*
12th	4	0	1	0	0	IR	4*
13th	3	0	0	1	1	UV,TLC	3*
14th	2	0	0	1	0	UV	2*
15th	1	0	0	0	1	TLC	1*

The asterisks were used to permit rapid visual identification of each combined match printed on the teletype. The ranking of MS$\longrightarrow$IR$\longrightarrow$UV$\longrightarrow$TLC was arbitrary and determined by the nature of the binary scoring system.

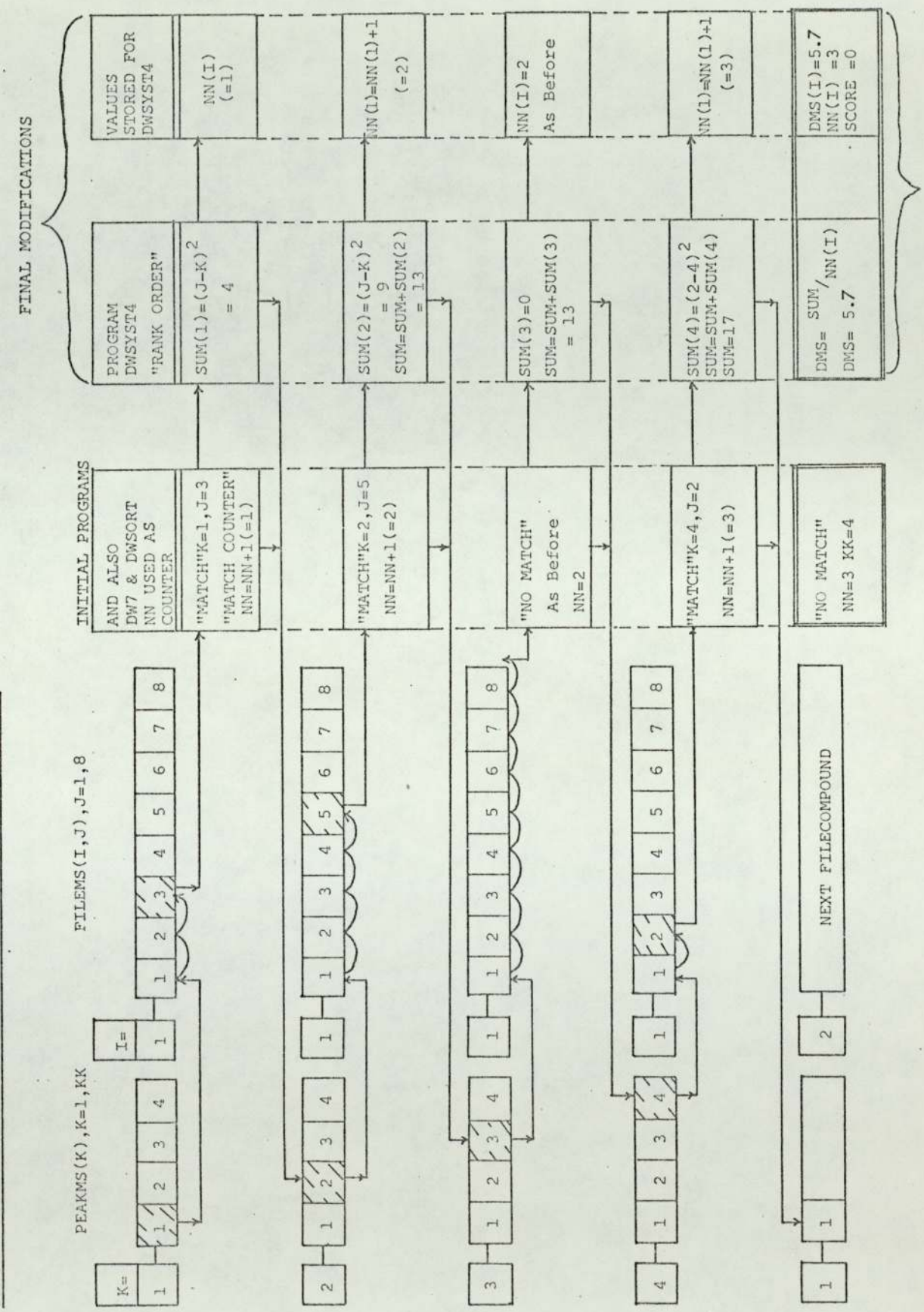
intensities within the group. Initially this was felt to be an appropriate method since, although peaks at high $^{m}/_{e}$ values were often not as intense as those at lower $^{m}/_{e}$ values, they were in fact more important. Coding in this way, however, completely lost any additional (intensity) information which could have been utilised within the comparison routine. The file was, therefore, re-structured so that spectra were coded for position and relative intensity, by coding the peaks in their decreasing order of intensity. This was termed coding in "Rank Order". Comparison of these ordered peaks in the file against those of the unknown, also coded in the same way, established not only the identity of peaks present within the file spectrum but also provided an evaluation of the quality of "fit" of the one with the other. A mathematical means of computing this "quality of fit" was devised.

The initial infra-red data file had been coded in "rank order" although within the original comparison routines this additional information had not been utilised.

The comparison routines MS and IR were modified (FIG: 6.4) so that they compared the peak values $^{m}/_{e}$ for MS, microns for IR) and also identified the positions within the "rank orders" of the unknown and the file at which the respective peaks were identical. These were essentially the first modifications to the subroutines MS and IR since their initial development. FIG:6.4 illustrates the processes involved using MS data as the example. For

FIG: 6.4

DIAGRAMMATIC REPRESENTATION OF PEAKMATCHING (MS AS EXAMPLE)



infra-red data the comparisons were carried out in the same manner except that only six peaks were coded within the file and a window of $\pm$ 0.2 micron was included on each comparison (Chapter 4). In FIG:6,4 the value SUM was used to provide a numerical evaluation of the quality of the match for <u>each</u> individual element of the array (PEAKMS). The DMS value (difference value) was used to provide a correlation value for <u>all</u> of the elements in the array (PEAKMS) when compared against the file (FILEMS), in a similar way to that used for calculating standard deviations.

Each value in PEAKMS (total of four peaks) was compared against all the peaks within FILEMS.

PEAKMS(1) = FILEMS(3)

$\therefore$ SUM(1) = the square of the difference between the respective J and K positions of the matching peaks,

$$SUM(1) = (3 - 1)^2 = 4$$

Similarly for the second peak:-

PEAKMS(2) = FILEMS(5)

$\therefore$ SUM(2) = 9

and so on for all the peaks:-

SUM(3) = 0 (no match)

and SUM(4) = 4

The DMS value was then computed as the mean of all the SUM values for <u>matching</u> peaks only, as illustrated in FIG:6,4

$$DMS = \frac{\sum_{J=1}^{KK} SUM(J)}{NN}$$

For example DMS . = $\frac{17}{3}$ = $\frac{5.7}{}$

Only three of the possible four peaks in the unknown were found to match therefore a "full match" had not been obtained and the SCORE value was accordingly set to zero. For each comparison involving infra-red or mass-spectral data an appropriate "Difference Value" was calculated and stored with an array for later use. The "Difference Values" for infra-red data were stored within the array DIR.

The minimum possible value for DMS was zero, i.e. when all of the peaks in the unknown were identical in position and value to those of the file. The maximum value possible was DMS = 49 i.e. when only one peak for the unknown was identical to a peak at position 8 within the file.

The maximum value possible for DIR was DIR = 25, when only one peak for the unknown was identical with a peak at position 6 within the file.

For combinations of MS and IR data where full matches were obtained, the D values DMS and DIR were transferred back to the main program and combined in the array D. This facilitated a greater ease of manipulation when used later in the program (sorting area).

3. Threshold Value for DIR and DMS

(i) DIR Threshold

For practical purposes it was necessary to determine the threshold limits at which the probability of retrieving the correct compound was as near to 100% as possible and

the probability of retrieving other compounds in which the peak match positions were not similar was as near to zero as possible.

For infra-red data the quality control study (Chapter 4) provided 12 coded spectra from different laboratories for each of two chemically different compounds. FIG:6.5a,b The extent to which the rank order correlation (DIR) varied from source to source gave an empirical indication of the threshold value at which DIR should be set within the program, in order to be certain of retrieving the correct compound.

The results are illustrated below:-

Zoxazolamine 6 peaks compared against 6.

The respective spectra from each of the laboratories were compared against an arbitrary standard, those of infra-red spectra recorded at C.R.E.

7 Spectra had	DIR = 0
3 Spectra had	DIR = 0.33
1 Spectrum had	DIR = 1.00

Cyclizine

7 Spectra	DIR = 0.0
1 Spectrum	DIR = 0.15
1 Spectrum	DIR = 0.33
1 Spectrum	DIR = 1.00
1 Spectrum	DIR = 1.33
(1 Spectrum	DIR = 0.33 5 out of 6 peaks only)

In Chapter 4 the coding difficulties encountered for IR data, in terms of peak shape and partially resolved peaks, have been illustrated. The two compounds Zoxazolamine and

FIG: 6.5a

Rank Order Comparison of 12 Infra-Red Spectra Obtained From Different Regional Forensic Science Laboratories against a Standard

Cyclizine HCL 0.2μ window

Lab. No.	CRE Stand	1	2	3	4	5	6	7	8	9	10(a)	(b)	(c)
Spectrometer	PE 137	Beckm.	PE 137	SP 200	SP 200	SP 200	PE 197	Grubb Parsons	SP 200	SP 200	SP 200	PE 457	PE 157
Peak Positions Matching Against Standard	1	1	2	3	1	2	1	1	1	1	1	1	1
	2	2	3	2	2	1	2	2	2	2	2	2	2
	3	3	1	1	3	3	3	3	3	3	3	3	3
	4	4	4	4	5	4	4	4	5	4	4	4	4
	5	5	5	5	6	5	5	5	4	5	5	5	5
	6	6	6	6	*	6	6	6	6	6	6	6	6

* Peak 4 out of range

DIR_{T_4} MAX = 2.0

FIG: 6.5b

Rank Order Comparison of 12 Infra-Red Spectra Obtained from Different Regional Forensic Science Laboratories against a Standard

Zoxazolamine base, 0.2 μ window

Lab. No.	CRE Stand	1	2	3	4	5	6	7	8	9	10(a)	(b)	(c)
Spectrometer	PE 137	Beckm.	PE 137	SP 200	SP 200	SP 200	PE 157	Grubb Parsons	SP 200	SP 200	SP 200	PE 457	PE 157
Peak Positions Matching Against Standard	1	1	1	1	1	1	1	1	1	1	1	1	1
	2	2	2	2	2	2	2	2	2	3	2	2	2
	3	4	3	5	5	4	3	3	3	2	3	4	3
	4	3	4	3	3	3	4	4	4	4	4	5	4
	5	5	5	4	4	5	5	5	5	5	5	5	5
	6	6	6	6	6	6	6	6	6	6	6	6	6

DIR_{T_4} MAX = 1.25

Cyclizine were chosen to illustrate the need for and size of comparison windows. Both demonstrated the two extremes of the ease and difficulties involved in coding. Zoxazolamine provided an evenly distributed spectrum with six obvious peaks and Cyclizine a much less evenly distributed spectrum with peaks that were close in intensity. These differences are illustrated by the total extent of all the DIR values for each spectrum and particularly for one of the Cyclizine spectra in which 5 out of the possible 6 peaks matched against the standard.

An attempt was made to identify the sources of difference which enabled infra-red spectra of the same compound to have different coded sets of data.

(ii) Possible Sources of Difference which could Produce Different Coded Spectra of the Same Compound

There were 5 sources which were apparent:-

(a) Machine variations.

(b) Different recording conditions and sample preparation.

(c) Different chemical forms of the samples.

(d) Different physical forms of the samples.

(e) Human factors involved in the choice of the largest peaks.

(a) Machine Variations

The variations encountered from spectra recorded on well maintained machines was slight and compensated for by the inclusion of comparison "windows". These probably compensated for transfer differences incurred when reading the peak positions, particularly in ambiguous situations.

e.g. when a peak falls between calibration lines, rather than machine variations. Polystyrene calibration peaks were also used on all recorded spectra. Although calibration peaks were not required as input to the program, the slight calibration differences were neutralised by each operator, when a spectrum was manually coded.

(b) Different Recording Conditions - Particularly the Type of Method Chosen for Presenting the Sample to the Spectrometer

There are three principle methods of sample handling solution in chloroform or carbon tetrachloride, potassium bromide or potassium chloride compressed disc, and nujol (liquid paraffin) mull. Each method produced spectra which had some visual dissimilarities to each other. In forensic science the two methods of KBr disc and nujol mull were the only ones used routinely. Comparison of the coded spectra for the same compound produced by each of these two methods are illustrated below:-

KBr. Morphine HCL:	12.7,	9.3,	8.2,	9.9,	6.7,	10.4
Nujol Morphine HCL:	9.4,	6.7,	7.6,	12.7,	9.0,	10.6

WINDOW (0.2μ)

Matches obtained =	1	2	3	4	5	6
	4	1	x	x	2	6

4 peaks out of 6 DIR = 4.75

Differences in the coded spectra were observed.

For most practical forensic purposes (Chapter 4) the infra-red spectra were determined as KBr discs. The spectra obtained from the regional laboratories for the determination of the DIR threshold were all recorded by this means. It was concluded that for accurate results

all spectra must be compared against spectra obtained using the same sample preparation techniques.

(c) Different Chemical Forms

The coded spectra for chemical forms of each of three morphine based compounds were compared to establish the extent of dissimilarity.

(The following spectra were obtained as nujol mulls.)

Morphine HCL:	9.4,	6.7,	7.6,	12.7,	9.0,	10.6	
Morphine Sulphate:	9.3,	8.8,	6.7,	12.5,	6.1,	7.8	
Window (0.2μ)							
Matches Obtained	1,	2,	3,	4,	5,	6	(UNKNOWN)
	1	3	6	4	2	x	(FILE)
5 peaks out of 6			DIR = 3.8				
Dihydrocodeine base:	7.9,	6.7,	9.6,	9.3,	8.3,	8.8	
Dihydrocodeine Tartrate:	9.3,	8.9,	7.8,	8.4,	8.1,	6.6	
Window (0.2μ)							
Matches Obtained	1,	2,	3,	4,	5,	6	(UNKNOWN)
	3	6	x	1	4	2	(FILE)
5 peaks out of 6			DIR = 9.2				

Finally:-

Codeine base:	9.4,	6.7,	8.9,	7.8,	10.6,	12.5
Codeine phosphate:	9.3,	10.4,	6.6,	7.9,	12.5,	8.9
Window (0.2μ)						

Matches Obtained	1,	2,	3,	4,	5,	6	(UNKNOWN)
	1	3	6	4	2	5	(FILE)
6 peaks out of 6			DIR = 3.3				

From these results it was concluded that significant differences were obtained from coded spectra of different

salts and that for practical purposes the retrieval system had to include data on all the possible salts of each compound likely to be routinely encountered. Usual extraction procedures normally gave the organic base, therefore it was most important that this was always included within the file.

(d) Different Physical Forms

From an extended study of barbiturates[45] it was noted that considerable differences were obtained in the infra-red spectra produced from different polymorphic (crystal) forms of the same compound. A standardised method of sample preparation, basically involving recrystallisation from selected solvents was proposed, prior to compression with potassium bromide.

Within the retrieval system no allowance was made for polymorphic variations of this kind, although for future, larger systems, they may be felt necessary.

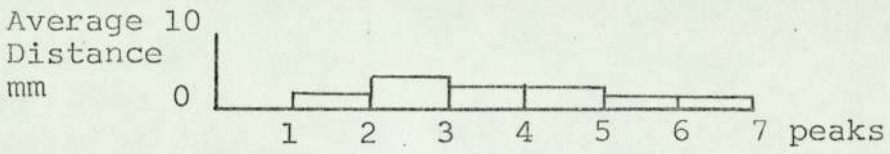
(e) Human Factors Involved in Choosing the Largest Peaks

Experiments were performed to establish the minimum measurable difference between the intensities of the six coded infra-red peaks in rank order, for two series of drugs related to Morphine and Pethidine. The results are illustrated in FIG: 6.6. 1 mm was regarded as the smallest possible distance measurable by a ruler and that distances less than 2 mm were visually discernable with difficulty. It can be seen from the results that the measurable distances between respective intensities and the coded peaks rapidly reduced from the peak coded at position 4 onwards in each case. This meant that the degree of coding

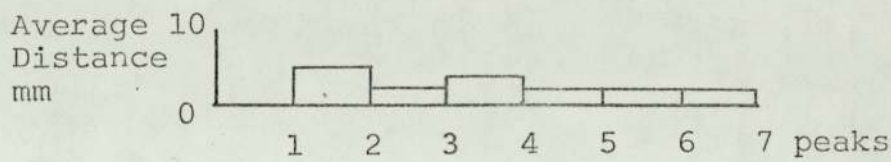
FIG: 6.6

The Average Measurable Distances $\geq$1 mm between the Intensities of the Six Coded Infra-Red Peaks for Each of Two Series of Compounds

PETHIDINE SERIES		Distance Between Intensities mm 1-2	2-3	3-4	4-5	5-6	6-7
HYDROXYPETHIDINE		1	9	2	3	2	2
DIPHENOXYLATE		4	4	2	4	3	5
ANILERIDINE		1	2	1	1	2	1
KETOBEMIDONE		1	3	3	5	2	3
ALPHAMEPRODINE		1	4	7	1	1	2
ETOXERIDINE		5	1	4	1	4	1
AVERAGE OF 6	=	2	4	3	3	2	2 mm



MORPHINE SERIES		1-2	2-3	3-4	4-5	5-6	6-7
NICOCODINE		1	3	6	3	2	2
NICODICODINE		1	1	2	1	1	1
HYDROMORPHONE		4	6	1	1	2	1
DIHYDROMORPHINONE		5	1	6	1	1	1
MORPHINE-N-OXIDE		16	1	1	3	2	5
RACEMETHORPHAN		2	1	2	1	2	1
AVERAGE OF 6	=	5	2	3	2	2	2



ambiguity would almost definitely have increased from this point. In situations where there was ambiguity of choice particularly at the 6th and 7th peak level both spectra were coded within the file. A system based on only the fully resolved peaks (i.e. easily distinguished in terms of size, or relative intensity, from the other peaks) was more likely to retrieve the correct compound than one based on 6 peaks of which the final 2 were speculative). This could only be utilised if it has no significant effect on the rank order correlation.

The data for Zoxazolamine and Cyclizine were re-examined using only the first 4 peaks in each "unknown" spectrum.

The following results were obtained:-

Zoxazolamine,

7 spectra	D = 0
3 spectra	D = 0.5
2 spectra	D = 1.25

DIR_{T_4} MAX = 1.25

Cyclizine,

5 spectra	D = 0
4 spectra	D = 0.25
one spectrum	D = 1.5
one spectrum	D = 2.0

DIR_{T_4} MAX = 2

Comparison of these results with those obtained previously for 6 peaks established that no significant difference was apparent and it was concluded that for most circumstances the use of only 4 peaks, comparing against 6 in the file

with the maximum DIR threshold set to 3 ($DIR_{T_4} = 3$) was as specific as the comparison of 6 against 6, but with the major practical advantage that coding errors produced by ambiguity of choice were minimised.

(iii) Results of a Test on the Infra-Red Retrieval Program to Determine if the Threshold Level of DIR_{T_4} was Set to its Optimum Value

The previously determined optimum experimental value for DIR_{T_4} was $DIR_{T_4} \leq 3$. The size of this value ensured that the probability of retrieving the correct spectrum from a file, if present in that file, was the maximum. An experiment was devised to determine if this value (≤ 3) was sufficiently small to ensure that the probability of retrieving additional spectra from the file was as near to zero per cent as possible.

Each of 3 spectra (present on the file) were compared against the full data file to establish, in each case the number of extra replies obtained at each match level (1 - 6 peaks). The results are represented graphically in FIG: 6.7. It is clearly illustrated that an average of 8 additional spectra were retrieved at the recommended 4 peak level. The additional spectra, on average were composed of 70% closely related compounds.

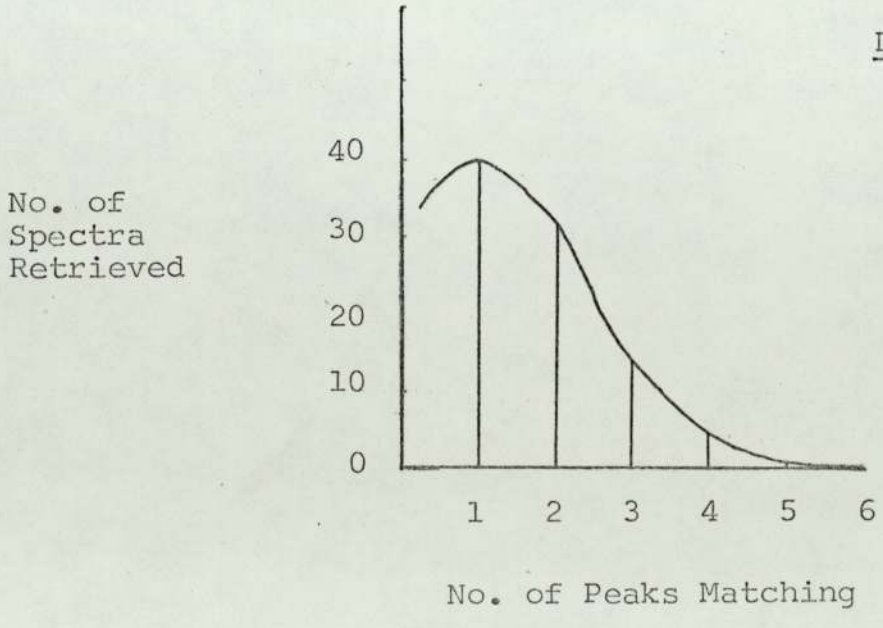
It was concluded that, taking into account all the previously described possible sources of difference, encountered within the 6 peak coding system, that it was not possible to have a more specific search than 8 replies from 190 spectra (including duplicates), in order to maintain 100% retrieval of the correct compound.

FIG: 6.7

Infra-Red

The Average Number of Spectra Retrieved for 1-6 matching Peaks When DIR ≤ 3, for 3 Compounds

Compounds Tested Against the File	Total Number of Possibilities where D ≤ 3 at each match level					
	1	2	3	4	5	6
Hydromorphinol	62	43	17	6	1	1
Oxycodone	123	106	45	13	3	1
Amphetamine	56	40	13	11	3	1
Average of 3 =	80	63	28	10	2	1



Reducing DIR_{T_4} would have decreased the number of additional replies but would have also proportionately decreased the probability of retrieving the correct reply.

Direct visual comparison of the full spectra on all the replies was the only means of complete identification using infra-red data alone.

This experiment is an excellent illustration of why in chemical and forensic analyses the use of several analytical methods is always recommended. A combined retrieval system of the type herein described overcomes this problem.

(iv) DMS Threshold

This threshold value was far more difficult to establish because facilities were not available for obtaining several mass-spectra of the same compound on different machines. A compromise experiment was performed. Five spectra of the M.I.T. collection were compared peak for peak, position for position against the same five compounds in the Aston file (spectra obtained on an A.E.I. MS9 instrument). The results of these comparisons are illustrated below:-

8 peaks M.I.T. (as the unknown) against 8 peaks Aston.

Morphine

M.I.T.:	285,	162,	42,	28,	44,	31,	215,	70
Aston:	285,	28,	32,	42,	44,	162,	215,	41
Matches Obtained	1,	2,	3,	4,	5,	6,	7,	8
	1	6	4	2	5	x	7	x

6 out of 8 peaks DMS = 2.15

Amphetamine

M.I.T.:	44,	91,	65,	42,	45,	120,	46,	92
Aston:	44,	43,	91,	65,	42,	39,	45,	92
Matches Obtained	1,	2,	3,	4,	5,	6,	7,	8
	1	3	4	5	7	x	x	8

6 out of 8 peaks DMS = 1.15

Pethidine

M.I.T.:	71,	70,	42,	28,	57,	43,	172,	247
Aston:	71,	247,	70,	57,	36,	42,	246,	172
Matches Obtained	1,	2,	3,	4,	5,	6,	7,	8
	1	3	6	x	4	x	8	2

6 out of 8 peaks DMS = 7.81

Codeine

M.I.T.:	299,	162,	229,	42,	214,	300,	124,	128
Aston:	299,	162,	42,	229,	124,	44,	115,	300
Matches Obtained	1,	2,	3,	4,	5,	6,	7,	8
	1	2	4	3	x	8	5	x

6 out of 8 peaks DMS = 1.66

Alphaprodine

M.I.T.:	172,	187,	42,	84,	129,	144,	44,	91
Aston:	29,	172,	42,	187,	84,	57,	43,	28
Matches Obtained	1,	2,	3,	4,	5,	6,	7,	8
	2	4	3	5	x	x	x	x

4 out of 8 peaks DMS = 1.5

(v) Background Peaks

It was observed that many of the spectra (for both Aston and M.I.T.) contained coded peaks at less than $^{m}/_{e}$ 42. This was understandable for the Aston file since the starting position of coding was originally $^{m}/_{e}$ 28, however, many of

the spectra in the M.I.T. collection also contained coded peaks in this region. Peaks less than $^{m}/_{e}$ 42 could have been produced from background contamination of the vacuum system by air. A typical background spectrum obtained on the Micromass 12B contained the following:-

$^{m}/_{e}$	Relative Intensity	(Source)
18	8%	(H_2O)
28	100%	(N_2)
32	59%	(O_2)
44	3%	(CO_2)

(vi) Recoding of Spectra

The peaks at $^{m}/_{e}$ 44, although present in the background at the 3% level was, for the majority of organic bases, a characteristic breakdown peak $CH_2 = \overset{+}{N} - CH_3$ particularly for the aromatic amines of the Amphetamine series. The peaks at $^{m}/_{e}$ 43, $\cdot CH_2 - \overset{+}{N} = CH_3$ and $^{m}/_{e}$ 42 $CH_2 = \overset{+}{N} = CH_2$ were also similarly characteristic. The spectra were recoded to include the largest 8 peaks greater than or equal to $^{m}/_{e}$ 42 and the Aston and M.I.T. spectra recompared, as shown:-

Morphine

M.I.T.:	285,	162,	42,	44,	215,	70,	200,	115
Aston:	285,	42,	44,	162,	215,	70,	286,	124
Matches Obtained	1,	2,	3,	4,	5,	6,	7,	8
	1	4	2	3	5	6	x	x

6 out of 8 peaks D = 1.00

Amphetamine

M.I.T.:	44,	91,	65,	42,	43,	77,	92,	51
Aston:	44,	43,	91,	65,	42,	45,	92,	117
Matches Obtained	1,	2,	3,	4,	5,	6,	7,	8
	1	3	4	5	2	x	7	x

6 out of 8 peaks D = 2.00

Pethidine

M.I.T.:	71,	70,	42,	57,	43,	172,	247,	103
Aston:	71,	247,	70,	42,	57,	246,	172,	44
Matches Obtained	1,	2,	3,	4,	5,	6,	7,	8
	1	3	4	5	x	7	2	x

6 out of 8 peaks D = 4.4

Codeine

M.I.T.:	299,	162,	229,	42,	214,	300,	124,	128
Aston:	299,	162,	42,	229,	124,	44,	115,	300
Matches Obtained	1,	2,	3,	4,	5,	6,	7,	8
	1	2	4	3	x	8	5	x

6 out of 8 peaks D = 1.66

Alphaprodine

M.I.T.:	172,	187,	42,	84,	129,	144,	44,	91
Aston:	172,	42,	187,	84,	57,	43,	77,	44
Matches Obtained	1,	2,	3,	4,	5,	6,	7,	8
	1	3	2	4	x	x	8	x

5 out of 8 peaks D = 0.6

From comparison of the previous data, coded from $^{m}/_{e}$ 28, it can be seen that for 3 of the drugs, Morphine, Pethidine and Alphaprodine, there was a considerable improvement in the quality of the "fit". For Codeine there was no change in the quality and only a marginal deterioration in quality

for Amphetamine. In all cases major differences in quality appeared only after the comparison of the fourth peak.

(vii) Possible Factors Responsible for Producing Differences in Coded Mass-Spectra

The seemingly non-reproducibility of mass-spectra from different sources was investigated with a view to itemising the possible causes and establishing additional routines within the retrieval system to eradicate them.

There were 4 major areas which were apparent sources of differences:-

(a) Machine Variation.

(b) Chemical Variation of the Sample.

(c) Physical Variation of the Sample. (Particularly Thermal Instability).

(d) Human Factors involved in choosing the largest peaks.

(a) Machine Variation

It had previously been illustrated[40] in a study on computer data retrieval methods that intensity variations (and hence rank order differences), were obtained when spectra of the same compound were obtained on different mass spectrometers. Three compounds had been analysed on 12 instruments of 4 different types. The 10 strongest peaks in each spectrum were coded. In one example the peak $^{m}/_{e}$ 43 on different instruments varied from the second strongest to the sixth strongest and the relative intensity from 12.8% to 50.6%. Previous attention[46] had also been drawn to the fact that there were variations in the duplicate standard spectra of farnesol taken on different instruments.

It was felt that the vague term "machine variations" hid a multitude of sins and that probably the other factors (**b**), (**c**) and (**d**) were also involved, however, in order to avoid the possibility of machine variations it was concluded that for optimum use spectra obtained from the unknown and the file should be recorded if at all possible on the same instruments for the retrieval system, since the reference data collection at C.R.E. was to be based on the Micromass mass-spectrometer ; the complete file of drugs was re-recorded on a Micromass 12B instrument at C.R.E., coding the 8 largest peaks $\geq {}^{m}/_{e}$ 42 in their order of decreasing importance, (rank order).

(b) Chemical Variation of the Sample

For the initial data file it was felt that different salts of the same compound behaved in a very similar way in the mass-spectrometer. A study of the mass-spectral breakdown of Morphine base and 5 closely related derivatives was undertaken to test this assumption. The results obtained are illustraded below:-

Morphine Spectra obtained on Micromass 12B
Probe Temperature 100°

Base	285,	162,	215,	44,	70,	124,	59,	286
HCL	285,	162,	215,	44,	42,	286,	124,	70
Sulphate	285,	162,	215,	44,	70,	57,	124,	45

and the quaternary salts:-

Metho-bromide	45,	58,	73,	285,	72,	80,	82,	42
Methoiodide	285,	226,	72,	58,	45,	42,	44,	162
N-Oxide	58,	285,	72,	42,	71,	59,	186,	44

Taking the base spectrum as the file standard the following correlations were obtained:-

Morphine HCL	7 out of 8 peaks	D = 2.0
Morphine Sulphate	6 out of 8 peaks	D = 0.16
Morphine Methobromide	1 out of 8 peaks	D = 9.0
Morphine Methoiodide	3 out of 8 peaks	D = 14.6
Morphine N-Oxide	3 out of 8 peaks	D = 6.0

From these results it was observed that for the 2 salts, Sulphate and Hydrochloride, there was in fact very little difference from the coded mass-spectrum of the base and certainly only slightly more than that obtained from spectra of the same compound on different machines.

The other (quaternary) derivatives did produce grossly different spectra and it was concluded that whenever possible all derivatives likely to be encountered by the system should be separately coded within the data files.

(c) Physical Variation of the Sample

Three possible sources of sample degradation were isolated:-

- the cracking produced by the high energy electron beam (70 ev.), discussed in Chapter 3
- the temperature of the ionising source (usually 200-250^{o}) - Chapter 3
- the temperature at which the direct insertion probe was heated in order to ensure the volatility of the sample.

The volatility of different chemical compounds varied greatly depending on the sample. In order to obtain good quality mass spectra external heating of the probe was

often required. The extent to which the probe was heated (i.e. the effective temperature) was arbitrary and often not recorded. For most circumstances it was felt that different temperatures had no effect on the final spectrum, however, to confirm or question this assumption spectra of Morphine Sulphate and Alphaprodine HCL were recorded on the Micromass 12B instrument at probe temperatures from 75° - 125° and 20° - 100° respectively. The initial temperature was determined by the compounds volatility, Morphine Sulphate being far less volatile than Alphaprodine.

The following results were obtained:-

Morphine Sulphate

$75^{\circ}C$:	70,	81,	57,	285,	44,	43,	56,	72
$100^{\circ}C$:	285,	162,	57,	44,	70,	215,	45,	69
$125^{\circ}C$:	285,	162,	215,	44,	70,	57,	45,	124

Alphaprodine HCL

$40^{\circ}C$:	172,	187,	84,	188,	173,	57,	144,	44
$60^{\circ}C$:	172,	187,	84,	188,	57,	173,	144,	44
$100^{\circ}C$:	172,	187,	84,	188,	57,	144,	173,	261

It can be seen from these results that different coded spectra (8 peaks) were obtained for the same compound at different probe temperatures. These differences could have been produced by competitive chemical breakdown pathways, one being preferentially more stable than the other at increased temperatures or, a more likely explanation was that there was some inherent physical difficulty in choosing the 8 largest peaks.

Some degree of temperature standardisation for all the samples handled by the system would probably have marginally

increased the total degree of correlation, however, for files containing samples of such varied volatilities this was impossible. As a result of this study, for the mass-spectral data file compiled at C.R.E. some degree of standardisation was obtained by allowing the probe sample to be slowly heated by the source until the spectrum was optimised. No form of external heating was applied to the probe.

(d) Human Factors Involved in Choosing the Largest Peaks

The spectral data utilised previously for the experiments on temperature variations were re-used to illustrate the degree of ease or difficulty involved in manually coding the raw spectral data. The results are illustrated graphically in FIG:6,8. These results established clearly that the most probable source of coding differences were produced by difficulties of choice, particularly since the previous correlation data had established that in all cases (for the 5 drugs observed) the major differences in quality of "fit" of the spectra were encountered after the fourth peak in each set.

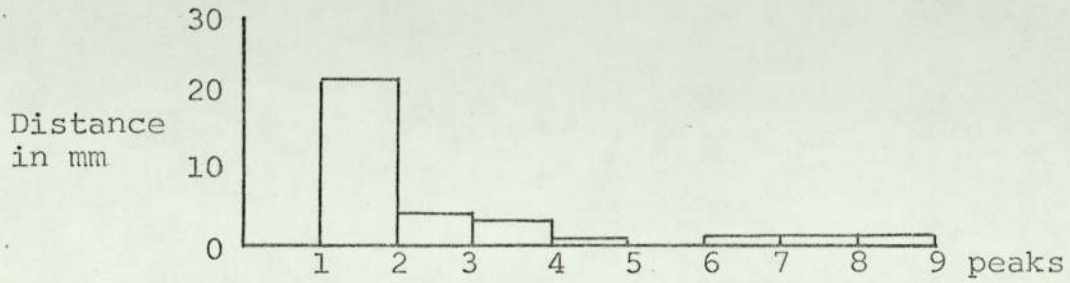
In situations where coding ambiguities were encountered both mass spectra were coded.

As for infra-red retrieval it was concluded that a system which compared only the fully resolved (4 major peaks) for the "unknown" against 8 in the file was the most appropriate practical solution. This overcame the major sources of coding difference and also compensated to some extent for the other sources of difference itemised in (a), (b) and (c).

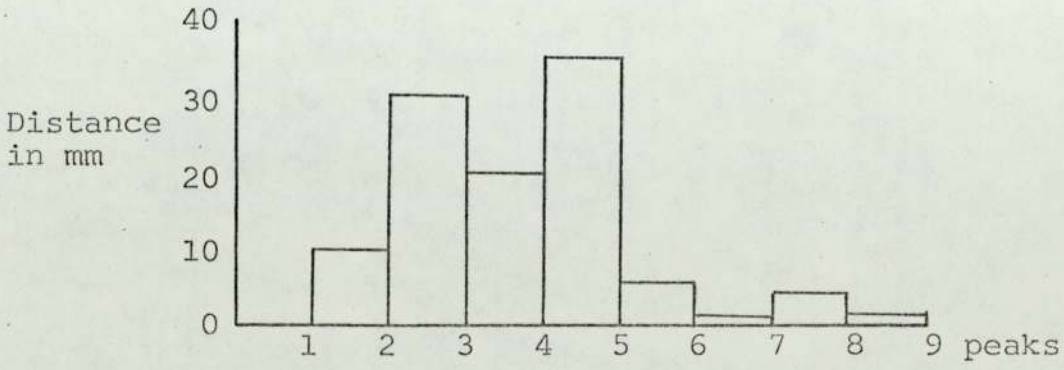
FIG: 6.8

The Measurable Distance $\geq$ 1 mm Between the Intensities of the Eight Coded Mass-Spectral Peaks for Each of Two Compounds

100°C, MICROMASS 12B	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9
MORPHINE SULPHATE	22	4	3	3	1	0	1	1



100°C MICROMASS 12B	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9
ALPHA PRODINE HCL	10	30	20	35	5	1	4	1



The recalculated correlation values for 4 peaks on each of the 5 spectra for M.I.T. against Aston are listed below:-

Morphine 4 peaks	D = 2.25
Amphetamine	D = 0.75
Pethidine	D = 0.75
Codeine	D = 0.5
Alphaprodine	D = 0.50

A small increase in the DMS value for Morphine was observed with the other correlation values for the compounds being markedly improved. For operational purposes the DMS_{T_4} was set to $DMS_{T_4} \leq 3$ within the program.

(viii) Results of a Test on the Mass-Spectral Retrieval Program to Determine if the Threshold Level DMS_{T_4} was set to its Optimum Value

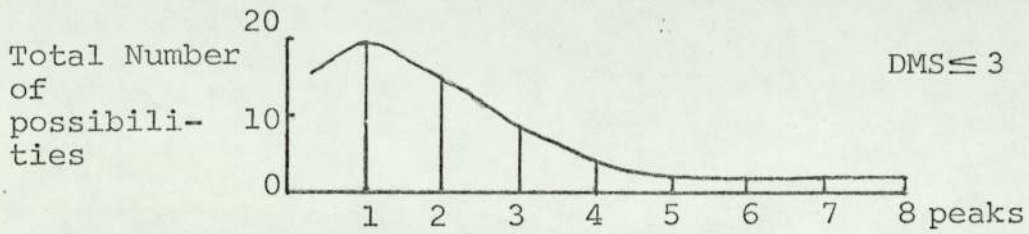
DMS_{T_4}, like DIR_{T_4} had been set to ≤ 3 as a result of experimental investigation. At this level the probability of retrieving the correct compound was the maximum. An identical study to that undertaken on the infra-red data was performed. Two spectra (both present on the file) were compared against the full data file to determine in each case the number of extra replies obtained. The results are represented graphically in FIG:6,9.

It can be seen from the results that at the 4 peak level Oxymorphone gave two additional replies (both closely related) and Amphetamine no extra replies. From these results it was concluded that the threshold value was indeed set at the optimim level. Additional replies of the order of 2 from 190 spectra were easily distinguished by the visual comparison of extra peaks.

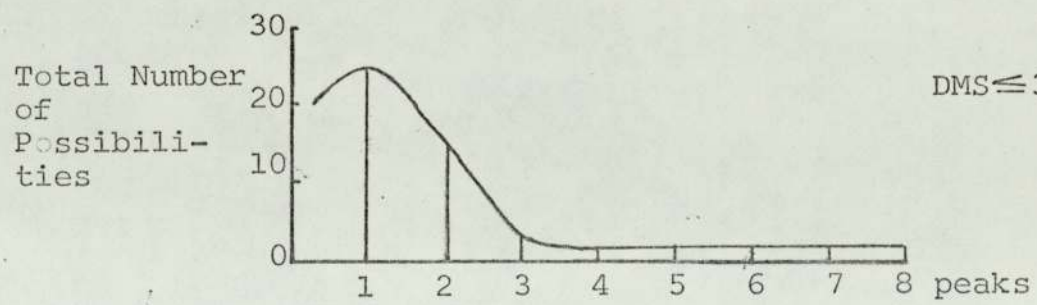
FIG: 6.9

The Number of Mass-Spectra Retreived for 1-8 when DMS $\leq$3 for Two Compounds

	Number of possibilities where DMS $\leq$ 3 at each match level							
	1	2	3	4	5	6	7	8
OXYMORPHONE	19	15	8	4	2	2	2	2



	Number of possibilities where DMS $\leq$ 3 at each match level							
	1	2	3	4	5	6	7	8
AMPHETAMINE	25	15	3	2	2	2	2	2



Combining these results with those obtained from tests on the infra-red matching program the comparison of 4 peaks for each of the 2 analytical techniques in combination enabled the system to have a combined degree of selectivity of the order of 1:1,805. [This value was obtained by multiplying the degree of selectivity for IR (1:19) by the degree of selectivity for MS (1:95).]

(ix) Coding Errors

Although the program and data files were now designed to cope with the majority of coding differences for MS and IR data they were still not adequately equipped to handle the possibility that a gross coding error had been made when either the file or unknown data had been coded. A solution was found to this problem by modifying the comparison routines MS and IR and including two additional subroutines MSMISMATCH and IRMISMATCH.

4. Mismatch Routines - Partial Match Search

The subroutines MS and IR were further modified as shown in FIG:6.4 , not only to compute and store the rank order correlation values, DMS and DIR, but also to store the match counter (Mismatch) values NN and NI.

Two additional subroutines were developed, one MSMISMATCH to sort the computed NN(MS) values in combination with their related rank order correlations DMS and the other IRMISMATCH to sort the NI(IR) values in combination with their related DIR values. By these means it was possible to output to the terminal if required the partial matches obtained in order of their decreasing importance. The Mismatch routines were only utilised if either, the unknown data for MS and IR had not produced a "full match" from

within the file or, a full match of poor quality, as defined by the size of the respective D value, had been obtained.

E. The Structure of the Final "Peak Matching" System

The program had now evolved into four major operational areas FIG:6,10.

1. Input area - where the unknown data was read into the program and stored alongside the file data in the core memory.
2. Screening area - where each of the compounds on file were compared repetitively against the coded data on file and the appropriate SCORE, DMS, DIR, NN and NI values computed.
3. Sorting area - where the previously computed values were sorted in combination into their decreasing order of importance. The appropriate Mismatch routines MSMISMATCH and IRMISMATCH were utilised if required.
4. Output area - where the appropriate format was attached to the equivalent SCORE value for output to the terminal.

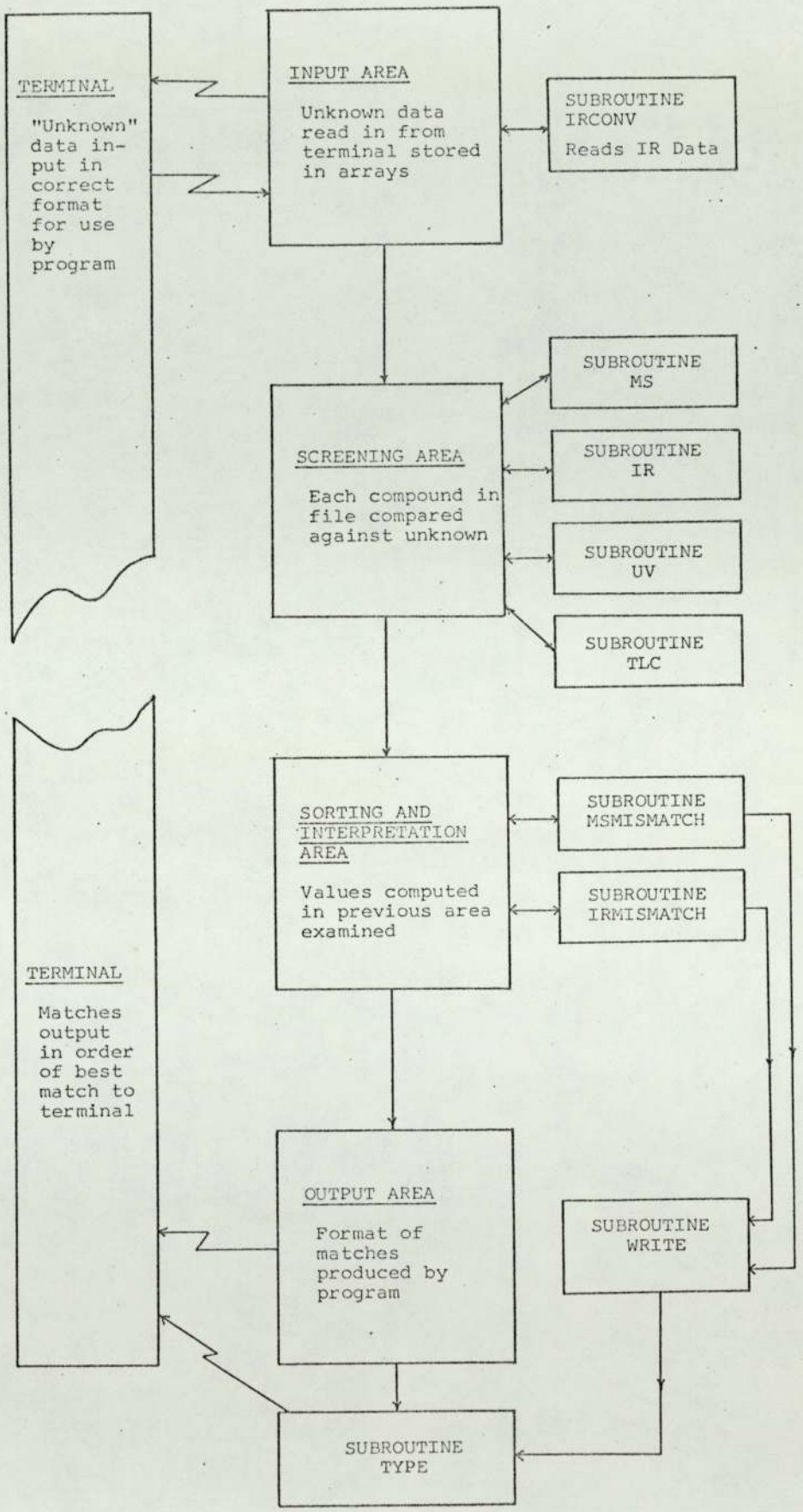
F. The Data Retrieval Package DWSYST4 FIG:6,11.

To complete the system three additional subroutines were developed to:-

1. Retrieve the analytical data stored on any named compound, Subroutine NAM.
2. Retrieve the analytical data stored for compounds of the same molecular weight, Subroutine MASS.
3. Retrieve the analytical data stored for compounds

FIG: 6.10

STRUCTURE OF SUBROUTINE ANAL



of the same full or partial molecular formulae, Subroutine FORM.

The incorporation of the additional subroutines within the program necessitated the inclusion of extra lines within the data file to indicate the molecular formula and molecular weight, (subsequently renamed FILEDATA FIG:6.12) and a modified MASTER segment. The "Peak Match" routines subsequently became renamed Subroutine ANAL. as shown in FIG:6.10

The detailed programming methodology required by Subroutine ANAL. and the three additional subroutines are fully described in Chapter 6, Section 2.

FIG: 6.11

TOTAL
STRUCTURE OF DSYST4

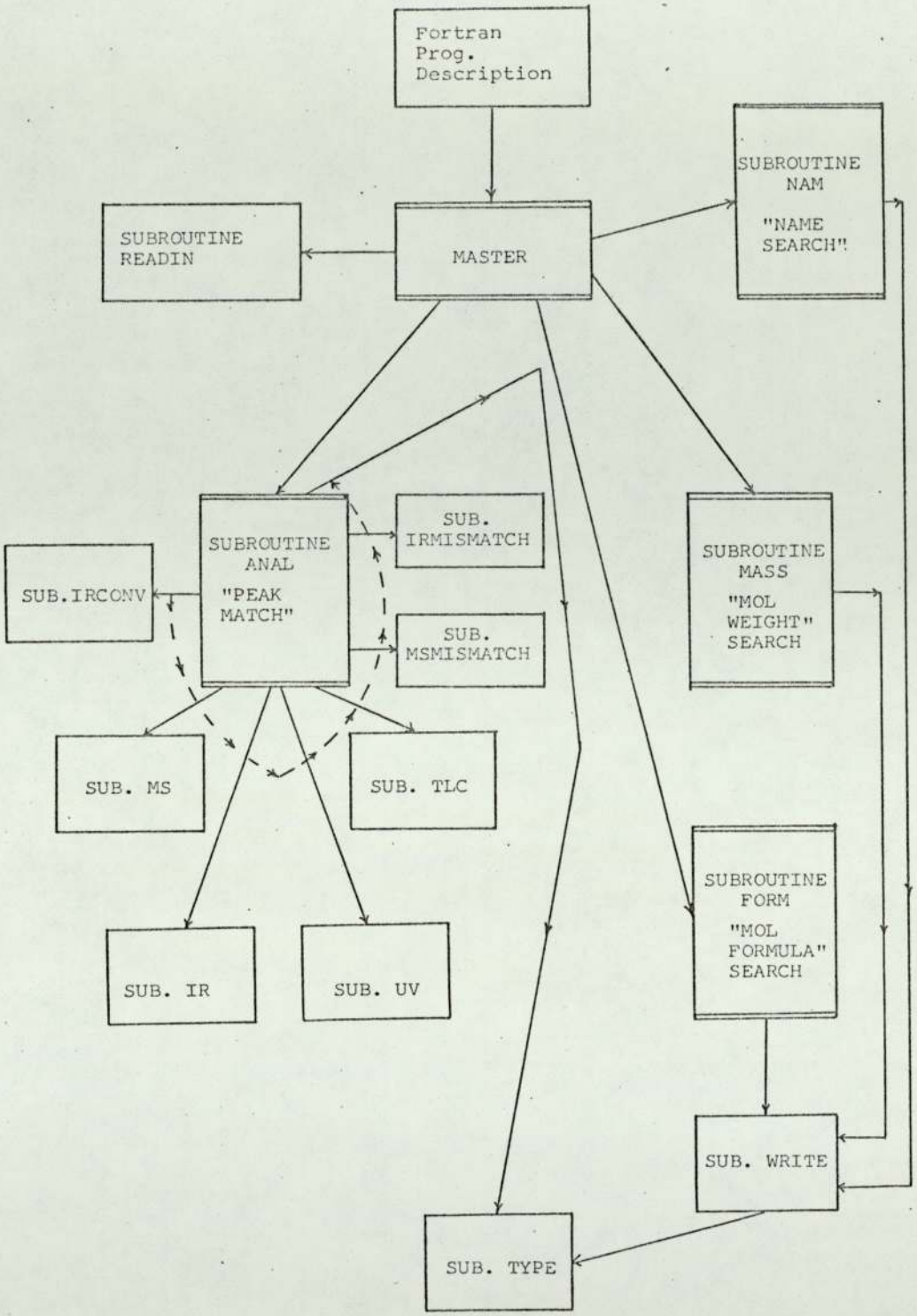


FIG: 6.12

DOCUMENT FILEDATA

```
 0  27 35  1  5
 1 453.0
 2    0   0   0   0   0   0   0   0
 3   0.0  0.0  0.0  0.0  0.0  0.0   0.0
 4  283
 5 0.68
 6 ACETORPHINE
 7  1
 8  18  25  1  2
 9 287.0
10    0   0   0   0   0   0   0   0
11   5.8  8.5  8.8  8.7 14.3 13.2
12  257
13 0.75
14 ALLYLPRODINE BASE
15  2
16  23 31  1  2
17 353.0.0
18   72  31  73  43  57  60  61  29
19   5.8  8.1 14.2  9.8 13.8 13.1
20 259
21 0.75
22 ALPHACETYLMETHADOL DI HCL
23  4
24  23 31  1  2
25 353.0
26    0   0   0   0   0   0   0   0
27   8.1  5.8 14.2  6.6  9.9  9.7
28  259
29 0.75
30 ALPHACETYLMETHADOL BASE
31  4
32  23 31  1  2
33 353.0
34   72  28  36  43  44  32  91  278
35   8.1  5.8 14.3  9.8 13.9  9.1
36  259
37 0.00
38 BETACETYLMETHADOL HCL
39  4
```

Chapter 6 Section 2 Full Description of the System DWSYST4

This section fully describes the programming methodology used within the retrieval system.

(I) Operating Levels

Within the operating capabilities of the ICL 1905E computer there were three "levels" of operation. FIG:6.13.

(A) Level 1

This involved switching on the terminal and typing a single "Log-in" command. Users were identified by a user number previously registered within the operating systems directory. The computer was then available for use at its lowest level, that of the operating system GEORGE 3Mk7.

A combination of GEORGE 3 commands was used to produce a small MACRO program which enabled the computer to be used at the second level.

(B) Level 2 Macro Program SYSTEM4

The Macro program was stored on tape (or disk) within the file-store of the computer and was utilised by typing a single Macro command "SYSTEM4" on the terminal. This program carried out the fundamental preparations required for the total operation of the retrieval system. The flow diagram and listing of the Macro are shown in FIG:6.14 and Appendix 2(MACRO)

The Macro's principal function was to load the compiled binary version of the Fortran object program and connect the necessary input/output devices.

(C) Level 3 Fortran Object Program DWSYST4

This program was responsible for all the data retrieval operations required by the system. The

FIG: 6.13

DIAGRAM: LEVELS OF COMPUTER OPERATION

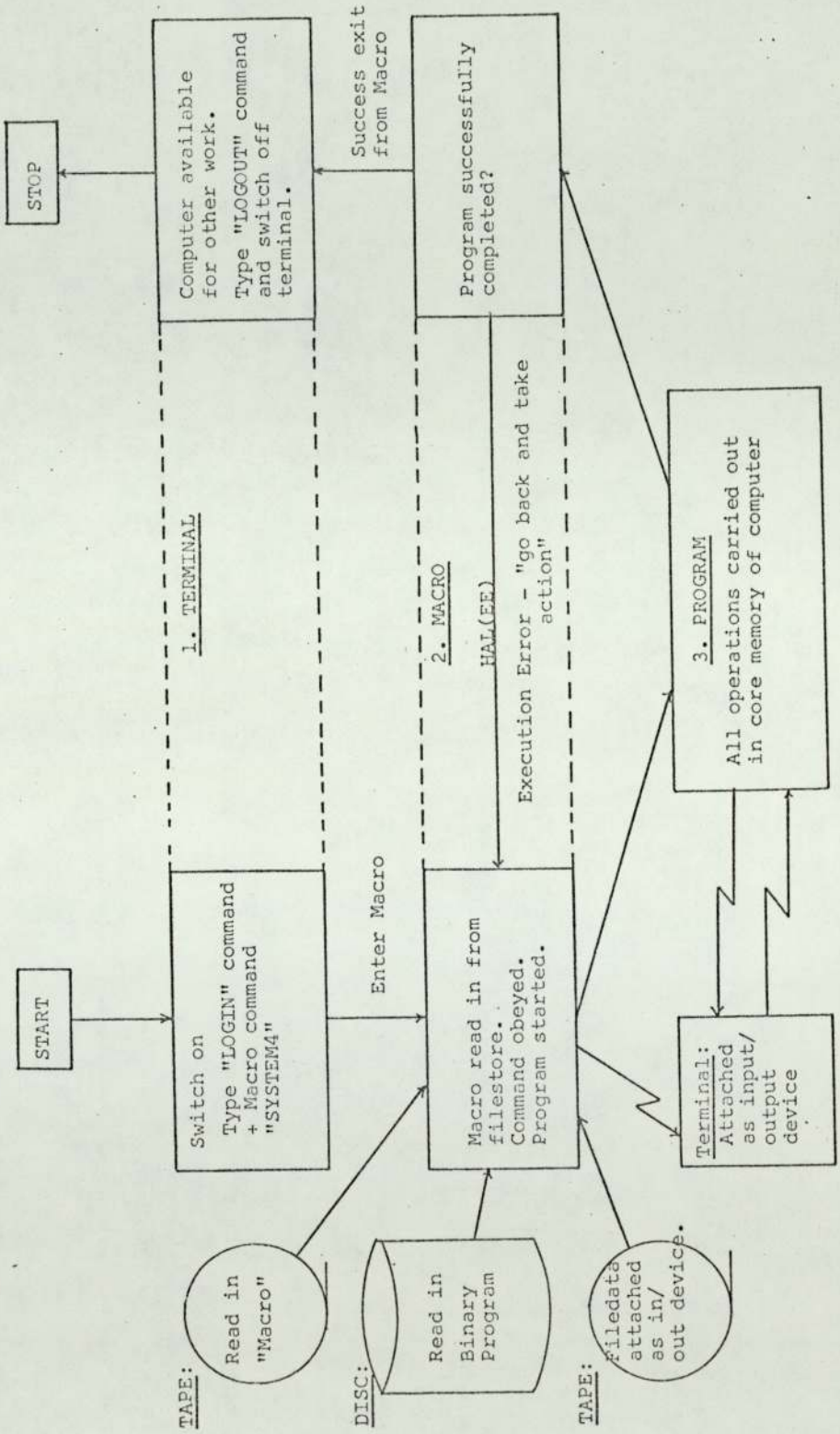
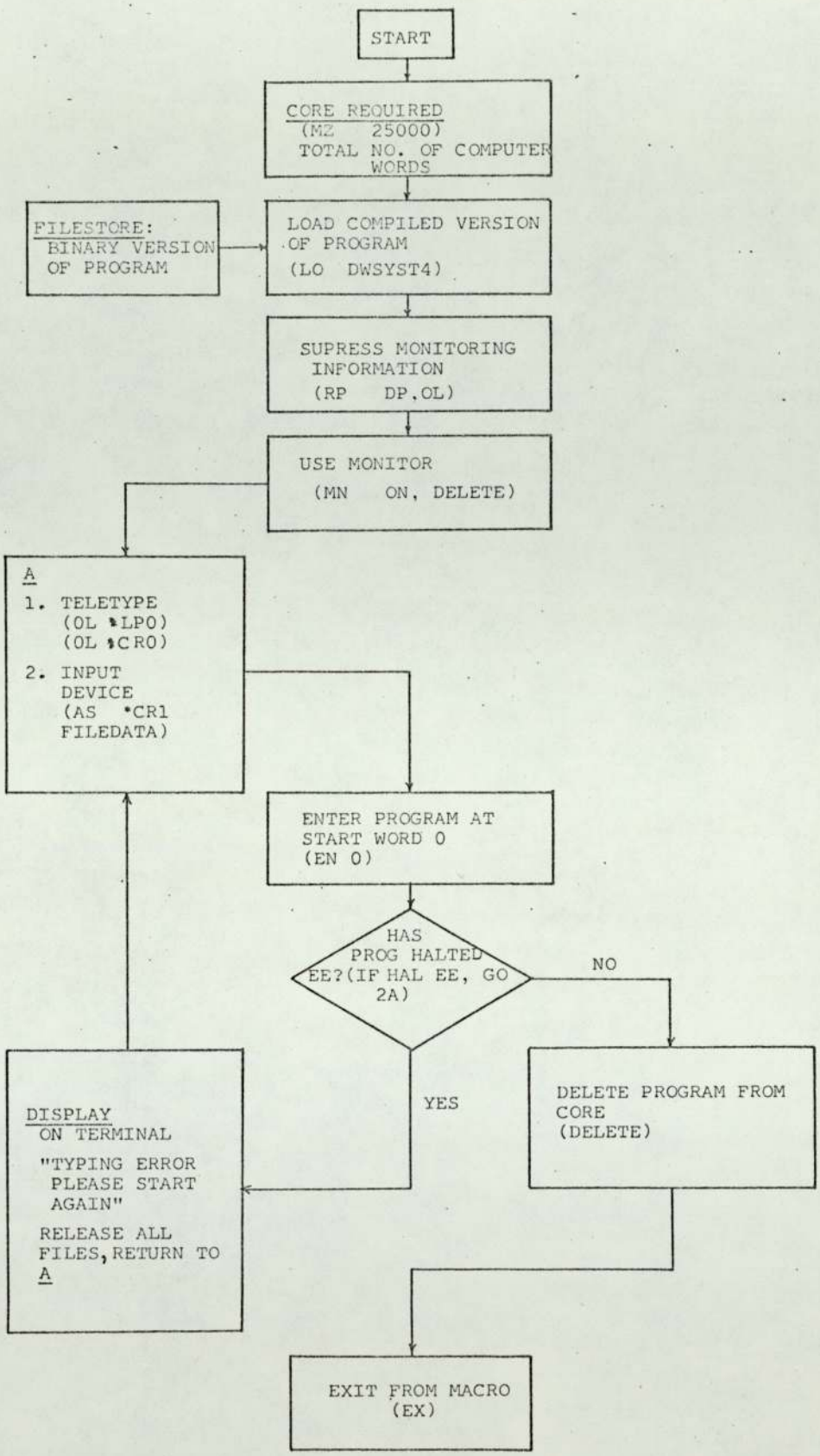


DIAGRAM: LEVELS OF COMPUTER OPERATION

FIG. 8.14

MACRO PROGRAM
OPERATED BY TYPING: SYSTEM4



program was utilised within the CORE MEMORY of the computer. Up to 36K of core was available for terminal use on the ICL 1905E system.

Within the earlier programs DW7 and DWSORT, statements were included within the program which permitted interaction with the MACRO program at level 2. These facilitated file rewinds, etc. The final program, DWSYST4 did not include any statements of this kind. Control was only returned to the MACRO program either if:-

1. the program had halted due to an execution error. The operator making a serious typing error on one of the inputs to the program was the only situation in which it was possible for the program to halt EE. The following statement was output to the terminal: "DISPLAY : TYPING ERROR PLEASE START AGAIN". The MACRO program then released all the input/output devices, re-attached them and re-started the program from the beginning, or

2. the program had been successfully completed, as in the majority of situations. Control was then returned first to the MACRO, which was responsible for deleting the program from core and finally back to the basic operating level, level 1 of GEORGE 3. If no further work was required a "LOG OUT" command was typed and the terminal switched off.

(II) The Program DWSYST4 FIG:6.11.

The program consisted of:-

A. A FORTRAN program description.

B. A MASTER segment

and 4 major subroutines:-

C. Subroutine READIN was the initial subroutine called by the MASTER segment. Responsible for reading the filedata into the program.

D. Subroutine ANAL "Peak Match routines". Responsible for the retrieval of analytical data.

E. Subroutine NAM "Name Search routine". Responsible for the retrieval of analytical data on named compounds.

F. Subroutine MASS "Molecular Weight Search". Responsible for the retrieval of analytical data associated with a particular molecular weight.

G. Subroutine FORM "Molecular Formula Search". Responsible for the retrieval of analytical data associated with a particular molecular formula.

These individual subroutines were responsible for using an assortment of other subroutines.

Subroutine ANAL was essentially self contained, a complete program within a program, only the additional subroutines READIN and TYPE were utilised from the full system. The other three major routines, NAM, FORM and MASS all used the WRITE subroutine as a standard method for providing output of the required format to the terminal.

A. The Fortran Program Description

This section of the program although small was important and its function was closely related to that of the MACRO program. A full listing is shown in Appendix 2(0-8) The most important lines were those of 2, 3 and 4 shown

below:- line (2) Input 1 = CR0

line (3) Input 3 = CR1

line (4) Output 6 = LP0

The remainder were machine specific statements required for compilation purposes. These three lines defined the input/output channels used within the program and established a cross relationship with those in the MACRO, as shown below:-

Prog. Description	Macro Command
INPUT 1 = CR0	OL *CR0)
OUTPUT 6 = LP0	OL *LP0) to terminal
INPUT 3 = CR1	AS *CR1, Filedata

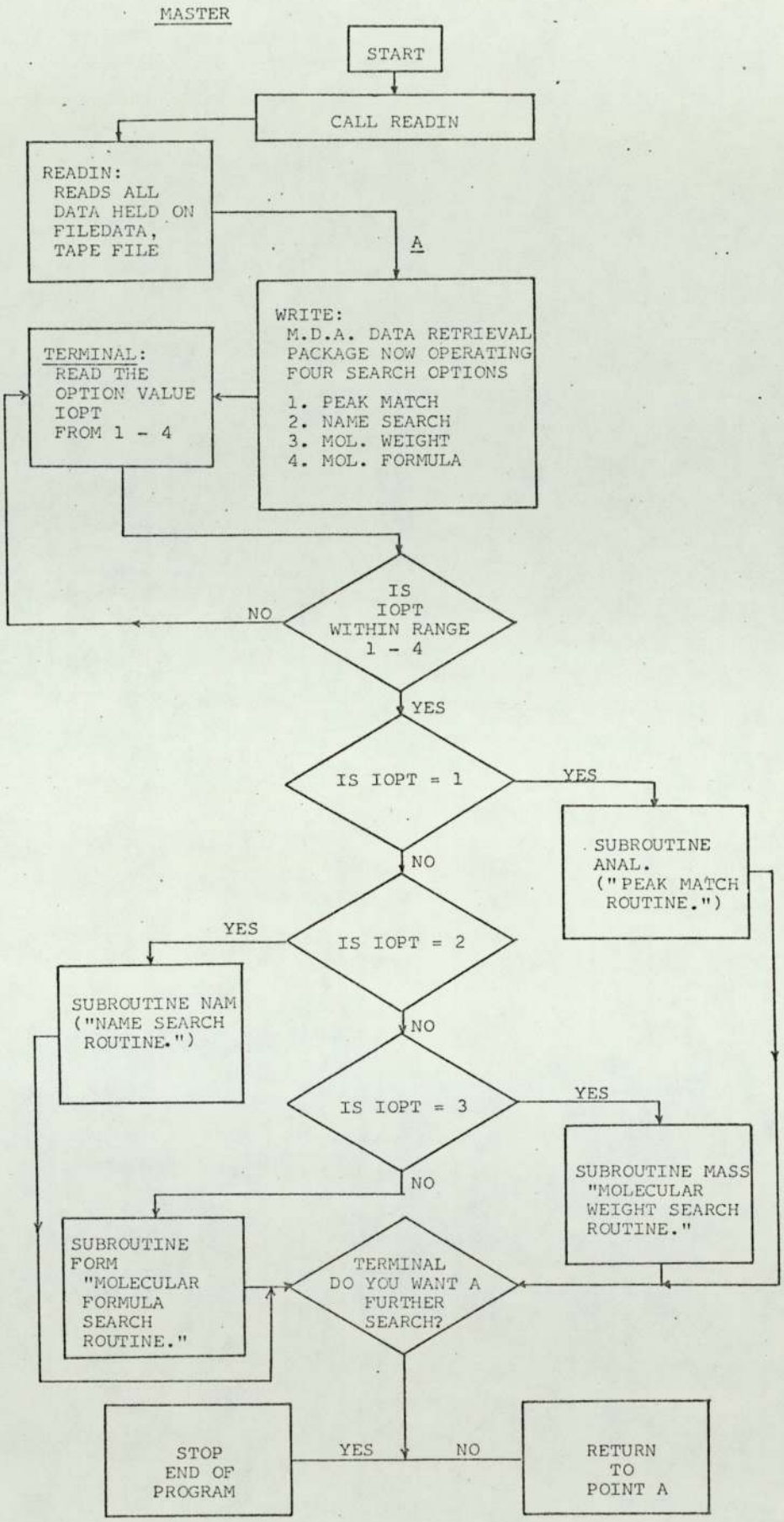
Every time a FORTRAN statement was written with a READ(1,N) or WRITE(6,N) (where N = format statement number), the input was received from the terminal and the output directed to the terminal. The statement READ(3,N) was only used for data read from the file FILEDATA within the subroutine READIN.

B. FORTRAN Master Segment

The function of this section of the program is illustrated in detailed flow diagram FIG:6.15 and the associated program listing Appendix 2(10-53).

The master segment controlled the access to the 4 major search options available. After each subroutine had been fully utilised control returned back to the MASTER. A loop was included within the program for repeat searches if required. The program was terminated if a repeat search was not required and control returned to the MACRO program.

FIG: 6.15


MASTER
START
CALL READIN
READIN:
READS ALL
DATA HELD ON
FILEDATA,
TAPE FILE
A
WRITE:
M.D.A. DATA RETRIEVAL
PACKAGE NOW OPERATING
FOUR SEARCH OPTIONS
1. PEAK MATCH
2. NAME SEARCH
3. MOL. WEIGHT
4. MOL. FORMULA
TERMINAL:
READ THE
OPTION VALUE
IOPT
FROM 1 - 4
IS
IOPT
WITHIN RANGE
1 - 4
NO
YES
IS IOPT = 1
YES
SUBROUTINE
ANAL.
("PEAK MATCH
ROUTINE.")
NO
IS IOPT = 2
YES
SUBROUTINE NAM
("NAME SEARCH
ROUTINE.")
NO
IS IOPT = 3
YES
SUBROUTINE MASS
"MOLECULAR
WEIGHT SEARCH
ROUTINE."
NO
SUBROUTINE
FORM
"MOLECULAR
FORMULA
SEARCH
ROUTINE."
TERMINAL
DO YOU WANT A
FURTHER
SEARCH?
STOP
END OF
PROGRAM
YES
NO
RETURN
TO
POINT A

The Basic Core Requirements of the System

The arrays storing the computed values and the file data were held in COMMON as shown below:-

IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
1. FILEUV(200),FILESP(200),D(200),NAME(200,10), ITYPE(200)
2. NN(200),NI(200),DMS(200),DIR(200)

The Contents of the Arrays in COMMON,

IFORM - seven integer numbers indicating the molecular formula (FILE).

SMASS - an integer number indicating the molecular weight (FILE).

FILEMS - 8 integer numbers indicating the coded mass-spectral data (FILE).

FILEIR - 6 real numbers indicating the coded infra-red spectral data (FILE).

FILEUV - an integer number indicating the coded UV spectral data (FILE).

FILESP - A number indicating the coded TLC Rf data. (FILE).

D - one real number indicating the combined MS and IR rank order correlation values obtained from "full matches".

NAME - 40 characters (10A4) indicating the names of the drugs on the file.

ITYPE - an integer number indicating the drug types - numbers from 1 - 5 for the 5 major drug types characterised (FILE).

NN - an integer number indicating the number of MS matches for the file spectra when compared against the unknown (MSMISMATCH values)

NI - an integer number indicating the number of IR

matches for the file spectra when compared against the unknown (IRMISMATCH values).

DMS - a real number indicating the rank order correlation values for the mass spectra matching for any number of peaks within the file (Degree of fit).

DIR - a real number indicating the rank order correlation values for the infra-red spectra matching for any number of peaks within the file (Degree of fit).

For files of up to 200 monographs this provided a rapid and efficient means of transferring data from sub-routine to subroutine.

The file arrays - IFORM(integer), SMASS(real), FILEMS(integer), FILEIR(real), FILEUV(integer), FILESP(real), NAME(integer) and ITYPE(integer) required 8,600 words of core. The computed values - D(real), NN(integer), NI(integer), DMS(real), DIR(real) required a further 1,600 words.

Total Core Requirement for COMMON = 10,200 Words

Data only utilised by specific subroutines was stored in arrays using DIMENSION statements.

Subroutine Anal utilised SCORE(200)integer, PEAKMS(8)integer, PEAKIR(6)real, NUM(16)integer.

SCORE - indicating the computed SCORE values for all the monographs on file.

PEAKMS - Space for a maximum of 8 integer numbers for storing the coded mass-spectral data for the unknown.

PEAKIR - Space for a maximum of 6 real numbers for storing the coded infra-red data for the unknown.

NUM - An array containing 16 integer numbers from 15 → 0, all the SCORE possibilities.

Subroutine MS - required the transfer array PEAKMS(8), and

Subroutine IR - also required a transfer array PEAKIR(6),

Subroutine NAM - required UNAME(10)integer.

UNAME - Space for a maximum of 40 characters (10A4) for storing the unknown name.

Subroutine FORM - utilised NFORM(7)integer, and the DATA statement arrays C(3), H(3), N(3), O(3), CL(3), S(3), P(3), all integer.

NFORM - Space for a maximum of 7 integer numbers used for storing the unknown molecular formula.

The Data statement arrays were used for storing format information within the program associated with the appropriate atomic symbol.

These additional arrays required a further 292 words of core. Giving a total of 10,492 words of core required for storing the arrays of the system.

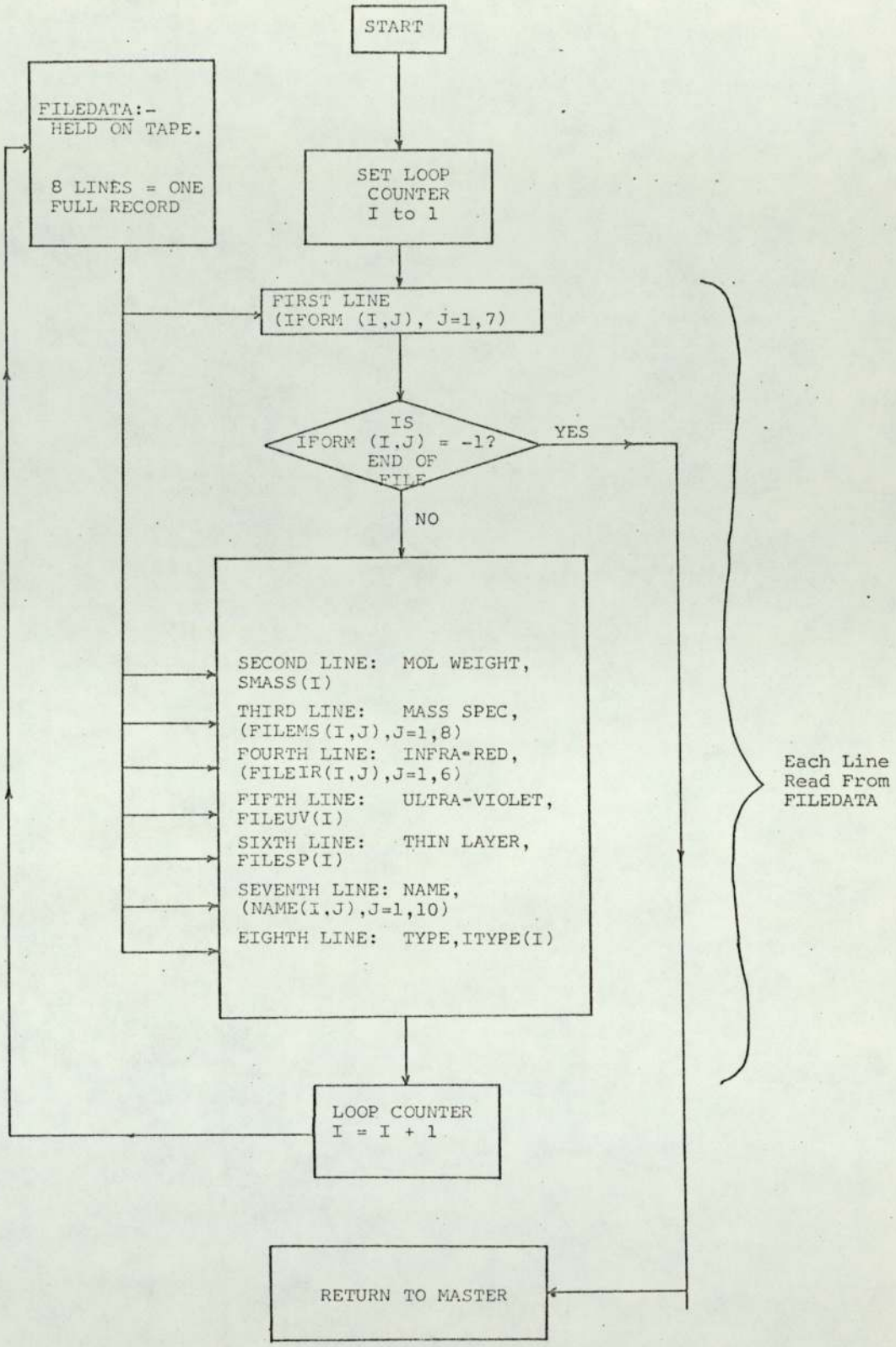
C. Subroutine READIN

The first subroutine called by the MASTER, READIN was a short subroutine responsible for storing in COMMON all the data read from the tape file FILEDATA. This program was also used as a means of ensuring that the format of the file was correct.

The end of file mark was IFORM(I,1) = -1. Each block of data (8 lines of the file) was read into the program, repetitively until the end of file mark was encountered. Control was then transferred back to the MASTER.

FIG: 6.16

SUBROUTINE READIN



The following subroutine was called by the MASTER in response to the value of IOPT (See FIG:6,15) being = 1.

D. Subroutine ANAL - "Peak Match Routines"

Subroutine ANAL was constructed of 4 major operational areas:-

1. Input Area

Responsible for reading from the terminal all the "unknown" data and storing it within the core memory for use within:-

2. Screening and Processing Area

This area was responsible for comparing all the "unknown" data repetitively against the data stored on file and computing the SCORE, NN, NI, DMS, DIR values for use within the next area:-

3. Sorting and Interpretation Area

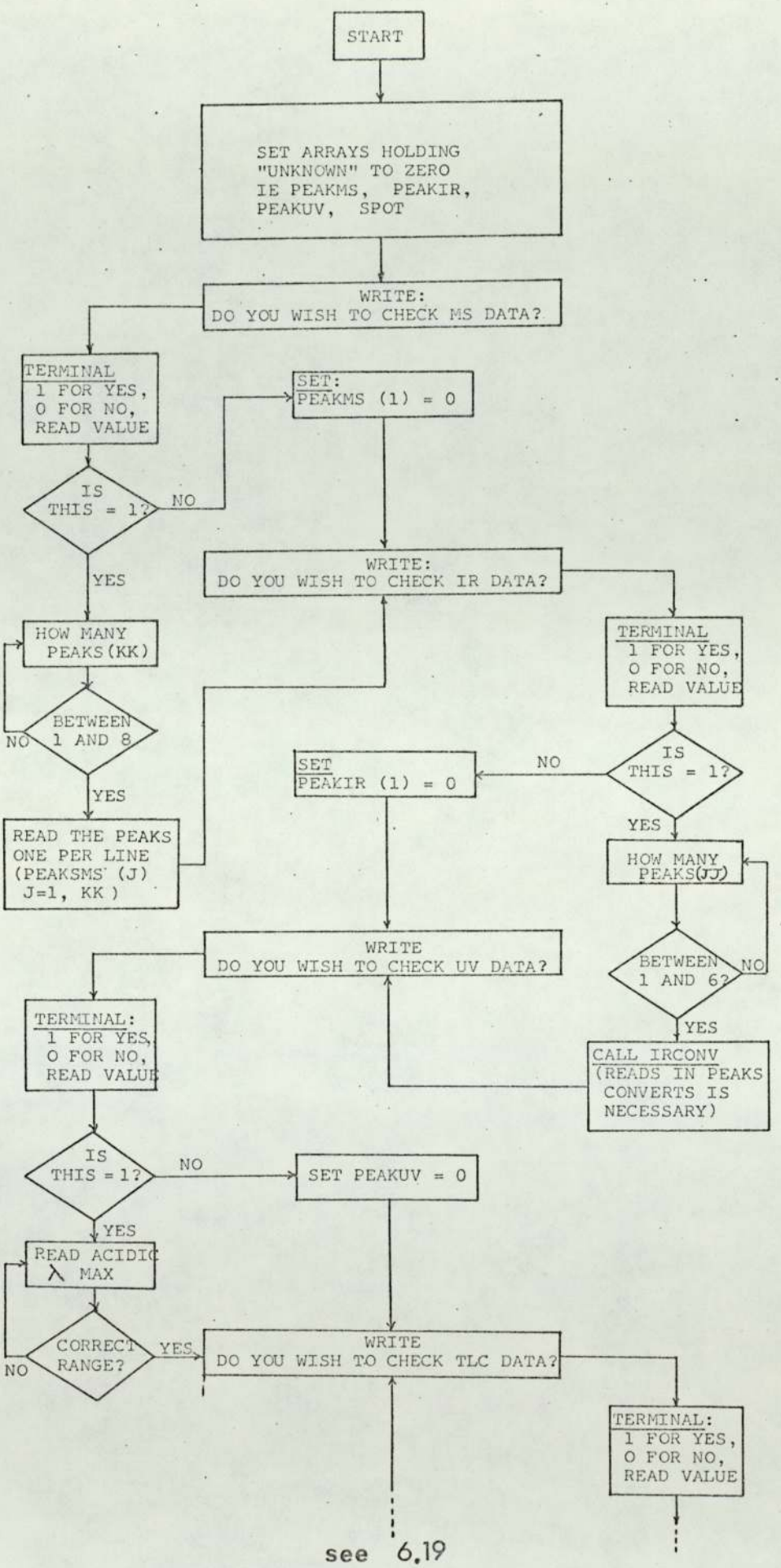
This area was responsible for examining all the previously computed values to establish the quality of the matches obtained and to sort them so that they were presented in decreasing order of quality to the next area of the program:-

4. Output Area

This area was responsible for delivering the sorted match combinations to the terminal with the appropriate format for final examination by the operator.

1. Input Area

This area, using the appropriate teletype outputs and formatted inputs, read from the terminal all the coded data for the unknown and stored it in the appropriate arrays. See FIG:6.17 and Appendix 2(147-243)


START
SET ARRAYS HOLDING "UNKNOWN" TO ZERO IE PEAKMS, PEAKIR, PEAKUV, SPOT
WRITE: DO YOU WISH TO CHECK MS DATA?
TERMINAL 1 FOR YES, 0 FOR NO, READ VALUE
IS THIS = 1?
NO
SET: PEAKMS (1) = 0
YES
HOW MANY PEAKS(KK)
BETWEEN 1 AND 8
NO
YES
READ THE PEAKS ONE PER LINE (PEAKSMS (J) J=1, KK)
WRITE: DO YOU WISH TO CHECK IR DATA?
TERMINAL 1 FOR YES, 0 FOR NO, READ VALUE
IS THIS = 1?
NO
SET PEAKIR (1) = 0
YES
HOW MANY PEAKS(JJ)
BETWEEN 1 AND 6?
NO
YES
CALL IRCONV (READS IN PEAKS CONVERTS IS NECESSARY)
WRITE DO YOU WISH TO CHECK UV DATA?
TERMINAL: 1 FOR YES, 0 FOR NO, READ VALUE
IS THIS = 1?
NO
SET PEAKUV = 0
YES
READ ACIDIC λ MAX
CORRECT RANGE?
NO
YES
WRITE DO YOU WISH TO CHECK TLC DATA?
TERMINAL: 1 FOR YES, 0 FOR NO, READ VALUE

see 6.19

Initially the two arrays which stored the data for the unknown - (PEAKMS(K),K = 1,KK),KK = 1,8(max)

(PEAKIR(J),J = 1,JJ),JJ = 1,6(max)

and the two individual values PEAKUV and SPOT(TLC) were set to zero. This prevented the interference of carry-over values from a previous search when several searches were required.

It can be seen from FIG:6.17 that the coded unknown data was requested by the program in the order, mass spectrum, infra-red, ultra-violet and thin layer chromatography.

For MS and IR data, in response to the appropriate program output the values KK and JJ, respectively were read from the terminal to indicate the total number of peaks within the unknown to be compared against the 8(MS) or 6(IR) peaks within each file spectrum.

If no mass-spectral data was available or a search not required then PEAKMS(1) = 0.

The infra-red data; because of the two distinct coding conventions in general use was read into the program using an additional subroutine IRCONV.

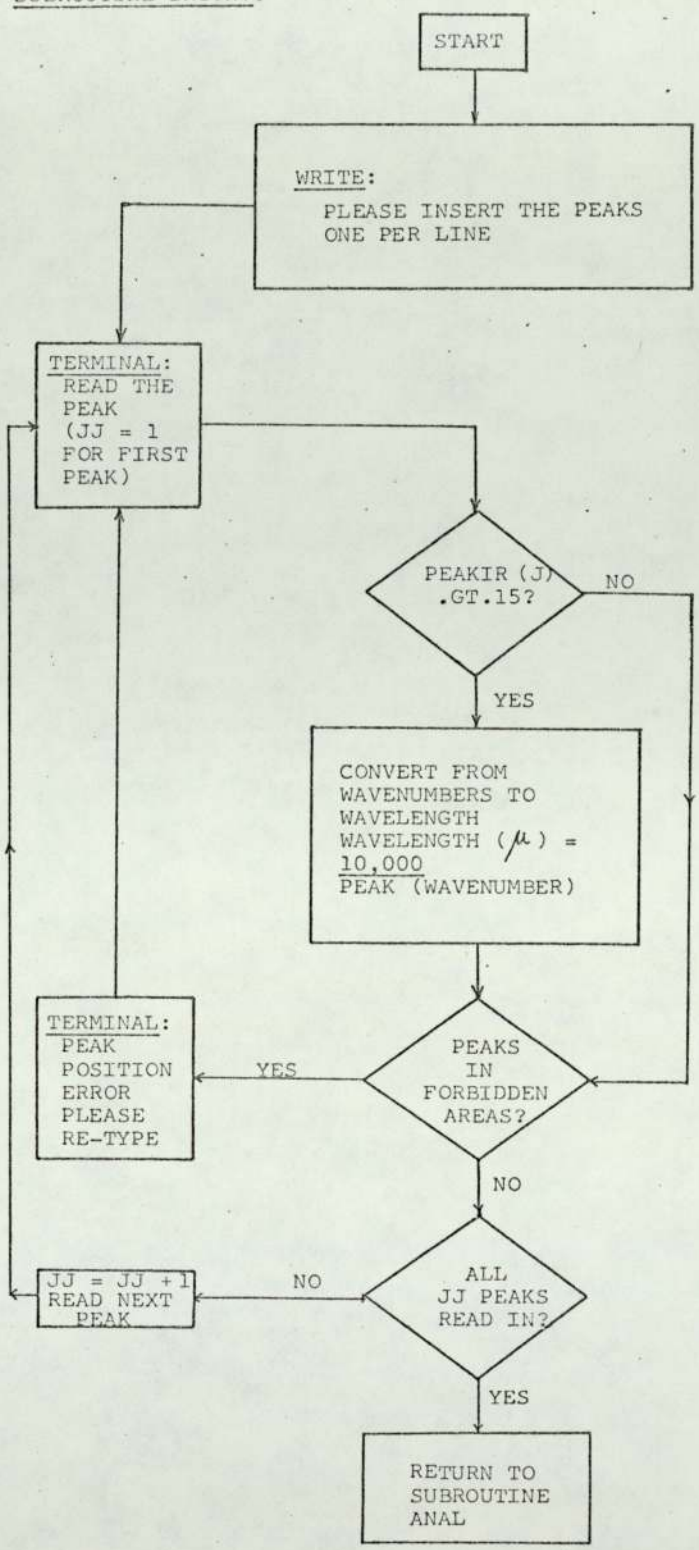
(i) Subroutine IRCONV

The function of this routine FIGS:6.18 and Appendix 2(723-75) was twofold:-

Initially to ascertain if the value of PEAKIR(J) was in wavelength or wavenumbers, i.e. if PEAKIR(J) $\geq$15 microns. If so it was treated as a value in wavenumbers and converted,- wavelength(microns) = $\frac{10,000}{\text{wavenumber}(cm^{-1})}$, and secondly to ascertain if the converted or non-converted

FIG: 6,18

SUBROUTINE IRCONV.



PEAKIR(J) was:-

(a) Still $>$15 microns (667cm^{-1}) which was outside the coding range, or

(b) Within the other non-coded areas of the spectrum, i.e. PEAKIR(J) $<$ 5.0 microns or 6.7$\leq$ PEAKIR(J) $\leq$ 7.5 microns (nujol). If either of these situations (a) or (b) were encountered the following statement was output tothe terminal:-

"PEAK POSITION ERROR PLEASE RETYPE" and the incorrect peak was either ignored or modified by the operator. This process was repeated until (JJ) peaks were obtained within the required range. Control was then returned to Subroutine ANAL.

As before for mass-spectral data if no IR search was required then PEAKIR(1) = 0.

The remaining two values λ max for UV and Rf, for TLC were successively read into the program. An initial comparison was carried on each value to determine if they were within the expected range for each technique. If not the program returned to re-request the operator to input correct data from the terminal.

If no searches were required the values of PEAKUV and SPOT respectively were set to zero.

The data transferred to the next area of the program consisted of any one of 15 possible data combinations for the four analytical techniques.

2. Screening and Processing Area

This area of the program compared all the possible combinations of unknown data against FILEDATA. The

numerical values of SCORE, NN, NI, DIR and DMS were computed for later use within the sorting and interpretation area.

The program was designed to compare the unknown against a maximum set of 199 monographs.

The common block holding the filedata was terminated by IFORM(I,1) = -1. The screening process was performed repetitively on the filedata until the "end of data" was encountered. The program then progressed to the "sorting and interpretation area". FIGS:6.19 Appendix 2(244-286) illustrate the flow of the screening area and the program listing.

This screening section of the program together with its associated subroutines established:-

the value of SCORE for each of the compounds on the file as in FIG:6.2 , indicating the <u>total</u> combined match, and also

within the subroutines MS and IR established the computed values, the rank order correlation, DMS and DIR and the mismatch NN and NI, which provided both a qualititative and quantitative indication of the "fit" of the unknown spectrum to those of the file.

These values (i) and (ii) were stored within COMMON for easy transfer to the next area of the program.

The four associated subroutines of Anal were called in the order MS ⟶ IR ⟶ UV ⟶ TLC.

(i) <u>Subroutine MS</u> FIG:6.20 and Appendix 2(433-472)

This routine compared all the mass spectral <u>$^{m}/_{e}$</u> values coded for one file monograph FILEMS(I,J),J = 1,8

FIG: 6.19

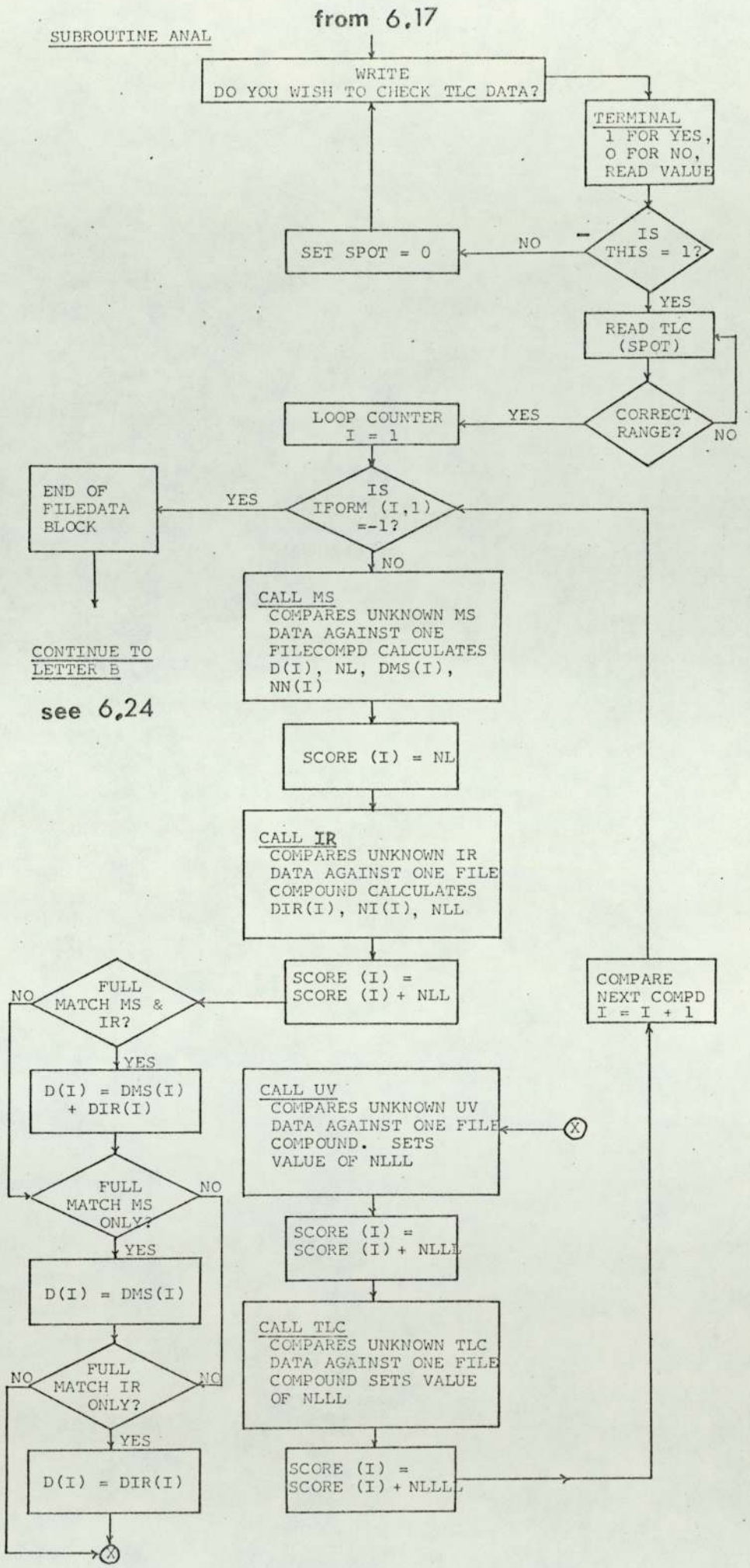
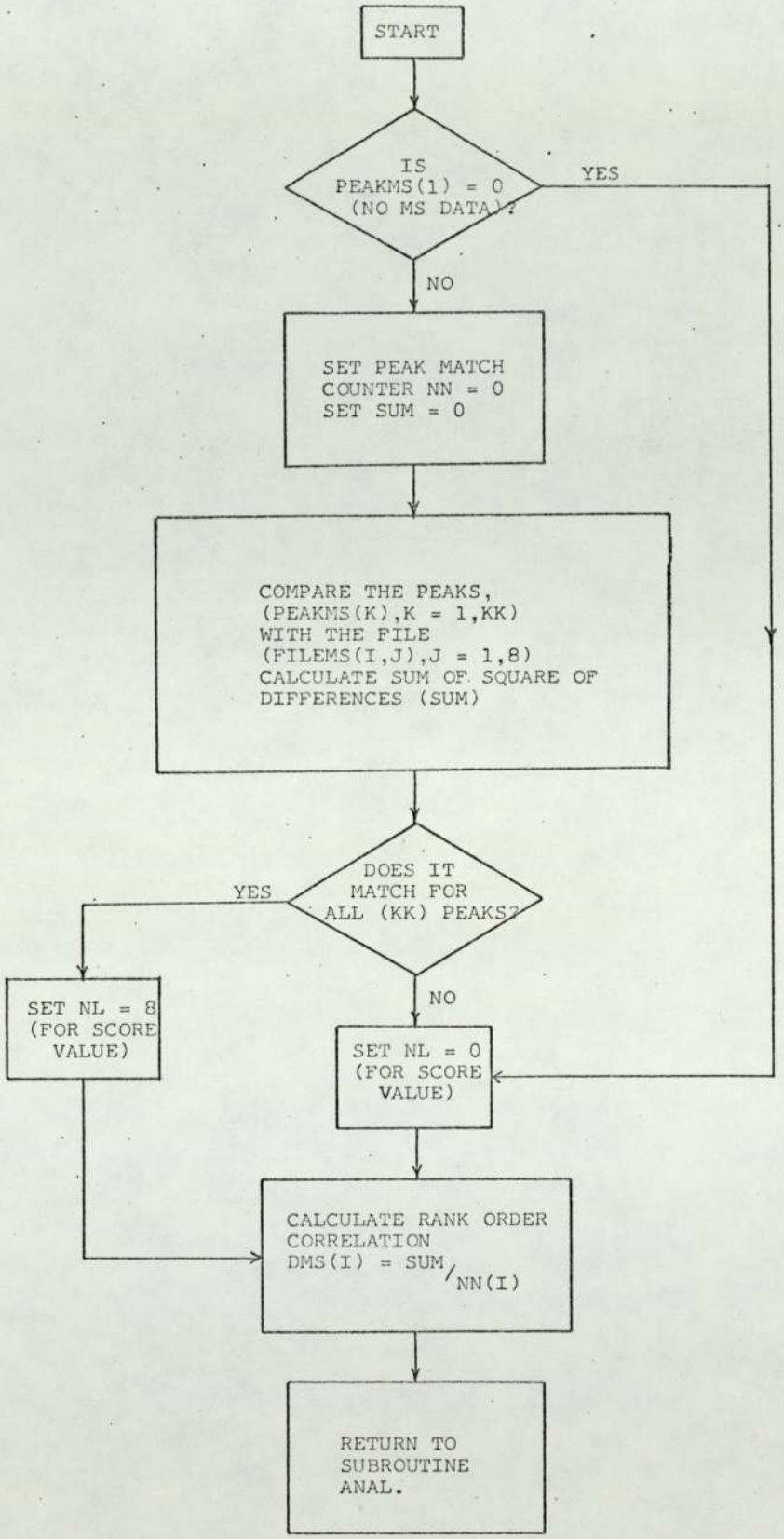

from 6.17
SUBROUTINE ANAL
WRITE
DO YOU WISH TO CHECK TLC DATA?
TERMINAL
1 FOR YES,
0 FOR NO,
READ VALUE
IS
THIS = 1?
NO
YES
SET SPOT = 0
READ TLC
(SPOT)
CORRECT
RANGE?
NO
YES
LOOP COUNTER
I = 1
IS
IFORM (I,1)
=-1?
YES
END OF
FILEDATA
BLOCK
NO
CALL MS
COMPARES UNKNOWN MS
DATA AGAINST ONE
FILECOMPD CALCULATES
D(I), NL, DMS(I),
NN(I)
SCORE (I) = NL
CALL IR
COMPARES UNKNOWN IR
DATA AGAINST ONE FILE
COMPOUND CALCULATES
DIR(I), NI(I), NLL
SCORE (I) =
SCORE (I) + NLL
FULL
MATCH MS &
IR?
NO
YES
D(I) = DMS(I)
+ DIR(I)
FULL
MATCH MS
ONLY?
NO
YES
D(I) = DMS(I)
FULL
MATCH IR
ONLY?
NO
NO
YES
D(I) = DIR(I)
CALL UV
COMPARES UNKNOWN UV
DATA AGAINST ONE FILE
COMPOUND. SETS
VALUE OF NLLL
X
SCORE (I) =
SCORE (I) + NLLL
CALL TLC
COMPARES UNKNOWN TLC
DATA AGAINST ONE FILE
COMPOUND SETS VALUE
OF NLLL
SCORE (I) =
SCORE (I) + NLLLL
COMPARE
NEXT COMPD
I = I + 1
CONTINUE TO
LETTER B
see 6.24

FIG: 6.20

SUBROUTINE MS



against those in the unknown array PEAKMS(K),K = 1,KK, as shown in FIG:6.4 . The matching routine was described by the following algorithm.

Algorithm for MS Comparisons

Using the Kronecher delta function,(basic function used in Quantum mechanics when two values are compared for equality),the matching procedure was described as follows:-

δ = delta function

$$\delta f(I)p = \begin{cases} =1 & \text{if } f(I)=p \text{ i.e. FILEMS(I) = PEAKMS} \\ =0 & \text{if } f(I)\neq p \text{ i.e. FILEMS(I) not eq. PEAKMS} \end{cases}$$

Let f(I,J) = file entry FILEMS(I,J)

Let p(K) = peak entry PEAKMS(K)

The number of matches was given by:-

$$\text{match counter NN(I)} = \sum_{K=1}^{KK} \sum_{J=1}^{8} \delta f(I,J),p(K)$$

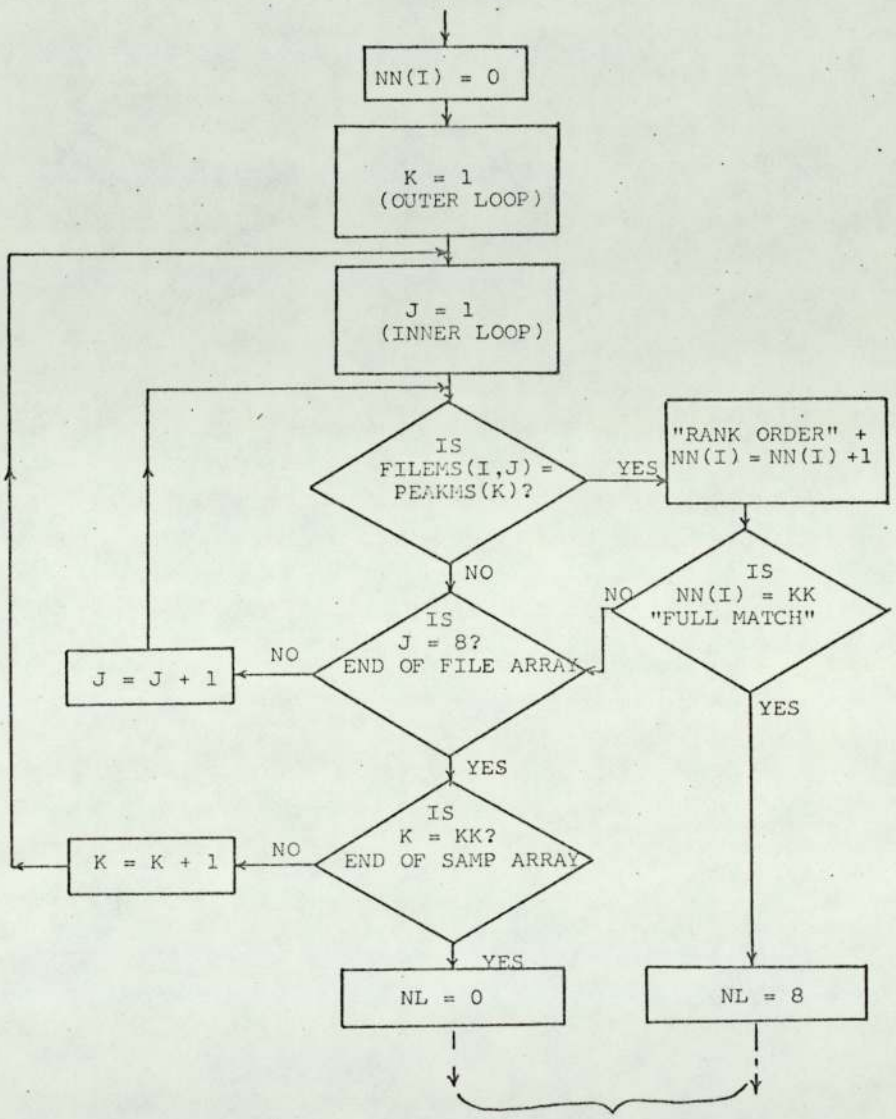
The rank order correlation value DMS(I) was then determined by the sum of the square of the differences of the KK positions of the matching J and Kth peaks by the following equation:-

$$DMS(I) = \frac{\sum_{K=1}^{KK} \sum_{J=1}^{8} \delta f(I,J),p(K)(J-K)^2}{NN(I)}$$

If the value NN(I) was equal to the total number of peaks(KK) required for a match within the unknown then the

FIG: 6.20a

EXPANDED SUBROUTINE MS



see 6,20

transfer value NL was set to 8 and converted directly to the SCORE value in Subroutine ANAL. If NN(I) was not equal to KK then NL was set to zero and likewise transferred to SCORE. If a full match had been obtained (i.e. NL = 8) then the DMS value, on transfer back to Subroutine ANAL also became the value held in D (the combined MS and IR "full" match value).

The function of this routine was now completed for one complete file monograph therefore control was returned to Subroutine ANAL, which progressed to the next comparison routine.

(ii) Subroutine IR FIG:6.21 and Appendix 2 (473-506)

This routine was based on exactly the same method of comparison as for mass-spectral data, except that a "window" was included within each comparison.

The routine compared the infra-red data within one monograph FILE IR(I,J),J = 1,6 against those in the unknown array PEAKIR(K),K = 1,JJ.

The matching routine was described by the following algorithm:-

Algorithm for IR Comparisons

Using the Kronecher delta function (δ)

$$\delta_{f(I),p} = \begin{cases} 1 \text{ if } f(I)=p \text{ i.e. } (FILEIR(I) - PEAKIR) \leq \pm 0.2\mu \\ \text{or} \\ 0 \text{ if } f(I)\neq p \text{ i.e. } (FILEIR(I) - PEAKIR) \geq \pm 0.2\mu \end{cases}$$

We let f(I,J) = file entry FILEIR(I,J)

and p(K) = peak entry PEAKIR(K)

FIG: 6.21

SUBROUTINE IR

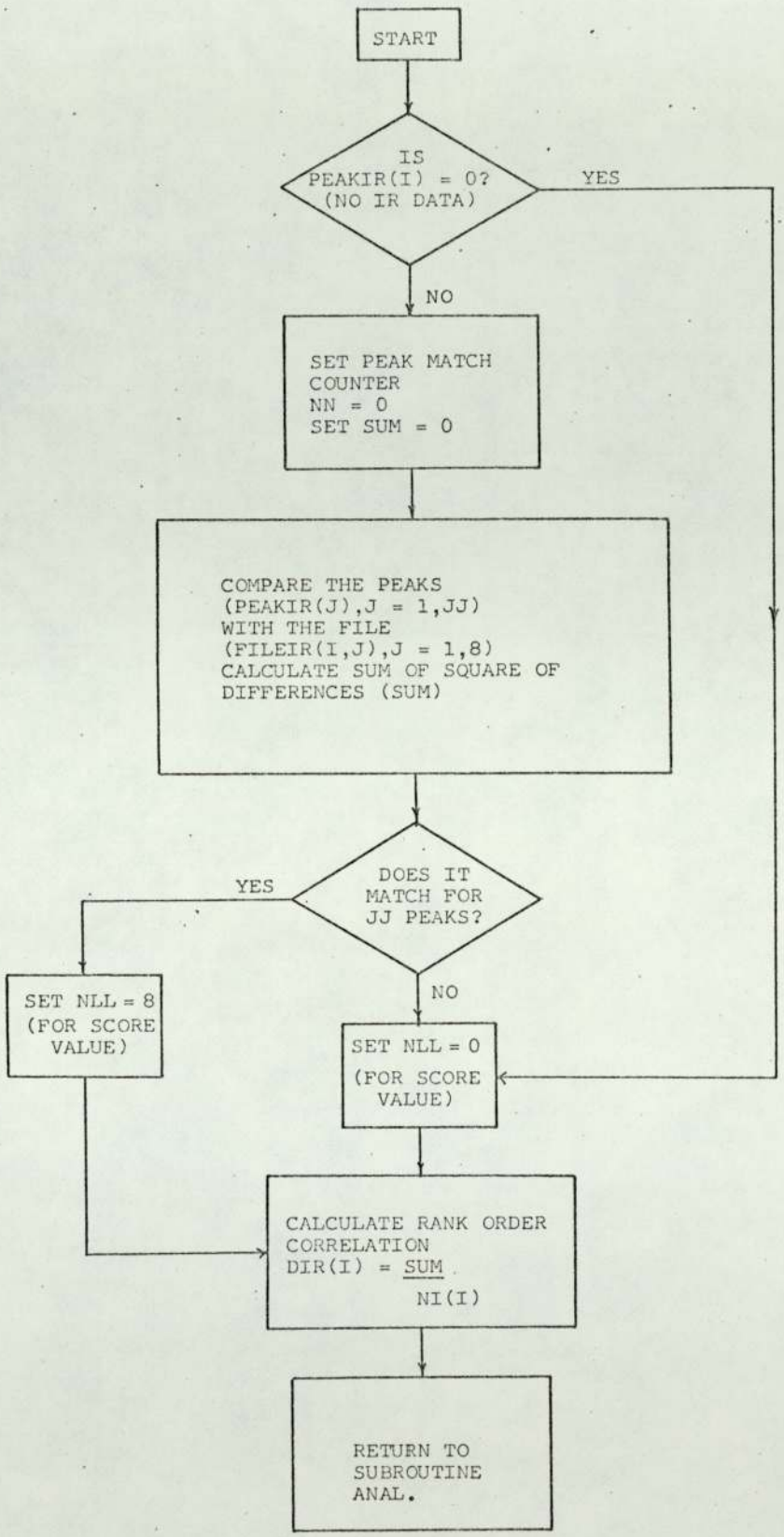
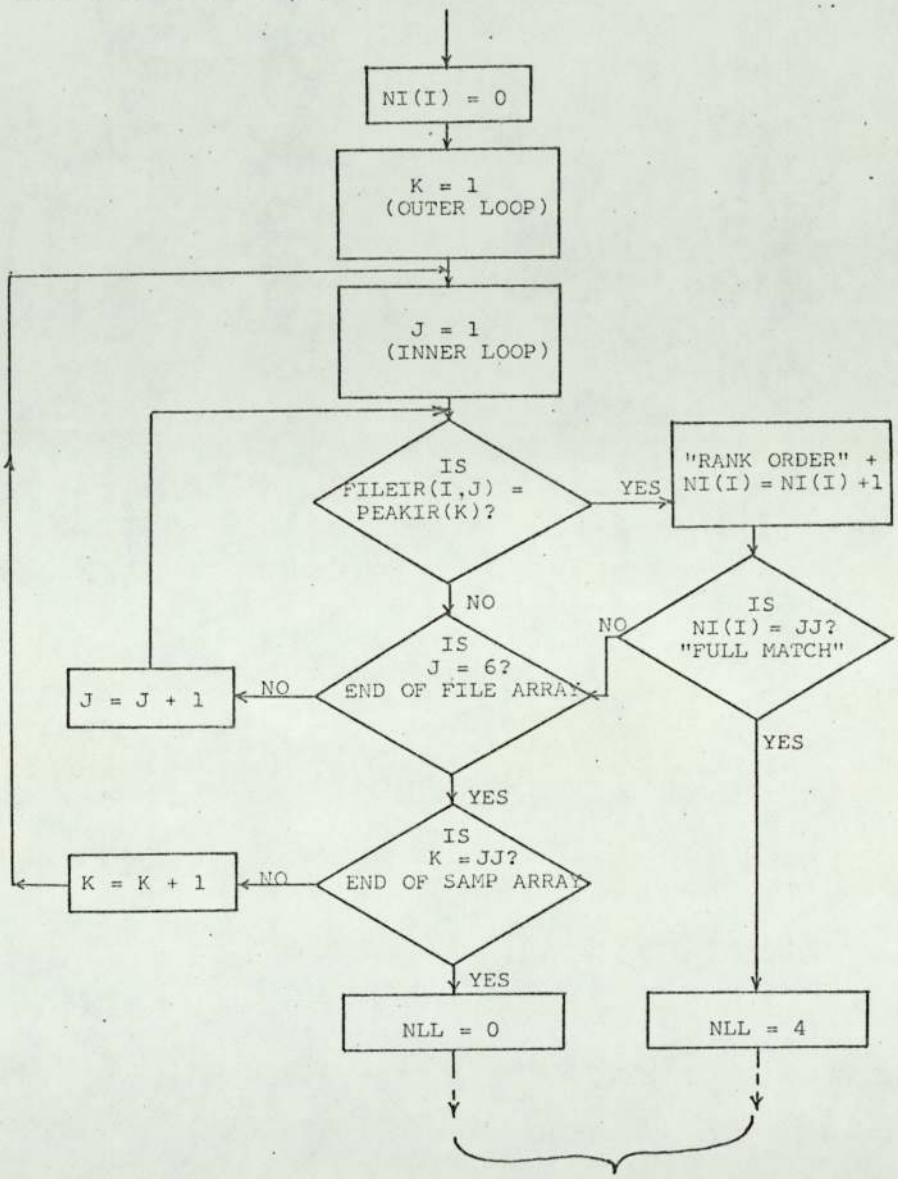


FIG: 6.21a

EXPANDED SUBROUTINE IR



see 6.20

Then the number of matches NI(I) was determined by:-

$$NI(I) = \sum_{K=1}^{JJ} \sum_{J=1}^{6} \delta f(I,J),p(K)$$

∴ The rank order correlation was computed by:-

$$DI(I) = \frac{\sum_{K=1}^{JJ} \sum_{J=1}^{6} \delta f(I,J),p(K)(J-K)^2}{NI(I)}$$

If the value NI = JJ (total number of peaks for the unknown), a full match had been obtained and NLL = 4. This was transferred back to Subroutine ANAL and incremented to SCORE. If NLL = 4 then the rank order value DIR was also transferred back to Subroutine ANAL and the value in the array D (rank order value for the combined MS and IR full match) was incremented. If no full match had been obtained NLL = 0 was transferred back to Subroutine ANAL and also incremented to the SCORE value.

The function of this routine was now completed for one complete file monograph. Control was returned to Subroutine ANAL which progressed to the next comparison routine.

(iii) Subroutine UV FIG 6.22 & Appendix 2 (560-575)

This routine compared the unknown, PEAKUV against the file value FILEUV(I) as shown below:-

if (FILEUV(I) - PEAKUV) $\leq \pm$ 2nm "match" NLLL = 2

if (FILEUV(I) - PEAKUV) $\geq \pm$ 2nm "no match" NLLL = 0

The appropriate value of NLLL was transferred back

FIG: 6.22

SUBROUTINE UV

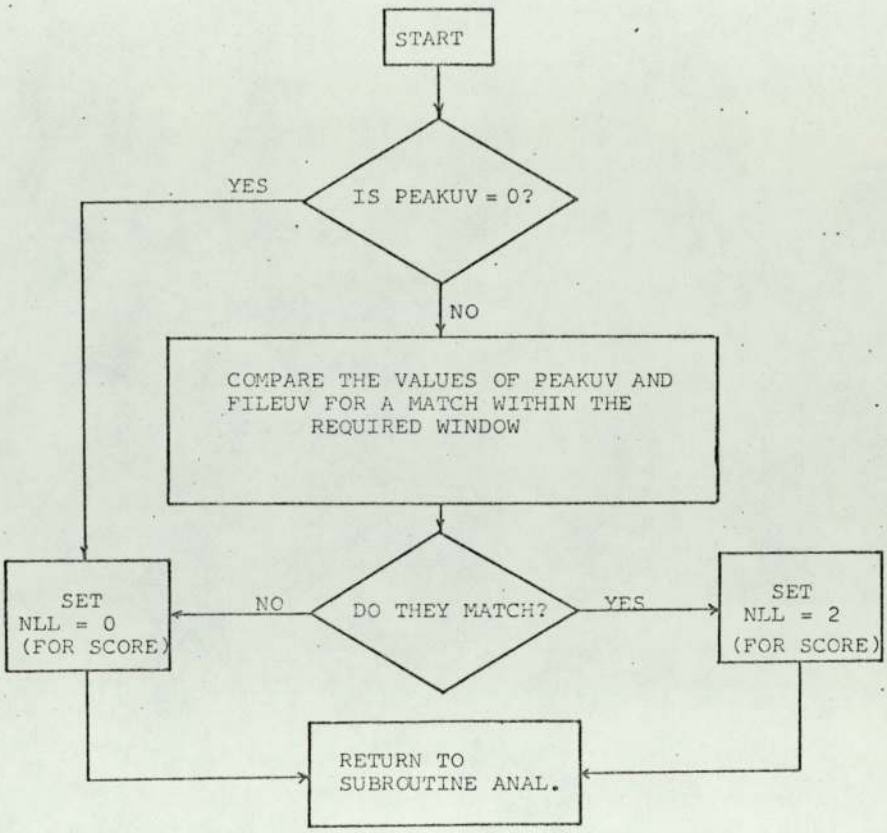
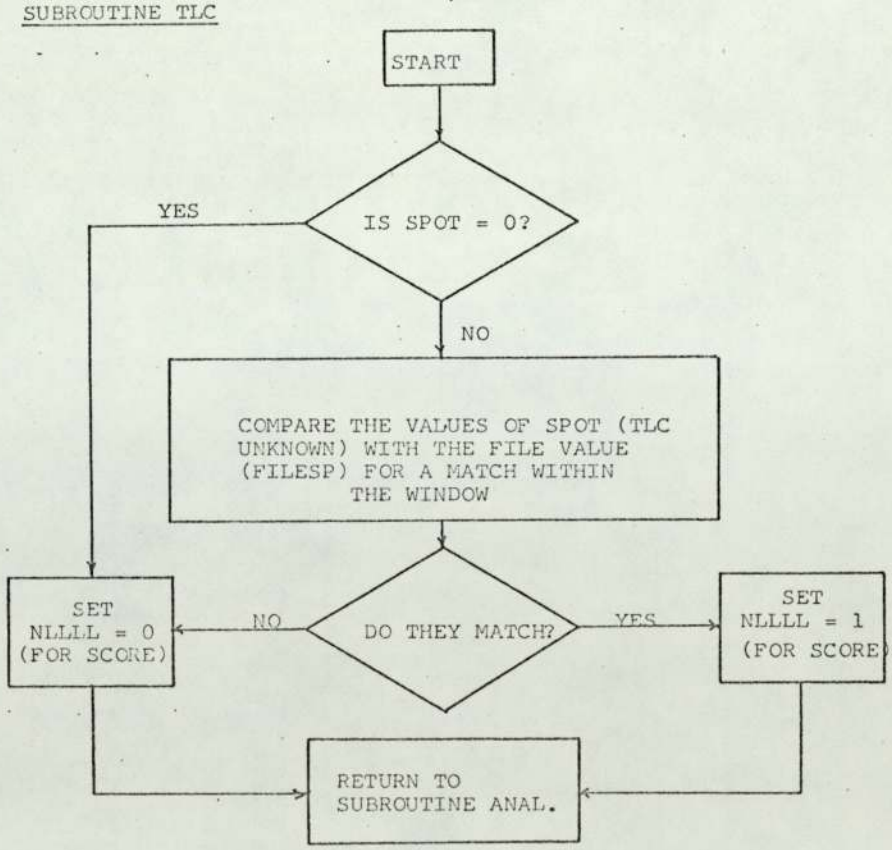


FIG: 6.23

SUBROUTINE TLC



to Subroutine ANAL and accumulated to the SCORE value. The final routine to be utilised within the screening was that of:-

(iv) Subroutine TLC FIG:6.23 and Appendix 2 (577-592)

This program, as for UV, also performed a direct comparison on two numbers (Rf values). The unknown value SPOT was compared against the file value FILESP(I) as shown below:-

if (FILESP - SPOT) $\leq \pm$ 0.15 "Match" NLLLL = 1

if (FILESP - SPOT) $\geq \pm$ 0.15 "no match" NLLLL = 0

The appropriate value of NLLLL was transferred back to ANAL and incremented to the SCORE value.

The full sequence of comparisons, for all the four analytical techniques was now completed. See FIG:6.2 "SCORE". The program returned to compare the next file monograph against the unknown data. The screening process was repeated for all the compounds on the file. When all the compounds had been successfully screened i.e. the end of data mark IFORM(I,1) = -1, had been encountered, the computed arrays SCORE, NN, NI, D, DMS, DIR were terminated with the value 100. The program now progressed to the next area.

3. The Sorting and Interpretation Area

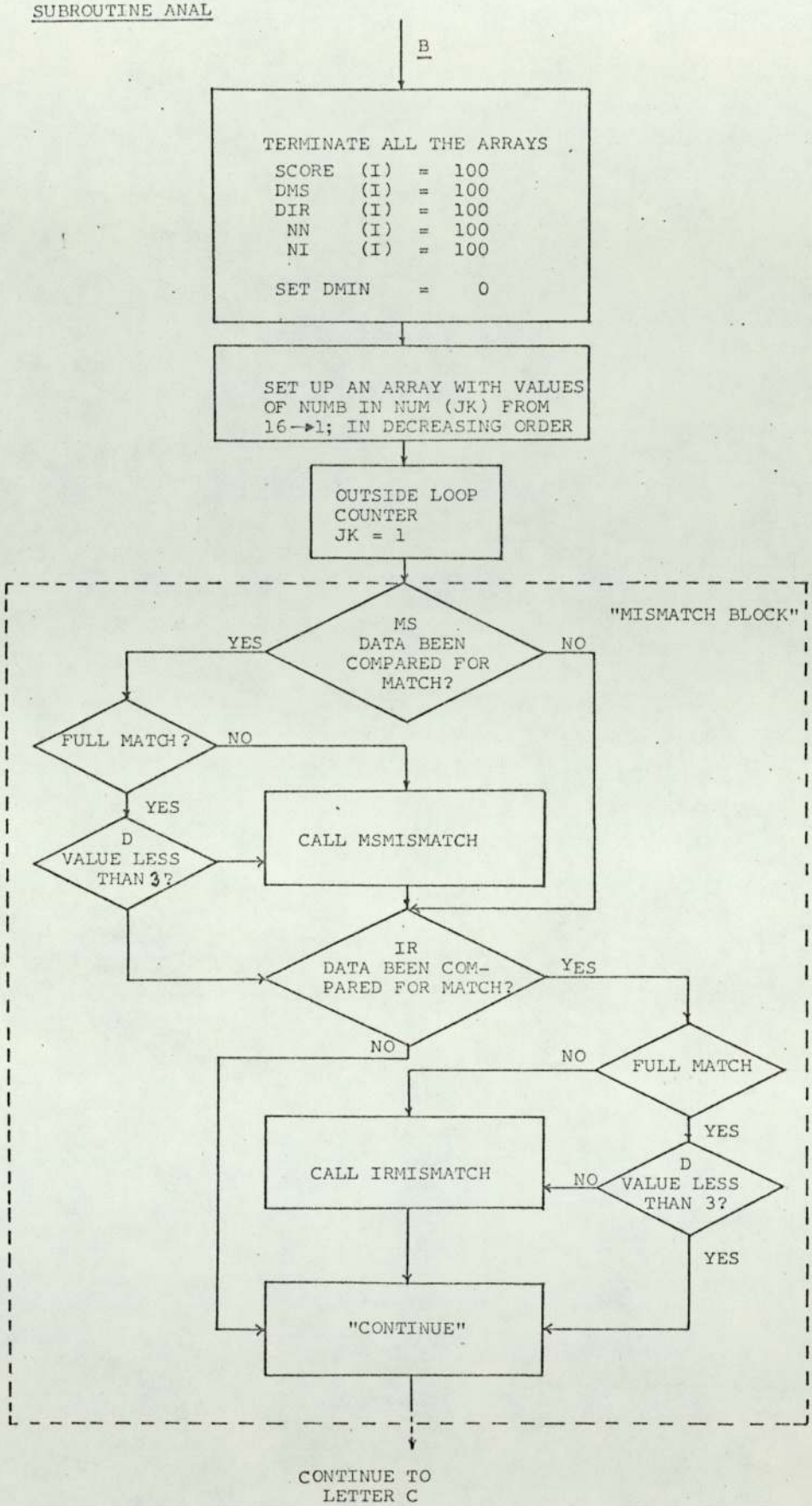
This area of the program, (FIGS:6.24,25. Appendix 2 (287-319)) was responsible for:-

(i) Sorting the "total match" SCORE values into decreasing order of size, so that the compound with highest SCORE value, i.e. best "total match" was output first to the terminal.

It sorted the rank order correlation values DMS and

FIG: 6.24

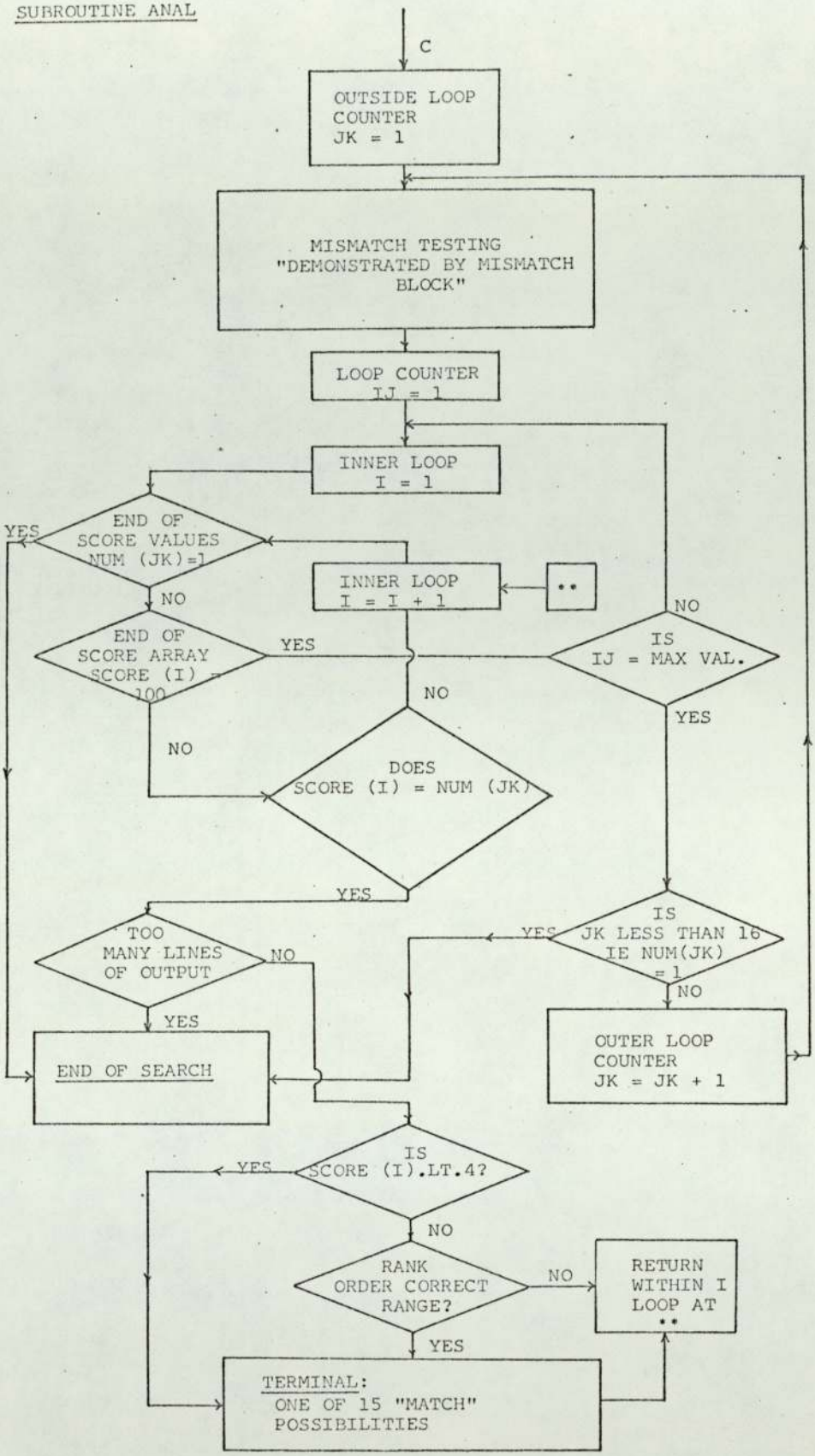
SUBROUTINE ANAL



see 6,25

FIG: 6.25

SUBROUTINE ANAL



DIR into decreasing order of size, so that not only the compound with best "total match", but also the best total "fit" was output first to the terminal, and

determined if either of the two situations which required the use of the MISMATCH routines had been encountered i.e. if there had not been a full match for MS and/or IR data, but input data for the unknowns

or there had been a full match but the quality, as defined by the D values was poor.

All three of the above processes were performed in close combination.

Initially the program created an array NUM(JK) JK = 1,16, which contained all the possible values of SCORE in reverse order from 15 ⟶ 0, i.e. NUM(1) = 15 and NUM(16) = 0, NUM(JK),JK = 1,16, was then compared against all the values stored in SCORE.

For the first loop the value of NUM(1) = 15. All the values within SCORE(I),I = 1,200 were compared repetitively against this value until either:-

a match was obtained

i.e. NUM(JK) = SCORE(I),

or the "end of data" mark SCORE(I) = 100 was encounted.

To cater for the possibility that several matches could have been obtained with the same SCORE value a secondary outer loop sorted the combined (MS, IR) rank order correlation values (D value), so that compounds with the same SCORE value were output to the terminal in their order of increasing D value, i.e. best "fit" first. If

the SCORE values were less than 4 (UV and TLC matches only) this loop did not apply.

The match was then directed towards its equivalent format "write" statement in the Output Area of the program. The match was output to the terminal and the program returned to compare against NUM(JK), the next SCORE (I + 1) to that previously output to the terminal. When the value SCORE (I) = 100 (end of array mark), was encountered the program returned to reduce the value of NUM(JK) to NUM(JK - 1). For example the first to second loop NUM(1) = 15 to NUM(2) = 14, instead of screening for MS, IR, UV, TLC matches, the program now screened for MS, IR, UV matches.

The comparison process continued until:-

The SCORE Value = 7 (i.e. NUM(9)). See FIG 6.24

At this point all possibilities which had contained MS matches had been output to the terminal. At this point within the program the quality of the data (if any) that had already been output to the terminal was examined in the following way:-

There had not been any MS data for the unknown. The program continued reducing the value of SCORE as before.

There had been MS for the unknown. Two situations could have applied:-

the unknown data had not produced a full match, i.e. some or all of the peaks in the unknown had not matched against those within the file. The MSMISMATCH subroutine was called. This

routine examined the previously computed rank order correlation values (DMS), in combination with the mismatch values (NN), in order to determine if any good quality (i.e. low D value) mismatch matches (e.g. 3 out of 4 peaks) had been obtained.

There had been a full match but the quality (D value) was outside the expected maximum. The MSMISMATCH subroutine was called and as above examined the DMS values in combination with the mismatch values (NN) to determine if possibly a partial match had been obtained of better quality (i.e. lower DMS value than the full match).

When these above tests had been performed and if the required MSMISMATCH subroutine called, the program continued to reduce and compare the values of SCORE.

This process continued until:-

SCORE Value = 3 (i.e. NUM(13))

At this point all the possibilities which had contained IR matches had been output to the terminal. The conditions were now re-examined for infra-red data. If required the IRMISMATCH routine was called to examine the combinations of NI and DIR values. See FIGS:6.24,25 .

The program again continued to reduce the value of SCORE until either:-

NUM(JK) = 0, end of the outer loop, all the SCORE possibilities had been examined, or

the output limit, the maximim number of lines of output sent to the terminal (10 full monographs) was reached.

The total search process of Subroutine ANAL had now been completed. The program asked the operator if a further search was required. If so the program returned to restart (See Input Area 6).

(ii) The Mismatch Routines

(a) MSMISMATCH FIGS: 6.26 and Appendix 2 (507-532).

The MSMISMATCH values NN(I),I = 1,200 were sorted. The number of peaks required by Subroutine MS for a full match = KK, therefore the program initially screened for mismatch values one less than KK, (i.e. LK = KK - 1) FIG: 6.26. If a match was observed, NN(I) = KK - 1, then a secondary test was performed on the related DMS(I) value computed for (KK - 1) peaks to determined:-

whether the value was within the expected range, and

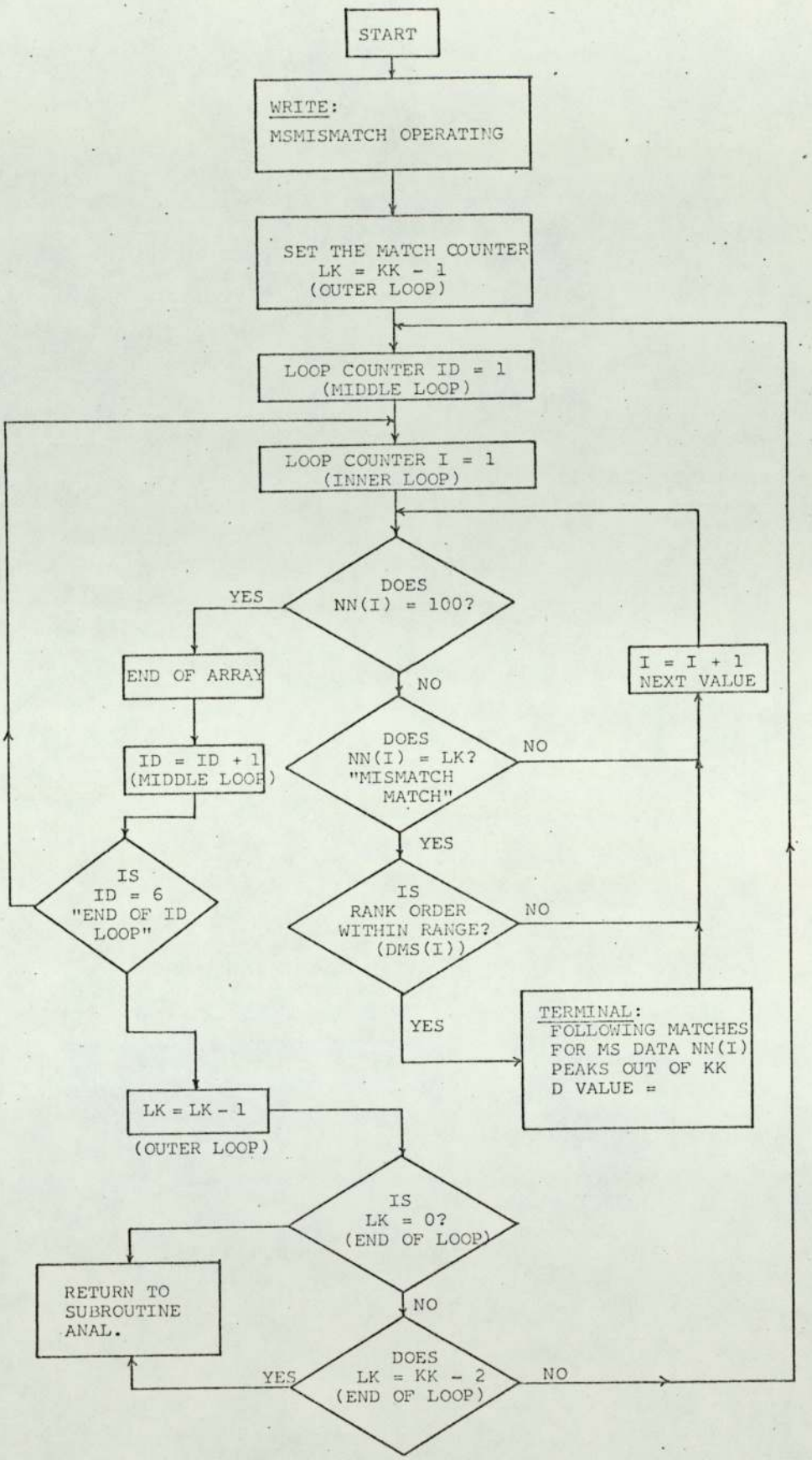
if there was more than one match with the same NN(I) value, if so the matches were output to the terminal first in increasing order of DMS(I).

At the end of the data mark, NN(I) = 100 the program returned to re-screen all the mismatch values = (KK - 2) i.e. two peaks less than the initial search (KK).

The routine was terminated when all the values of NN(I) had been re-screened.

FIG: 6.26

SUBROUTINE MSMISMATCH



Values of KK <4 were not utilised by this sub-routine to avoid situations where the total number of peaks input for the unknown was initially small.

Subroutine WRITE was used to format the output on the terminal.

(b) IRMISMATCH FIG:6.27 and Appendix 2 (533-559)

This program functioned in the same way as the previous routine MSMISMATCH. The value LK was substituted by LKK and JJ substituted for KK. Subroutine WRITE was again utilised for the terminal output. (6.28)

4. Output Area FIG:6.3 (output formats) Appendix 2 (320-433)

This area of the program was utilised for formatting the file data equivalent to the SCORE value previously screened in Area 3.

Each of the possible 15 SCORE values were unique to any combination of analytical data. The total number of possibilities are shown in FIG: 6.3 . Subroutine TYPE FIG:6.29 and Appendix 2 (593 625) wrote the drug type, indicated by the value of ITYPE(I), to the terminal. There were five possible drug types characterised. More values could have been included by increasing the range of ITYPE(I) and additional format statements.

When the appropriate matching monograph had been output to the terminal the program returned to the sorting area at a position (I + 1) to that of the previous match. See "Screening Area".

On completion of a full search this area of the program was terminated by indicating the total number of compounds compared i.e. N "COMPOUNDS SEARCHED"

FIG: 6.27

SUBROUTINE IRMISMATCH

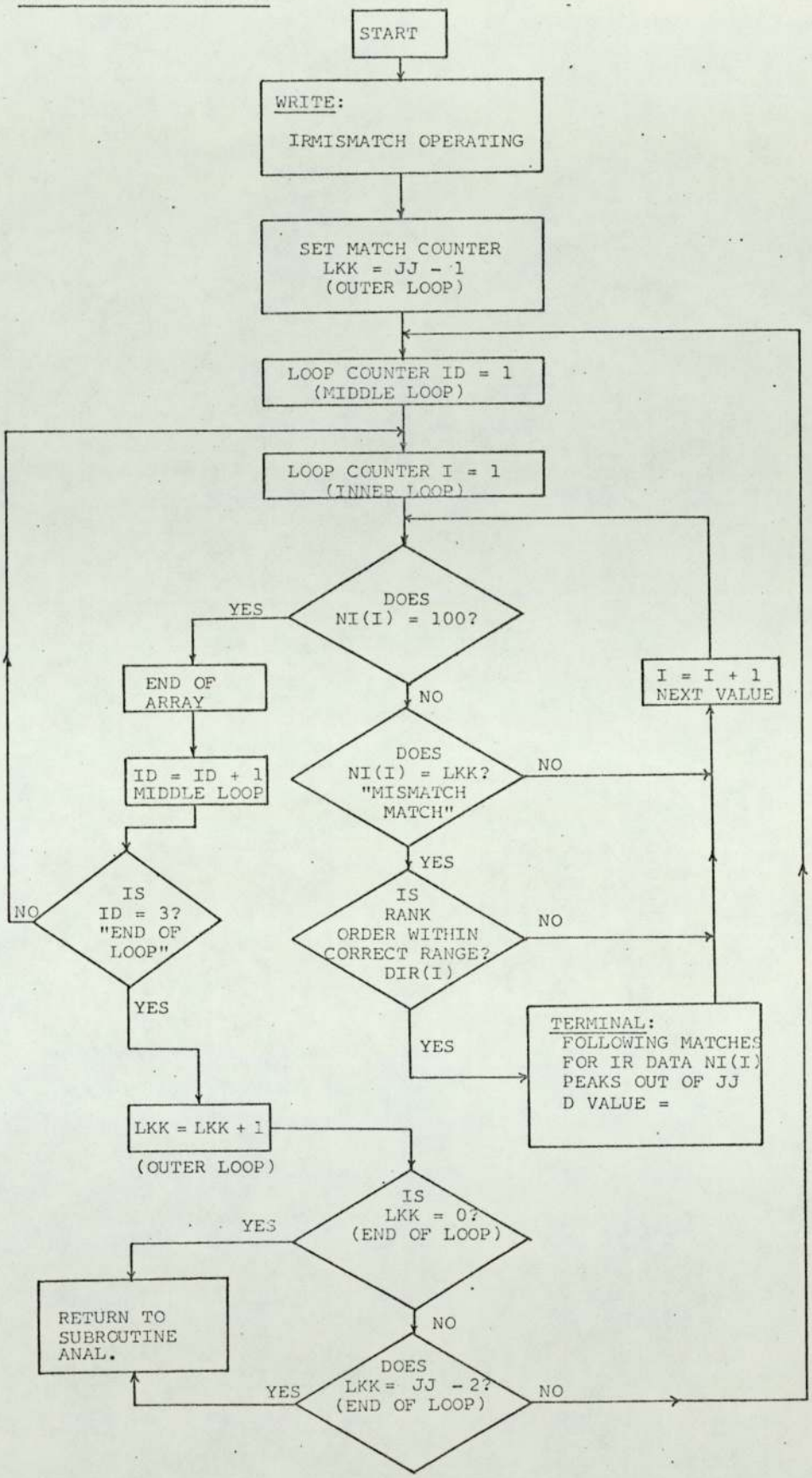


FIG: 6,28

SUBROUTINE WRITE

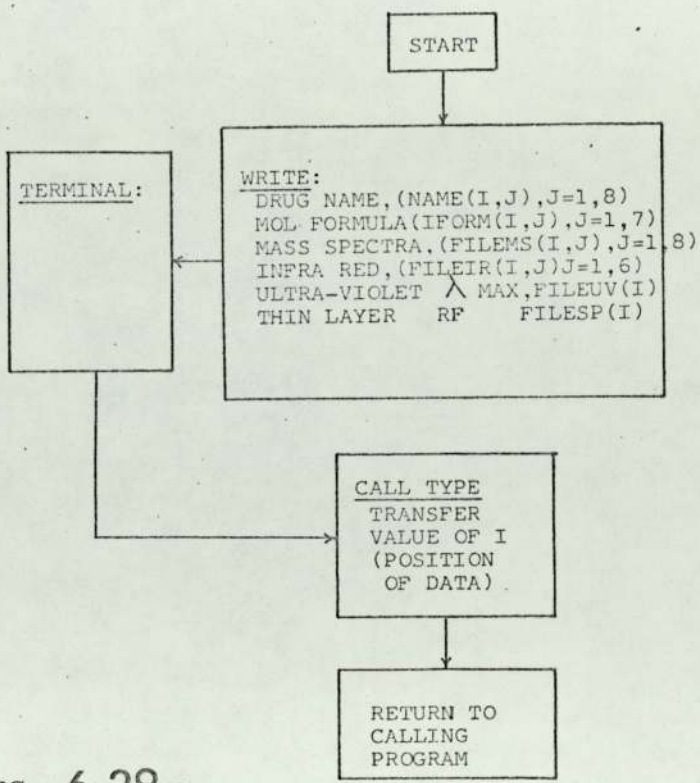
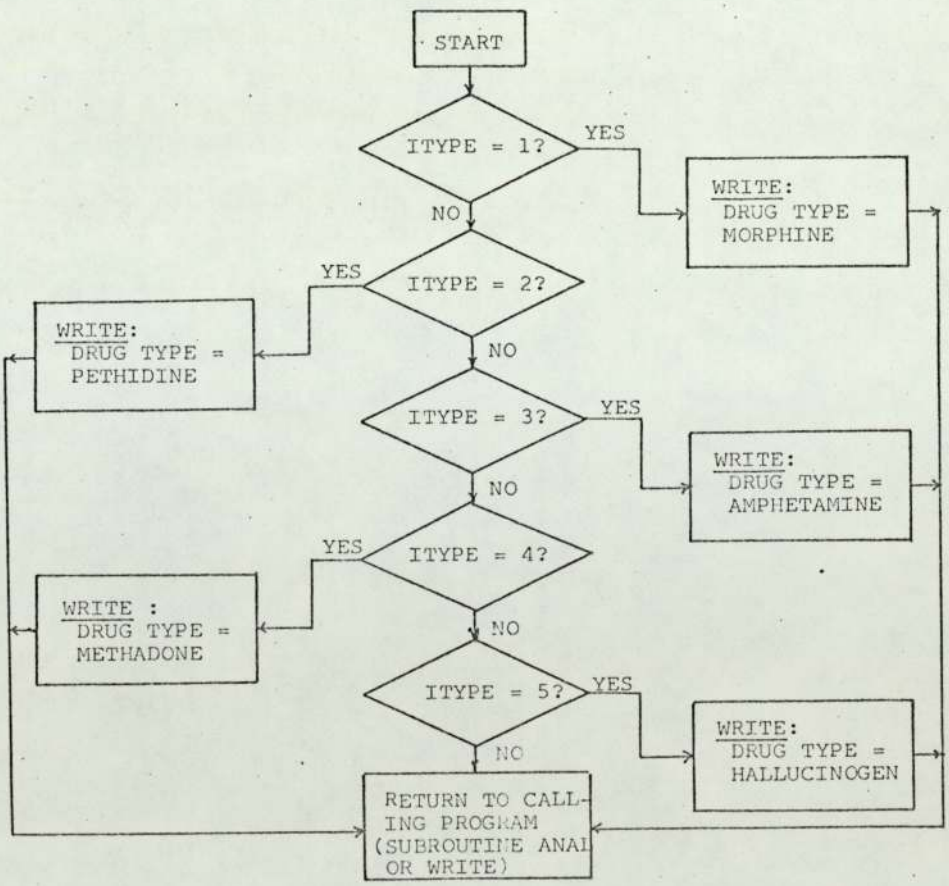


FIG: 6,29

SUBROUTINE TYPE



E. Subroutine NAM - Name Search Routine FIG:6,30 and Appendix 2 (84-117)

This was the second major subroutine of the system, operated in response to IOPT = 2 in the MASTER. The major feature of this routine was its use of the ICL library subroutine COMP. COMP facilitated the comparison of two character strings (name arrays) for equality.

The unknown name UNAME(J),J = 1,10, of a maximum 40 characters (10 words) was read from the terminal (format 10A4). The first and second words (8 characters) were then repeatedly compared against all the compound names held in FILEDATA, (NAME(I,J),J = 1,10)I = 1,200.

The first word (4 characters) of UNAME was compared against NAME using COMP. If a match was obtained the next four characters were compared. If a further match was obtained, the compound matching for 8 characters was output to the terminal using subroutine WRITE. Names within a file of this size were usually unique for 8 characters. More characters could have been compared for each name in the same way but this was felt to be unnecessary.

The routine repetitively compared all the names in the file until the "end of data" mark, IFORM(I,1) = -1 was encountered.

Control was then returned to the MASTER.

F. Subroutine MASS - Molecular Weight Search FIG:6,31 and Appendix 2 (626 - 654)

This was the third major subroutine of the system, operated in response to IOPT = 3 in the MASTER.

FIG:6.30

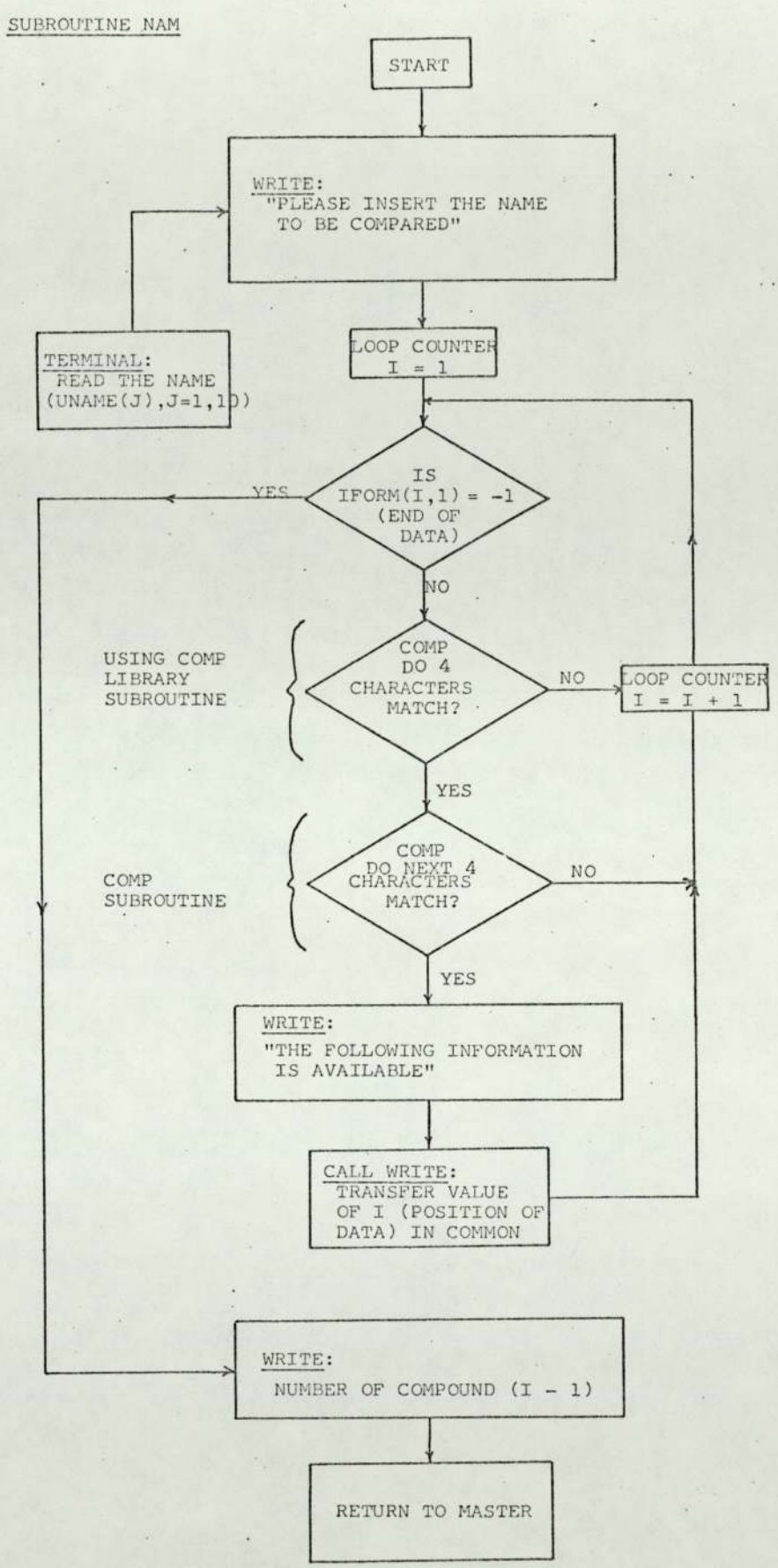
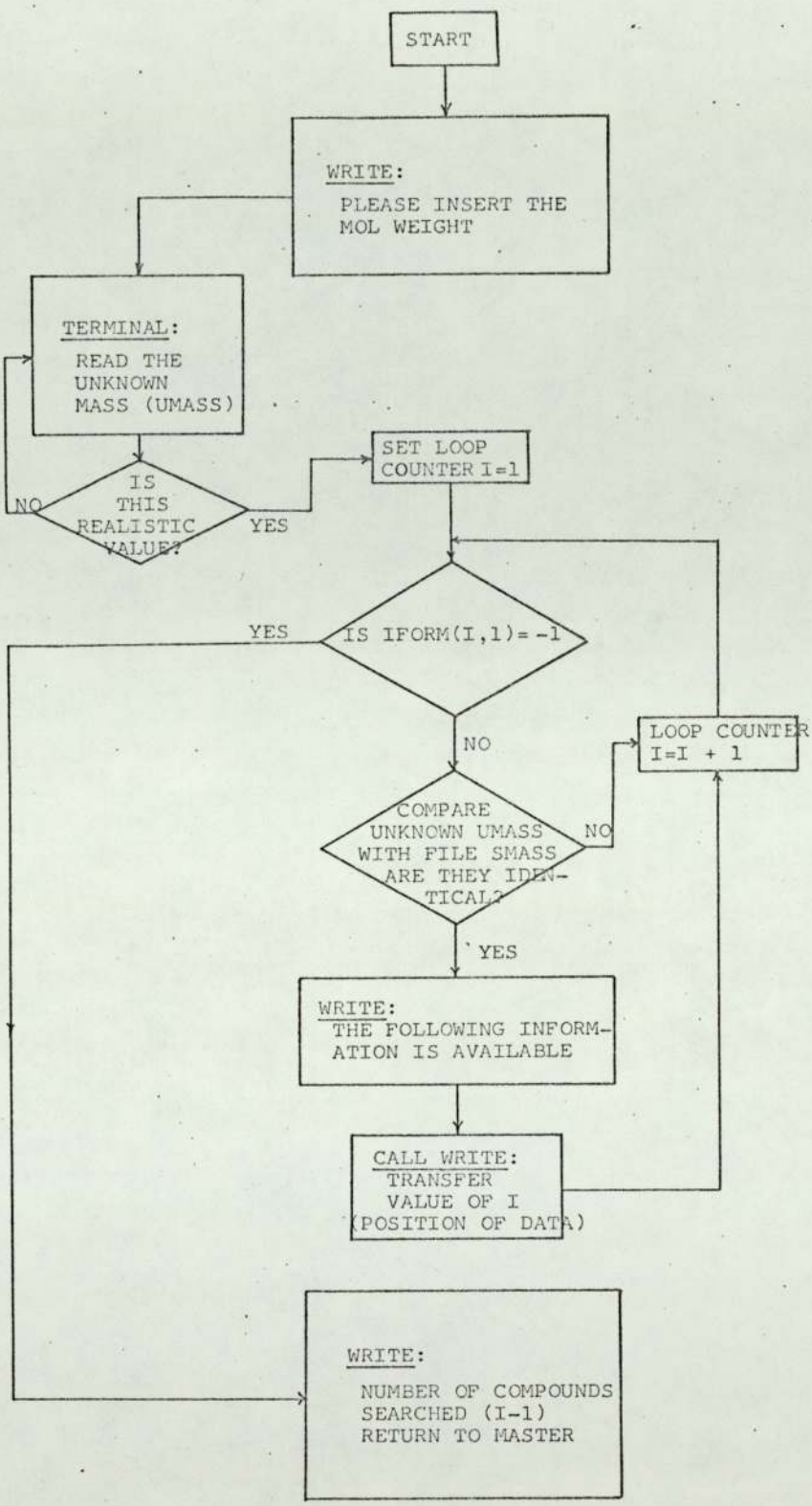

SUBROUTINE NAM
START
WRITE:
"PLEASE INSERT THE NAME
TO BE COMPARED"
TERMINAL:
READ THE NAME
(UNAME(J),J=1,10)
LOOP COUNTER
I = 1
IS
IFORM(I,1) = -1
(END OF
DATA)
YES
NO
USING COMP
LIBRARY
SUBROUTINE
COMP
DO 4
CHARACTERS
MATCH?
NO
LOOP COUNTER
I = I + 1
YES
COMP
SUBROUTINE
COMP
DO NEXT 4
CHARACTERS
MATCH?
NO
YES
WRITE:
"THE FOLLOWING INFORMATION
IS AVAILABLE"
CALL WRITE:
TRANSFER VALUE
OF I (POSITION OF
DATA) IN COMMON
WRITE:
NUMBER OF COMPOUND (I - 1)
RETURN TO MASTER

FIG: 6.31

SUBROUTINE MASS



The unknown molecular weight UMASS was compared against the molecular weights SMASS(I),I = 1,200 stored on file. This process involved repetitive direct comparison.

i.e. if (UMASS - SMASS) = 0 match

if (UMASS - SMASS) ≠ no match

The end of file IFORM(I,1) = -1. Subroutine WRITE was again used to output the matches to the terminal.

G. Subroutine FORM - Molecular Formula and Partial Molecular Formula Search FIGS:6.32,33 and Appendix 2 (655-722)

This program was operated in response to IOPT = 4 in the MASTER.

This program compared the unknown molecular formula or partial molecular formula repetitively against the molecular formulae of the file.

This program consisted of two sections:-

1. Input.

2. Matching and Sieving.

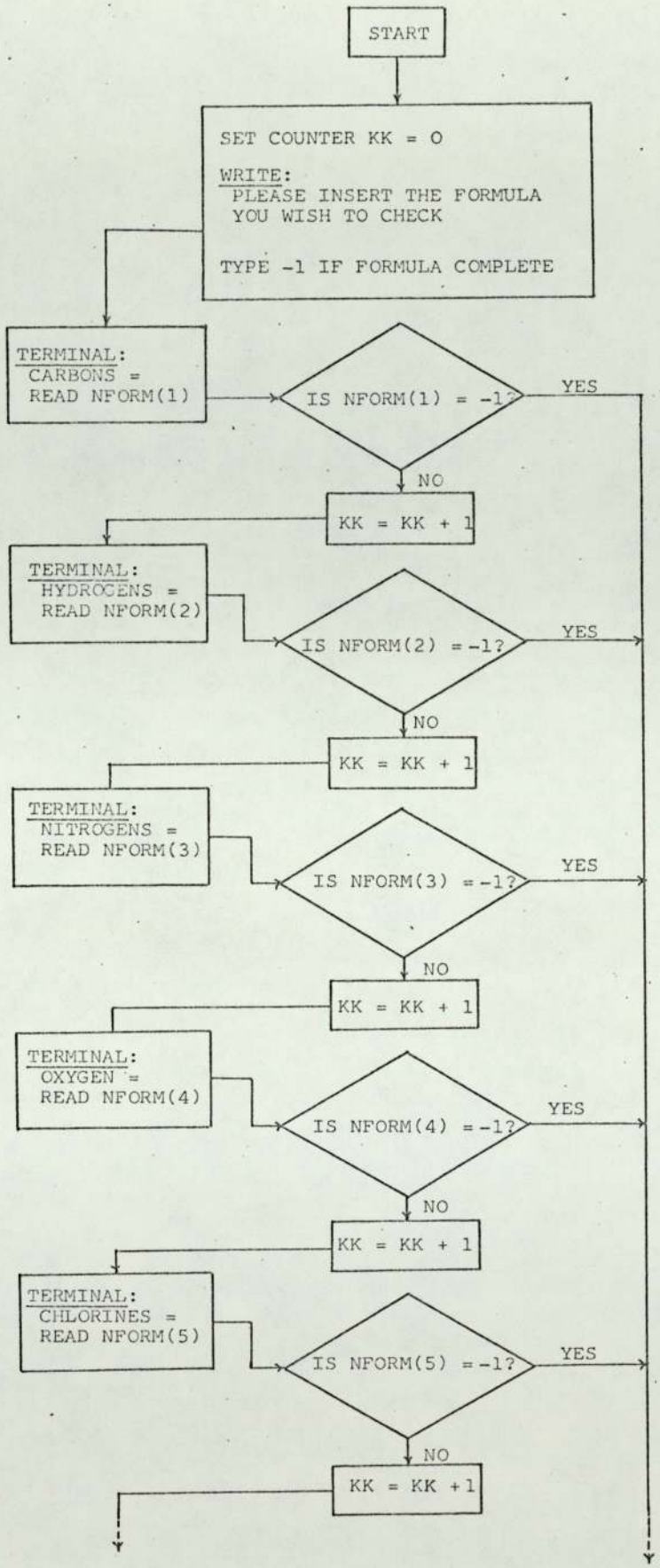
1. Input Section FIG:6,32 and Appendix 2(655-698)

The elements were read from the terminal in the order, Carbon, Hydrogen, Nitrogen, Oxygen, Chlorine, Sulphur and Phosphorous. This elemental group included all the possibilities within the file. To terminate the input array at any position after, carbon, a -1 was typed on the terminal.

Initially the value of KK (array counter) was set to zero. After each element of the unknown array NFORM(J) was read from the terminal KK was incremented

FIG: 6.32

SUBROUTINE FORM



see 6.33

to (KK + 1). If the value of NFORM(J) = -1 the input data was completed and the program continued to the matching and sieving area. If not, the program accepted further input until either -

NFORM(J) = -1 or

the final value NFORM(7) had been accepted.

The molecular formula for the unknown was then contained within the array NFORM(J),J = 1,KK.

2. Matching and Sieving Section FIGS:6.33

The program repetitively compared the elements of the "unknown" array NFORM(J),J = 1,KK against the file array IFORM(I,J), J = 1,7. The values held in the Jth position of each array were compared for equality (initial value J = 1). If the two elements matched then the program continued to compare the value at (J + 1), and so on until either:-

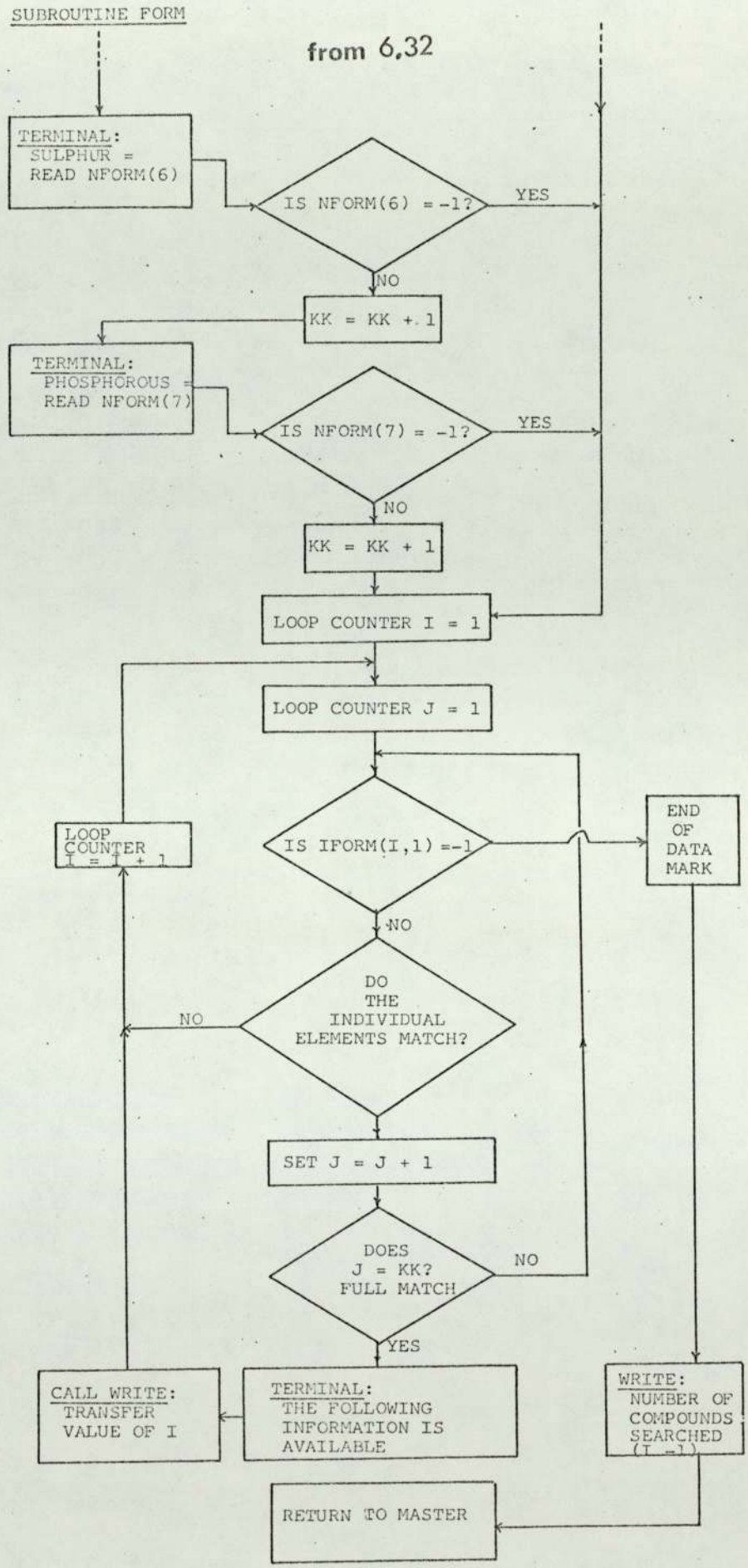
all the (KK) peaks had been compared and hence a match obtained or

The IFORM value at position J within the file array did not match. If so the compound was eliminated from the search and the next (I + 1) file array was compared.

The matching data was written to the terminal using the Subroutine WRITE.

3. Partial Molecular Formula Search

To facilitate partial molecular formula searching, zeros were permitted as input. They were treated as "neutral" values, i.e. any element within the file array IFORM(I,J),J = 1,7, would have matched against a zero.


SUBROUTINE FORM
from 6,32
TERMINAL:
SULPHUR =
READ NFORM(6)
IS NFORM(6) = -1?
YES
NO
KK = KK + 1
TERMINAL:
PHOSPHOROUS =
READ NFORM(7)
IS NFORM(7) = -1?
YES
NO
KK = KK + 1
LOOP COUNTER I = 1
LOOP COUNTER J = 1
IS IFORM(I,1) =-1
END OF DATA MARK
LOOP COUNTER I = I + 1
NO
DO THE INDIVIDUAL ELEMENTS MATCH?
NO
SET J = J + 1
DOES J = KK? FULL MATCH
NO
YES
CALL WRITE:
TRANSFER VALUE OF I
TERMINAL:
THE FOLLOWING INFORMATION IS AVAILABLE
WRITE:
NUMBER OF COMPOUNDS SEARCHED (I - 1)
RETURN TO MASTER

If the element NFORM(J) = 0 the compound was maintained within the sieve until either a match or no match was obtained with a later non-zero element.

If NFORM had consisted of all zeros, every compound within the file would have matched for all KK values. If NFORM contained zeros, all except for NFORM(5) which contained a 1 (1 chlorine atom), then only the compounds on the file which contained 1 chlorine atom would have been output to the terminal. This similarly applied for any other combinations of atoms.

On completion, control returned to the MASTER. This completes the full description of the programs. Terminal Sessions were used to illustrate the full facilities provided by the system.

H. Terminal Sessions

In each of the examples illustrated FIGS:6.34-42, the input data, typed on the terminal by the operator was preceded by a backward facing arrow (←—).

1. Session 1 FIG:6.34 "A Combined Search for all the four analytical techniques".

A full combined match was obtained 10 full monographs were output to the terminal of decreasing importance.

2. Session 2 FIG:6.35 "The Effectiveness of the error checking routines".

Incorrect input data, outside the permitted ranges for each analytical technique, were typed by the operator. The response of the program in each case is illustrated.

3. Session 3 FIG:6.36 "A combined search for MS and IR data".

No full matches were obtained therefore the mismatch routines, MSMISMATCH and IRMISMATCH were utilised.

4. Session 4 FIG:6.37 "A Search for IR Data only".

No full match was obtained, IRMISMATCH was utilised. Within the program the computed DIR values were sorted to the nearest whole number. Matches with DIR values in the range 0 - 0.99 were considered to be equivalent although on output to the terminal the actual DIR values, to two decimal places, were quoted.

5. Session 5 FIG:6.38 "A Name Search".

For this example Morphine was selected. The program compared for equality only the initial 8 characters of any name. Morphine contains exactly 8 characters therefore all compounds on file with morphine + (other characters) were output to the terminal.

6. Session 6 FIG:6.39 "A Molecular Weight Search".

All compounds with a molecular weight of 301 were retrieved.

Two monographs were retrieved for oxymorphone base. Both were included within the file because the infra-red spectra, one from Aston the other from C.R.E. were different. To avoid any possibility of rejecting a possible match both were included. The final decision on the analytical accuracy was made by manually comparing the full spectra of both.

7. Session 7 FIG: 6.40 "A complete Molecular Formula Search".

The two monographs of oxymorphone base were retrieved

8. Session 8 FIG: 6.41 "A Partial Molecular Formula Search".

A search for all the compounds on file containing 1 chlorine atom. Two compounds were retrieved.

FIG: 6.34a

```
          *****MISUSE OF DRUGS ACT*****
    DATA RETRIEVAL PACKAGE NOW OPERATING

FOUR SEARCH OPTIONS ARE AVAILABLE:-
          (1)PEAK MATCH
          (2)NAME SEARCH
          (3)MOLECULAR WEIGHT
          (4)MOLECULAR FORMULA


PLEASE INSERT THE OPTION YOU REQUIRE
NUMBER 1 TO 4 ONLY
← 1


THE PROGRAM RETRIEVES INFORMATION ON
ANY OF THE FOUR FOLLOWING ANALYTICAL TECHNIQUES
     (1) MASS-SPECTRAL DATA ONE TO EIGHT PEAKS
     (2) INFRA-RED DATA ONE TO SIX PEAKS
     (3) ULTRA-VIOLET DATA ACIDIC LAMBDA MAX
     (4) THIN LAYER DATA CURRY-POWELL RF
THE PROGRAM OPERATES ON A MATCH BASIS AND
OUTPUTS THE COMPOUNDS IN ORDER OF BEST MATCH


 DO YOU WISH TO CHECK MS DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 1
 HOW MANY PEAKS DO YOU WISH TO COMPARE?
PLEASE TYPE A NUMBER FROM 1 TO 8
← 5
PLEASE INSERT THE PEAKS ONE PER LINE
← 58
← 36
← 42
← 28
← 125
 DO YOU WISH TO CHECK IR DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 1
 HOW MANY PEAKS DO YOU WISH TO COMPARE?
PLEASE TYPE NUMBER FROM 1 TO 6
← 4
PLEASE INSERT THE PEAKS ONE PER LINE
← 12.3
← 9.2

← 9.9
← 11.8
 DO YOU WISH TO CHECK UV DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 1
 PLEASE INSERT THE ACIDIC LAMBDA MAX
← 267
 DO YOU WISH TO CHECK TLC DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 1
 PLEASE INSERT CURRY-POWELL RF
← 0.65
```

FIG: 6.34b

```
THE FOLLOWING COMPOUND MATCHES FOR MS,IR,UV,TLC DATA **************

COMPOUND NAME :CHLORPHENTERMINE HCL
CHEMICAL FORMULA(BASE):C10 H14 N1 O0 CL1 S0 P0
MOLECULAR WEIGHT(BASE):183.5
MASS-SPECTRA EIGHT PEAKS :  58  36  42  28 125  59 168  41
INFRA-RED SIX PEAKS : 12.3  9.2  9.9 11.8  7.8  8.6
ULTRA-VIOLET LAMBDA MAX : 267
CURRY-POWELL RF :0.65
D VALUE= 0.00
DRUG TYPE = AMPHETAMINE


THE FOLLOWING COMPOUND MATCHES FOR MS,IR,UV,TLC DATA **************

COMPOUND NAME :CHLORPHENTERMINE HCL
CHEMICAL FORMULA(BASE):C10 H14 N1 O0 CL1 S0 P0
MOLECULAR WEIGHT(BASE):183.5
MASS-SPECTRA EIGHT PEAKS :  58  36  42  28 125  59 168  41
INFRA-RED SIX PEAKS : 12.3  9.2  9.9 11.8  7.8 13.3
ULTRA-VIOLET LAMBDA MAX : 267
CURRY-POWELL RF :0.65
D VALUE= 0.00
DRUG TYPE = AMPHETAMINE


THE FOLLOWING MATCHES FOR UV AND TLC DATA              ***

COMPOUND NAME :ETHYLMETHYLTHIAMBUTENE HCL
CHEMICAL FORMULA(BASE):C25 H33 N1 O4 CL0 S0 P0
MOLECULAR WEIGHT(BASE):411.0
ULTRA-VIOLET LAMBDA MAX : 268
CURRY-POWELL RF :0.71
DRUG TYPE = METHADONE


THE FOLLOWING MATCHES FOR UV ONLY                      **

COMPOUND NAME :MESCALINE SULPHATE
CHEMICAL FORMULA(BASE):C11 H17 N1 O3 CL0 S0 P0
MOLECULAR WEIGHT(BASE):211.0
ULTRA-VIOLET LAMBDA MAX : 268
DRUG TYPE = AMPHETAMINE
```

```
THE FOLLOWING MATCHES FOR UV ONLY                              **

COMPOUND NAME :MESCALINE BASE
CHEMICAL FORMULA(BASE):C11 H17 N1 03 CL0 S0 P0
MOLECULAR WEIGHT(BASE):211.0
ULTRA-VIOLET LAMBDA MAX : 268
DRUG TYPE = AMPHETAMINE

THE FOLLOWING MATCHES FOR UV ONLY                              **

COMPOUND NAME :PSILOCIN
CHEMICAL FORMULA(BASE):C12 H16 N2 01 CL0 S0 P0
MOLECULAR WEIGHT(BASE):204.0
ULTRA-VIOLET LAMBDA MAX : 266
DRUG TYPE = HALLUCINOGEN

THE FOLLOWING MATCHES FOR UV ONLY                              **

COMPOUND NAME :PSILOCIN
CHEMICAL FORMULA(BASE):C12 H16 N2 01 CL0 S0 P0
MOLECULAR WEIGHT(BASE):204.0
ULTRA-VIOLET LAMBDA MAX : 266
DRUG TYPE = HALLUCINOGEN

THE FOLLOWING MATCHES FOR UV ONLY                              **

COMPOUND NAME :PSILOCYBIN
CHEMICAL FORMULA(BASE):C12 H17 N2 04 CL0 S0 P1
MOLECULAR WEIGHT(BASE):284.0
ULTRA-VIOLET LAMBDA MAX : 268
DRUG TYPE = HALLUCINOGEN

THE FOLLOWING MATCHES FOR UV ONLY                              **

COMPOUND NAME :METHAQUALONE HCL
CHEMICAL FORMULA(BASE):C16 H14 N2 01 CL0 S0 P0
MOLECULAR WEIGHT(BASE):250.0
ULTRA-VIOLET LAMBDA MAX : 269

THE FOLLOWING MATCHES FOR UV ONLY                              **

COMPOUND NAME :METHAQUALONE BASE
CHEMICAL FORMULA(BASE):C16 H14 N2 01 CL0 S0 P0
MOLECULAR WEIGHT(BASE):250.0
ULTRA-VIOLET LAMBDA MAX : 269

190 COMPOUNDS SEARCHED

 DO YOU WISH TO CHECK ANOTHER COMPOUND
INSERT 1 FOR YES 0 FOR NO
← 0
```

FIG: 6.35

```
 DO YOU WISH TO CHECK MS DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 1
 HOW MANY PEAKS DO YOU WISH TO COMPARE?
PLEASE TYPE A NUMBER FROM 1 TO 8
← 10
 HOW MANY PEAKS DO YOU WISH TO COMPARE?
PLEASE TYPE A NUMBER FROM 1 TO 8
← 4
PLEASE INSERT THE PEAKS ONE PER LINE
← 44
← 42
← 301
← 70
 DO YOU WISH TO CHECK IR DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 1
 HOW MANY PEAKS DO YOU WISH TO COMPARE?
PLEASE TYPE NUMBER FROM 1 TO 6
← -1
 HOW MANY PEAKS DO YOU WISH TO COMPARE?
PLEASE TYPE NUMBER FROM 1 TO 6
← 4
PLEASE INSERT THE PEAKS ONE PER LINE
← 9.1
← 4.9
 PEAK POSITION ERROR PLEASE RETYPE
← 6.3
← 6.8
 PEAK POSITION ERROR PLEASE RETYPE
← 1700
← 7.9
 DO YOU WISH TO CHECK UV DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 1
 PLEASE INSERT THE ACIDIC LAMBDA MAX
← 500
 PLEASE INSERT THE ACIDIC LAMBDA MAX
← 281
 DO YOU WISH TO CHECK TLC DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 1
 PLEASE INSERT CURRY-POWELL RF
← 2.0
 PLEASE INSERT CURRY-POWELL RF
← 0.1
```

FIG: 6,36a

```
      *****MISUSE OF DRUGS ACT*****
   DATA RETRIEVAL PACKAGE NOW OPERATING

FOUR SEARCH OPTIONS ARE AVAILABLE:-
        (1)PEAK MATCH
        (2)NAME SEARCH
        (3)MOLECULAR WEIGHT
        (4)MOLECULAR FORMULA

PLEASE INSERT THE OPTION YOU REQUIRE
NUMBER 1 TO 4 ONLY
← 1

THE PROGRAM RETRIEVES INFORMATION ON
ANY OF THE FOUR FOLLOWING ANALYTICAL TECHNIQUES
     (1) MASS-SPECTRAL DATA ONE TO EIGHT PEAKS
     (2) INFRA-RED DATA ONE TO SIX PEAKS
     (3) ULTRA-VIOLET DATA ACIDIC LAMBDA MAX
     (4) THIN LAYER DATA CURRY-POWELL RF
THE PROGRAM OPERATES ON A MATCH BASIS AND
OUTPUTS THE COMPOUNDS IN ORDER OF BEST MATCH

 DO YOU WISH TO CHECK MS DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 1
 HOW MANY PEAKS DO YOU WISH TO COMPARE?
PLEASE TYPE A NUMBER FROM 1 TO 8
← 5
PLEASE INSERT THE PEAKS ONE PER LINE
← 58
← 36
← 42
← 126
← 125
 DO YOU WISH TO CHECK IR DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 1
 HOW MANY PEAKS DO YOU WISH TO COMPARE?
PLEASE TYPE NUMBER FROM 1 TO 6
← 4
PLEASE INSERT THE PEAKS ONE PER LINE
← 12.3
← 9.2
← 10.0
← 11.5
 DO YOU WISH TO CHECK UV DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 0
 DO YOU WISH TO CHECK TLC DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 0
```

FIG: 6.36b

```
M SMISMATCH OPERATING

THE FOLLOWING MATCHES FOR MS DATA
  58   36   42   28 125   59 168   41 CHLORPHENTERMINE HCL
  4 PEAKS OUT OF 5      D VALUE= 0.00

THE FOLLOWING MATCHES FOR MS DATA
  58   36   42   28 125   59 168   41 CHLORPHENTERMINE HCL
  4 PEAKS OUT OF 5      D VALUE= 0.00
I RMISMATCH OPERATING

THE FOLLOWING MATCHES FOR IR DATA
12.3  9.2  9.9 11.8  7.8  8.6 CHLORPHENTERMINE HCL
  3 PEAKS OUT OF 4      D VALUE= 0.00

THE FOLLOWING MATCHES FOR IR DATA
12.3  9.2  9.9 11.8  7.8 13.3 CHLORPHENTERMINE HCL
  3 PEAKS OUT OF 4      D VALUE= 0.00

190 COMPOUNDS SEARCHED
```

6.37a

```
 DO YOU WISH TO CHECK ANOTHER COMPOUND
INSERT 1 FOR YES 0 FOR NO
← 1
 DO YOU WISH TO CHECK MS DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 0

 DO YOU WISH TO CHECK IR DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 1
 HOW MANY PEAKS DO YOU WISH TO COMPARE?
PLEASE TYPE NUMBER FROM 1 TO 6
← 4
PLEASE INSERT THE PEAKS ONE PER LINE
← 5.8
← 8.3
← 9.1
← 12.7
 DO YOU WISH TO CHECK UV DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 0
 DO YOU WISH TO CHECK TLC DATA?
PLEASE TYPE 1 FOR YES 0 FOR NO
← 0
```

```
IRMISMATCH OPERATING

THE FOLLOWING MATCHES FOR IR DATA
 5.8  8.3  8.9  6.6  8.1 14.4 ANILERIDINE DI HCL
 3 PEAKS OUT OF 4      D VALUE= 0.00

THE FOLLOWING MATCHES FOR IR DATA
 5.8  9.0  8.5 14.4  8.3 10.5 BENZETHIDINE BASE
 3 PEAKS OUT OF 4      D VALUE= 0.67

THE FOLLOWING MATCHES FOR IR DATA
 5.8  8.3  9.1 14.2 13.1  9.9 DIOXAPHETYL BUTYRATE
 3 PEAKS OUT OF 4      D VALUE= 0.00

THE FOLLOWING MATCHES FOR IR DATA
 5.8 10.4  8.5  8.9  8.2  6.6 DIPHENOXYLATE BASE
 3 PEAKS OUT OF 4      D VALUE= 0.67

THE FOLLOWING MATCHES FOR IR DATA
 5.8  8.2  8.9  8.5  9.4 14.3 ETOXERIDINE HCL
 3 PEAKS OUT OF 4      D VALUE= 0.00

THE FOLLOWING MATCHES FOR IR DATA
 5.8  8.9  8.5  8.3  9.5  7.7 ETOXERIDINE BASE
 3 PEAKS OUT OF 4      D VALUE= 0.67

THE FOLLOWING MATCHES FOR IR DATA
 5.8  8.9  8.5  8.3  9.3 14.4 FURETHIDINE BASE
 3 PEAKS OUT OF 4      D VALUE= 0.67

THE FOLLOWING MATCHES FOR IR DATA
 5.8  8.1  8.2  9.1  8.5 13.8 MORPHERIDINE HCL
 3 PEAKS OUT OF 4      D VALUE= 0.67

THE FOLLOWING MATCHES FOR IR DATA
 5.8  9.0  8.5  8.3  7.7 14.4 MORPHERIDINE BASE
 3 PEAKS OUT OF 4      D VALUE= 0.67

THE FOLLOWING MATCHES FOR IR DATA
 5.8  9.0  8.3  7.8  9.2 '8.8 PROPERIDINE BASE
 3 PEAKS OUT OF 4      D VALUE= 0.67

190 COMPOUNDS SEARCHED

 DO YOU WISH TO CHECK ANOTHER COMPOUND
INSERT 1 FOR YES 0 FOR NO
← 0
```

FIG: 6.38a

```
FOR A FURTHER SEARCH TYPE 1,0 TO FINISH
← 1
FOUR SEARCH OPTIONS ARE AVAILABLE:-

        (1)PEAK MATCH
        (2)NAME SEARCH
        (3)MOLECULAR WEIGHT
        (4)MOLECULAR FORMULA

PLEASE INSERT THE OPTION YOU REQUIRE
NUMBER 1 TO 4 ONLY
← 2
PLEASE INSERT THE NAME YOU WISH TO CHECK
← MORPHINE
```

```
THE FOLLOWING INFORMATION IS ON FILE

COMPOUND NAME:MORPHINE SULPHATE
CHEMICAL FORMULA(BASE):C17 H19 N1 03 CL0 S0 P0
MOLECULAR WEIGHT(BASE):285.0
MASS SPECTRAL EIGHT PEAKS: 285  28  32  42  44 162 215  41
INFRA RED SIX PEAKS:  9.0  9.3 12.7  7.6  8.5 10.6
ULTRA-VIOLET LAMBDA MAX: 284
THIN LAYER CURRY POWELL RF:0.14
DRUG TYPE = MORPHINE


COMPOUND NAME:MORPHINE BASE
CHEMICAL FORMULA(BASE):C17 H19 N1 03 CL0 S0 P0
MOLECULAR WEIGHT(BASE):285.0
MASS SPECTRAL EIGHT PEAKS:   0   0   0   0   0   0   0   0
INFRA RED SIX PEAKS:  8.0  8.9 12.4 10.6 12.0  9.2
ULTRA-VIOLET LAMBDA MAX: 284
THIN LAYER CURRY POWELL RF:0.14
DRUG TYPE = MORPHINE


COMPOUND NAME:MORPHINE HCL
CHEMICAL FORMULA(BASE):C17 H19 N1 03 CL0 S0 P0
MOLECULAR WEIGHT(BASE):285.0
MASS SPECTRAL EIGHT PEAKS:   0   0   0   0   0   0   0   0
INFRA RED SIX PEAKS: 12.7  7.6  9.3  9.0  8.9 10.6
ULTRA-VIOLET LAMBDA MAX: 284
THIN LAYER CURRY POWELL RF:0.14
DRUG TYPE = MORPHINE


COMPOUND NAME:MORPHINE METHOBROMIDE
CHEMICAL FORMULA(BASE):C17 H19 N1 03 CL0 S0 P0
MOLECULAR WEIGHT(BASE):285.0
MASS SPECTRAL EIGHT PEAKS:   0   0   0   0   0   0   0   0
INFRA RED SIX PEAKS:  9.1  7.6  9.4  7.9  9.5 10.7
ULTRA-VIOLET LAMBDA MAX:   0
THIN LAYER CURRY POWELL RF:0.00
DRUG TYPE = MORPHINE


COMPOUND NAME:MORPHINE-N-OXIDE
CHEMICAL FORMULA(BASE):C17 H19 N1 03 CL0 S0 P0
MOLECULAR WEIGHT(BASE):285.0
MASS SPECTRAL EIGHT PEAKS:  58  28 285  72  42  32  71  59
INFRA RED SIX PEAKS:  8.1  6.2 12.6 10.5  8.9  9.2
ULTRA-VIOLET LAMBDA MAX: 284
THIN LAYER CURRY POWELL RF:0.14
DRUG TYPE = MORPHINE


190 COMPOUNDS SEARCHED


FOR A FURTHER SEARCH TYPE 1,0 TO FINISH
← 1
```

```
FOUR SEARCH OPTIONS ARE AVAILABLE:-
        (1)PEAK MATCH
        (2)NAME SEARCH
        (3)MOLECULAR WEIGHT
        (4)MOLECULAR FORMULA

PLEASE INSERT THE OPTION YOU REQUIRE
NUMBER 1 TO 4 ONLY
← 3
 PLEASE INSERT THE MOL WEIGHT
← 301

THE FOLLOWING INFORMATION IS ON FILE

COMPOUND NAME:OXYMORPHONE BASE
CHEMICAL FORMULA(BASE):C17 H19 N1 04 CL0 S0 P0
MOLECULAR WEIGHT(BASE):301.0
MASS SPECTRAL EIGHT PEAKS:  44  42 301  70 216  57  58  28
INFRA RED SIX PEAKS:  5.8  8.1  8.2  8.8 10.6 10.5
ULTRA-VIOLET LAMBDA MAX: 281
THIN LAYER CURRY POWELL RF:0.09
DRUG TYPE = MORPHINE

COMPOUND NAME:OXYMORPHONE BASE
CHEMICAL FORMULA(BASE):C17 H19 N1 04 CL0 S0 P0
MOLECULAR WEIGHT(BASE):301.0
MASS SPECTRAL EIGHT PEAKS:  44  42 301  70 216  57  58  28
INFRA RED SIX PEAKS:  9.1  6.3  5.8  7.9  8.8  8.1
ULTRA-VIOLET LAMBDA MAX: 281
THIN LAYER CURRY POWELL RF:0.09
DRUG TYPE = MORPHINE

COMPOUND NAME:DIHYDROCODEINE TARTRATE
CHEMICAL FORMULA(BASE):C18 H23 N1 03 CL0 S0 P0
MOLECULAR WEIGHT(BASE):301.0
MASS SPECTRAL EIGHT PEAKS: 301  28  42 302 163 245  70  59
INFRA RED SIX PEAKS:  8.0  7.0  9.4  8.8  8.3 14.7
ULTRA-VIOLET LAMBDA MAX: 282
THIN LAYER CURRY POWELL RF:0.20
DRUG TYPE = MORPHINE

COMPOUND NAME:DIHYDROCODEINE BASE
CHEMICAL FORMULA(BASE):C18 H23 N1 03 CL0 S0 P0
MOLECULAR WEIGHT(BASE):301.0
MASS SPECTRAL EIGHT PEAKS:   0   0   0   0   0   0   0   0
INFRA RED SIX PEAKS:  6.6  7.9  9.7  8.0  8.7  9.5
ULTRA-VIOLET LAMBDA MAX: 282
THIN LAYER CURRY POWELL RF:0.20
DRUG TYPE = MORPHINE

190 COMPOUNDS SEARCHED
```

FIG: 6.40

```
FOUR SEARCH OPTIONS ARE AVAILABLE:-
        (1)PEAK MATCH
        (2)NAME SEARCH
        (3)MOLECULAR WEIGHT
        (4)MOLECULAR FORMULA

PLEASE INSERT THE OPTION YOU REQUIRE
NUMBER 1 TO 4 ONLY
← 4
 PLEASE INSERT THE FORMULA YOU WISH TO CHECK.
CARBONS=
← 17
HYDROGEN=     TYPE -1 IF FORMULA COMPLETE
← 19
NITROGEN=     TYPE -1 IF FORMULA COMPLETE
← 1
OXYGEN=       TYPE -1 IF FORMULA COMPLETE
← 4
CHLORINE=     TYPE -1 IF FORMULA COMPLETE
← -1

THE FOLLOWING INFORMATION IS ON FILE

COMPOUND NAME:OXYMORPHONE BASE
CHEMICAL FORMULA(BASE):C17 H19 N1 04 CL0 S0 P0
MOLECULAR WEIGHT(BASE):301.0
MASS SPECTRAL EIGHT PEAKS:  44  42 301  70 216  57  58  28
INFRA RED SIX PEAKS:  5.8  8.1  8.2  8.8 10.6 10.5
ULTRA-VIOLET LAMBDA MAX: 281
THIN LAYER,CURRY POWELL RF:0.09
DRUG TYPE = MORPHINE

COMPOUND NAME:OXYMORPHONE BASE
CHEMICAL FORMULA(BASE):C17 H19 N1 04 CL0 S0 P0
MOLECULAR WEIGHT(BASE):301.0
MASS SPECTRAL EIGHT PEAKS:  44  42 301  70 216  57  58  28
INFRA RED SIX PEAKS:  9.1  6.3  5.8  7.9  8.8  8.1
ULTRA-VIOLET LAMBDA MAX: 281
THIN LAYER CURRY POWELL RF:0.09
DRUG TYPE = MORPHINE

190 COMPOUNDS SEARCHED

FOR A FURTHER SEARCH TYPE 1,0 TO FINISH
← 1
```

FIG: 6.41a

```
FOUR SEARCH OPTIONS ARE AVAILABLE:-
        (1)PEAK MATCH
        (2)NAME SEARCH
        (3)MOLECULAR WEIGHT
        (4)MOLECULAR FORMULA

PLEASE INSERT THE OPTION YOU REQUIRE
NUMBER 1 TO 4 ONLY
← 4
 PLEASE INSERT THE FORMULA YOU WISH TO CHECK,
CARBONS=
← 0
HYDROGEN=     TYPE -1 IF FORMULA COMPLETE
← 0
NITROGEN=     TYPE -1 IF FORMULA COMPLETE
← 0
OXYGEN=       TYPE -1 IF FORMULA COMPLETE
← 0
CHLORINE=     TYPE -1 IF FORMULA COMPLETE
← 1
SULPHUR=      TYPE -1 IF FORMULA COMPLETE
← -1
```

FIG: 6.41b

```
THE FOLLOWING INFORMATION IS ON FILE

COMPOUND NAME:CLONITAZENE BASE
CHEMICAL FORMULA(BASE):C20 H23 N4 O2 CL1 S0 P0
MOLECULAR WEIGHT(BASE):386.5
MASS SPECTRAL EIGHT PEAKS:   0   0   0   0   0   0   0   0
INFRA RED SIX PEAKS:  7.6  6.6 13.6 12.5  9.2 12.0
ULTRA-VIOLET LAMBDA MAX: 283
THIN LAYER CURRY POWELL RF:0.68

COMPOUND NAME:CLONITAZENE HCL
CHEMICAL FORMULA(BASE):C20 H23 N4 O2 CL1 S0 P0
MOLECULAR WEIGHT(BASE):386.5
MASS SPECTRAL EIGHT PEAKS:   0   0   0   0   0   0   0   0
INFRA RED SIX PEAKS:  8.4  6.6  9.5  9.7 13.6 12.8
ULTRA-VIOLET LAMBDA MAX: 283
THIN LAYER CURRY POWELL RF:0.68

COMPOUND NAME:CHLORPHENTERMINE HCL
CHEMICAL FORMULA(BASE):C10 H14 N1 O0 CL1 S0 P0
MOLECULAR WEIGHT(BASE):183.5
MASS SPECTRAL EIGHT PEAKS:  58  36  42  28 125  59 168  41
INFRA RED SIX PEAKS: 12.3  9.2  9.9 11.8  7.8  8.6
ULTRA-VIOLET LAMBDA MAX: 267
THIN LAYER CURRY POWELL RF:0.65
DRUG TYPE = AMPHETAMINE

COMPOUND NAME:CHLORPHENTERMINE HCL
CHEMICAL FORMULA(BASE):C10 H14 N1 O0 CL1 S0 P0
MOLECULAR WEIGHT(BASE):183.5
MASS SPECTRAL EIGHT PEAKS:  58  36  42  28 125  59 168  41
INFRA RED SIX PEAKS: 12.3  9.2  9.9 11.8  7.8 13.3
ULTRA-VIOLET LAMBDA MAX: 267
THIN LAYER CURRY POWELL RF:0.65
DRUG TYPE = AMPHETAMINE

190 COMPOUNDS SEARCHED

FOR A FURTHER SEARCH TYPE 1,0 TO FINISH
← 1
```

APPENDIX 1

Synthetic Methods

APPENDIX 1

Synthetic Methods

The Prodines

The four compounds:-

Alpha and Betaprodine (I) and Alpha and Betameprodine (II) were all prepared by the same synthetic route[47,48]. The preparation of (I) involved a 4 stage synthesis from commercially available methyl α-methylacrylate. For the synthesis of II ethyl α-ethylacrylate was not readily available and, therefore, required an 8 stage preparation from ethyl diethylmalonate.

Synthetic Scheme for Alpha and Betaprodine (I)

(α,β-1,3-dimethyl-4-phenyl-4-propionyloxpiperidine)

Methyl-2-methyl-3-methylaminopropionate (1)

Methyl α-methylacrylate (85g) was gradually added to a solution of methylamine (20g) in 95% ethanol (180 cm^3). This solution was stored for 7 days at room temperature after which period the ethanol was removed in vacuo and the product (1) distilled at 97°/29mm Hg yield 78g.

Dimethyl α-methyl-β,β^1(methylimino)dipropionate (2)

Methylacrylate (100g) was added to 78g of (1) and the mixture left to stand at room temperature for 4 days to give the product (115g) (2) which distilled at 117°/5mm Hg.

1,3-Dimethyl-4-piperidone (3)

Compound (2) (20g) was cyclised[48] by dropwise addition with stirring to a suspension of sodium (2g) under refluxing dry toluene (40 cm^3). As the condensation reaction progressed the sodium salt of the piperidone

precipitated out. When the addition was complete the mixture was heated for 3 hours. The contents were cooled, water (20 cm^3) added, the toluene layer removed and the aqueous layer acidified with concentrated hydrochloric acid (17 cm^3). The acidified piperidone solution was refluxed until one drop gave a faint colour with ferric chloride. The water was removed *in vacuo* and the residue made alkaline with 40% sodium hydroxide solution to pH 11. The mixture was extracted into ether, dried over potassium carbonate and the ether removed. The residual oil on distillation gave 5.5g of the piperidone (3).

1,3-Dimethyl-4-hydroxy-4-phenylpiperidine (4)

The piperidone (3) was treated in the usual way[49] with phenyl lithium prepared from bromobenzene (15.7g) and lithium (1.5g) in excess dry ether. Subsequent work up and crystallisation from hexane gave 2g of the two α and β diasterioisomeric alcohols m.p. 72-82°.

1,3-Dimethyl-4-phenyl-4-propionoxypiperidine (5)

The alcohol (4) (2g) was dissolved in excess propionic anhydride (10 cm^3) and heated for 10 hours on a steam bath. The excess solvent was removed *in vacuo* and the residue made alkaline with 10% sodium carbonate solution. The oil was extracted into ether and dried over anhydrous potassium carbonate. After drying the ether solution was filtered and treated with hydrogen chloride gas. The resulting mass was filtered and dried over sodium hydroxide pellets *in vacuo* for 24 hours and finally crystallised from methanol/acetone. The α and β

isomers were separated by fractional crystallisation. The α isomer (1.2g m.p. 220-222°) was less soluble and crystallised immediately from methanol acetone and the β isomer (0.5g) m.p. 199-200° crystallised after two days in the refrigerator.

Synthetic Scheme for Alpha and Betameprodine (II)

(3-Ethyl-1-methyl-4-phenyl-4-propionoxypiperidine)

Mono acid of diethyl ethylmalonate (6)

(2-propionoxy-butyric acid)

Diethyl ethylmalonate (1 mol) stirred with potassium hydroxide (1 mol) in excess absolute alcohol for 12 hours at room temperature[50]. The potassium salt was then washed with ether to remove unchanged malonate and filtered. The residue was dissolved in a minimum volume of water and acidified with concentrated hydrochloric acid. The oily free acid was extracted into ether and washed with water to remove all traces of the di-acid. The ether was removed in vacuo to give the mono acid as a colourless oil.

Ethyl α-ethylacrylate (7)

This compound was prepared by a standard Mannich[51] base reaction . The acid (27g) was added dropwise to diethylamine (12g) and 30% formaldehyde (17g) with cooling. Two products the acrylate (7) boiling at 137° (60%) and an additional condensation product $CH_2(NC_2H_5)_2$ boiling at 167° were obtained and separated by fractional distillation.

Successive treatments of the acrylate (7) in the manner described for the preparation of Alpha and Betaprodines (I) 1-5 gave the following:-

Ethyl 2-ethyl-3-methylaminopropionate (8)

Prepared as in I(1), distilled at 97°/29mm Hg.

Diethyl α-ethyl-β,β^1-(methylimino)dipropionate (9)

Prepared as in I(2), distilled at 126°/2mm Hg.

3-Ethyl-1-methyl-4-piperidone (10)

Prepared as in I(3), distilled at 103°/33mm Hg.

1-Methyl-3-ethyl-4-pheny-4-hydroxypiperidine (11)

Prepared as in I(4), colourless crystals m.p. 96-97° from hexane.

1-Methyl-3-ethyl-4-phenyl-4-propionoxy-piperidine hydrochloride (12)

Prepared as in I(5), α-isomer m.p. 229-230° (1g), β isomer m.p. 201-203° (0.2g)

Acetyldihydrocodeine (III)

Dihydrocodeine anhydrous (5g) was dissolved in refluxing pyridine to which acetyl chloride (2g) was added dropwise. This mixture was refluxed for 1 hour. The pyridine was removed by distillation and the residue dissolved in water. The acidic solution was basified with 40% sodium hydroxide solution and the base extracted into ether, concentration of the dried ethereal extract gave III (4g) m.p. 120-122° from ethanol.

Nicocodine IV

(6-Nicotinoylcodeine)

Anhydrous codeine base (6g) was shaken in small amounts[52] into molten nicotinic anhydride (11.4g) at 125°. This mixture was stirred for 1 hour at 125-135°. The solid mass on cooling was triturated with water (100 cm^3) and sodium bicarbonate to decompose the excess nicotinic

anhydride and to obtain a complete solution. This solution was basified with sodium carbonate and extracted into ether. The ether was removed in vacuo and the residue recrystallised from ethanol to yield 6-nicotinoylcodeine (4g) m.p. 123-125°.

Nicodicodine (V)

(6-Nicotinoyldihydrocodeine)

This compound was prepared from anhydrous dihydrocodeine in exactly the same manner as for (IV) to yield 4g of (V), m.p.140 -142°

Normethadone (VI)

(6-Dimethylamino-4,4-diphenyl-3-hexanone)

Diphenylacetonitrile (20g) in dry benzene (100 cm^3) was stirred with 2-(N,N-dimethyl)ethylchloride (15g) in the presence of sodamide (15g) for 3-4 hours[53] at 50° to give 4-(N,N-dimethyl)-2,2-diphenyl-butyronitrile (21g) m.p. 66-67° from benzene. This compound when treated with the Grignard reagent Ethyl-magnesium bromide and subsequently worked up[54] produced the oily base (VI) which distilled at 164-167°. This base on treatment with ethanol, hydrochloric acid mixture gave the hydrochloride (10g) m.p. 174-175° from acetone.

Norpipanone (VII)

(4,4-Diphenyl-6-piperidino-3-hexanone)

To a solution of diphenylacetonitrile (20g) in dry benzene (100 cm^3) was added sodamide (5g) followed by 2-(1-piperidyl)ethyl chloride with 3-4 hours stirring at 50°[53]. This gave 2,2-diphenyl-4-(N-piperidyl)-butyronitrile (23g) from benzene.

Grignard reaction with ethylmagnesium bromide and subsequent hydrolysis[54] gave the ketone (VII) as an oily solid. Treatment with ethanol, hydrochloric acid mixture gave the hydrochloride salt (12g) m.p. 181-182° from acetone.

Alphamethadol (VIII)

(α-6-Dimethylamino-4,4-diphenyl-3-heptanol)

A solution of methadone (9g) in dry ether (50 cm^3) was added dropwise over 10 minutes to a suspension of lithium aluminium hydride (1.3g) in dry ether[55]. The reaction was stirred for 15 minutes. On completion of the reaction water (5 cm^3) was cautiously added to the suspension, followed by concentrated hydrochloric acid (20 cm^3). Two clear liquid phases were present and after standing for 1 hour the hydrochloride salt of (VIII) had crystallised in the aqueous phase. This was removed by filtration and recrystallised from water and ethanol/ether to give the alcohol hydrochloride (8g) m.p. 192-193°.

Alphacetylmethadol (IX)

(α-3-Acetoxy-6-dimethylamino-4,4-diphenylheptane)

The alcohol hydrochloride (VIII) (0.8g) was heated with acetic anhydride (10 cm^3) for 1 hour on a steam bath. The solvent was removed *in vacuo* and the hydrochloride salt of the product (IX) (0.6g) obtained m.p. 208-209° from ether/ethanol.

Betamethadol (X)

(β-6-Dimethylamino-4,4-diphenyl-3-heptanol)

Sodium (3.6g) was dissolved in absolute propanol[56]

($70\ cm^3$). To this solution methadone (3.6g) was added over a period of 15-20 minutes, maintaining a gentle refluxing solution. This solution was refluxed for a further 15 minutes after which it was carefully diluted with water and excess benzene. The benzene layer was washed with water and dried with anhydrous magnesium sulphate. The solvent was removed in vacuo and the residue acidified with ethanol, hydrochloric acid mixture, diluted with ether and stood overnight at 5° to give the hydrochloride salt of (X) (2.5g) m.p. 210-212° from acetone.

Betacetylmethadol (XI)

(β-3-Acetoxy-6-dimethylamino-4,4-diphenylheptane)

Betamethadol hydrochloride (100mg) was heated with acetic anhydride ($10\ cm^3$) as for the preparation of (IX) to yield the hydrochloride salt (XI) (50mg) m.p. 215-217° from acetone.

Diampromide (XII)

(N- 2-(Methylphenethylamino)propyl propionanilide)

An equimolar solution of methylphenethylamine and 2-bromopropionanilide[57] (prepared from 2-bromopropionyl bromide and aniline[58]) in dry benzene was heated under reflux for 4 hours to give 2-(N-methylphenethylamino)-propionanilide, 80% m.p. 65-67° from 40-60° petrol. Reduction of this compound with lithium aluminium hydride in dry tetrahydrofuran afforded an 80% yield of N^2-methyl-N^2-phenethyl-N^1-phenyl-1,2-propanediamine b.p. 138-140°/0.2mm Hg. This compound was acylated with excess propionic anhydride (2 hours reflux)and the solvent

removed in vacuo to yield 83% of the product (XII) which was distilled at 174-178°/0.5mm Hg.

Phenampromide (XIII)

(N-(1-Methyl-2-piperidinoethyl)propionanilide)

An equimolar benzene solution of aniline and 1-(2-brompropionyl)-piperidine[57] (prepared from 2-bromo-propionyl bromide and piperidine[59]) was heated under reflux for 4 hours to give 80% of 1-(2-anilinopropyl)piperidine m.p. 90-91° from 40-60° petrol. This compound on reduction with lithium aluminium hydride in dry tetra-hydrofuran afforded 75% of 1-(2-anilinopropyl)piperidine, 108-112°/0.4mm Hg. Acylation of this compound with propionic anhydride (2 hours reflux on a steam bath), removal of the solvent in vacuo gave 70% of (XIII) 124-128°/0.2mm Hg.

Dioxaphetyl butyrate (XIV)

(Ethyl-4-morpholino-2,2-diphenylbutyrate)

Diphenylacetonitrile (19.3g) was condensed with N-(2-chloroethyl)-morpholine (15g) in the presence of sodamide (4g) exactly as for the preparation of (VI) which gave 2,2-diphenyl-4-(N-morpholino)butyro nitrile (23g) recrystallised from 60-80° petrol.

This nitrile was hydrolysed and esterified in a combined reaction[60]. The nitrile (10g) was dissolved in a mixture of absolute ethanol (25 cm^3), conc. sulphuric acid (8 cm^3), water (0.1 cm^3) and ammonium chloride (1.8g). This was heated in a sealed glass tube for 16 hours at 150°. On completion of the reaction the contents were diluted, made alkaline with 40% sodium hydroxide and

and extracted into ether. The dense oily layer and the water layer were removed and discarded. The ether was removed in vacuo and the residual oil distilled at 175-180°/0.5mm Hg to yield the base (XIV) (4g) m.p. 65-70° from 40-60° petrol. The more stable hydrochloride salt was subsequently prepared by treatment with ethanol, hydrochloric acid mixture to give (XIV) hydrochloride m.p. 167-168° from acetone.

Prolintane (XV)

(1-(α-Propylphenethyl)pyrrolidine)

A solution of benzylpropyl ketone (12g) and pyrrolidine (5.5g) in methanol (50 cm^3) was shaken with hydrogen and platinic oxide catalyst (0.5g) at room temperature, 3 atmospheres[61] pressure until no further hydrogen was consumed. The catalyst was filtered off and the solvent removed in vacuo. The residual oil was dissolved in dilute hydrochloric acid and shaken with ether (to remove unreacted ketone), basified and the released amine taken up in ether. Concentration of the dried ethereal extract and subsequent distillation of the residual oil gave (XV) (9g) 153°/16mm Hg. From this the hydrochloride salt m.p. 133-134° from acetone was produced by treatment with ethanol, hydrochloric acid mixture.

Morphine methobromide (XVI)

A solution of equimolar quantities of anhydrous morphine and bromoethane in ethanol were heated under reflux for 1 hour. On cooling the methylbromide salt of morphine crystallised to give a 95% yield of (XVI) m.p.

265-266° from ethanol.

(The methyl iodide salt was prepared in exactly the same way m.p. 286-288°.)

APPENDIX 2

FORTRAN Source Program

2 (MACRO)

```
    LF SYSTEM4,NU


 0 MZ 25000
 1 LO DWSYST4
 2 RP DP,OL
 3 MN ON,DELETE
 4 1A OL *LP0
 5 OL *CR0
 6 AS *CR1,FILEDATA
 7 EN 0
 8 IF HAL(EE),GO 2A
 9 DELETE
10 EXIT
11 2A DP 0,TYPING ERROR PLEASE START AGAIN
12 RL *LP0
13 RL *CR0
14 RL *CR1
15 GO 1A
16 ****
17
```

```
      LIST(LP)
      PROGRAM(FXXXX)
      INPUT1=CR0
      INPUT3=CR1
      OUTPUT6=LP0
      COMPRESS INTEGER AND LOGICAL
      COMPACT
      TRACE0
      END
C     SMALL CORE RESIDENT MASTER RESPONSIBLE FOR
C     PRINTING THE SEARCH OPTIONS AVAILABLE AND CALLING THE REQUIRED
C     SUBROUTINE
      MASTER
      INTEGER NAME,FILEMS,FILEUV
      COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
     1FILEUV(200),FILESP(200),D(200),NAME(200,10),ITYPE(200),
     2NN(200),NI(200),DMS(200),DIR(200)
C     READIN READS ALL THE DATA HELD ON FILEDATA AND STORES
C      IT IN COMMON
      CALL READIN
      WRITE(6,10)
   10 FORMAT(1H0,10X,29H*****MISUSE OF DRUGS ACT*****,/,
     1 15X,36HDATA RETRIEVAL PACKAGE NOW OPERATING,/)
   11 WRITE(6,15)
   13 FORMAT(1H0,35HFOUR SEARCH OPTIONS ARE AVAILABLE:-,/,
     1 10X,13H(1)PEAK MATCH,/,
     2 10X,14H(2)NAME SEARCH,/,
     3 10X,19H(3)MOLECULAR WEIGHT,/,
     4 10X,20H(4)MOLECULAR FORMULA)
   12 WRITE(6,15)
   15 FORMAT(//,1X,36HPLEASE INSERT THE OPTION YOU REQUIRE,/,
     1 11X,18HNUMBER 1 TO 4 ONLY)
      READ(1,20)IOPT
   20 FORMAT(I0)
C     THE FOUR SEARCH OPTIONS ARE HELD IN FOUR SUBROUTINES
C     ANAL=PEAK MATCHING FOR MS,IR,UV,TLC DATA
C     NAM=NAME SEARCH(FIRST EIGHT CHARACTERS)
C     MASS=MOLECULAR WEIGHT SEARCH
C     FORM=MOLECULAR FORMULA SEARCH OR PARTIAL MOLECULAR
C     FORMULA SEARCH
      IF(IOPT.EQ.1) CALL ANAL
      IF(IOPT.EQ.2) CALL NAM
      IF(IOPT.EQ.3) CALL MASS
      IF(IOPT.EQ.4) CALL FORM
      IF((IOPT.LT.1).OR.(IOPT.GT.4)) GO TO 12
      WRITE(6,30)
   30 FORMAT(1H0,39HFOR A FURTHER SEARCH TYPE 1,0 TO FINISH)
      READ(1,40)IRET
   40 FORMAT(I0)
      IF(IRET.EQ.1) GO TO 11
      CONTINUE
      STOP
      END
```

```
C      READIN READS ALL THE DATA HELD ON FILEDATA AND STORES IT
C       IN COMMON
       SUBROUTINE READIN
       INTEGER FILEMS,FILEUV,NAME
       COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
      1FILEUV(200),FILESP(200),D(200),NAME(200,10),ITYPE(200),
      2NN(200),NI(200),DMS(200),DIR(200)
       DO 1000 I=1,200
       READ(3,5)(IFORM(I,J),J=1,7)
C      NEGATIVE VALUE FOR END OF FILE MARK
       IF(IFORM(I,1).EQ.-1) GO TO 150
       READ(3,6)SMASS(I)
       READ(3,10)(FILEMS(I,J),J=1,8)
       READ(3,20)(FILEIR(I,J),J=1,6)
       READ(3,30)FILEUV(I)
       READ(3,40)FILESP(I)
       READ(3,50)(NAME(I,J),J=1,10)
       READ(3,60)ITYPE(I)
 1000  CONTINUE
    5  FORMAT(7I3)
    6  FORMAT(F5.1)
   10  FORMAT(8I4)
   20  FORMAT(6F5.1)
   30  FORMAT(I4)
   40  FORMAT(F4.2)
   50  FORMAT(10A4)
   60  FORMAT(I2)
  150  CONTINUE
       RETURN
       END
```

```
C      NAM NAME SEARCH OPTION 2 IN MASTER
       SUBROUTINE NAM
       INTEGER UNAME,NAME,FILEMS,FILEUV
       COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
      1FILEUV(200),FILESP(200),D(200),NAME(200,10),ITYPE(200),
      2NN(200),NI(200),DMS(200),DIR(200)
       DIMENSION UNAME(10)
       WRITE(6,15)
   15  FORMAT(1H0,41HPLEASE INSERT THE NAME YOU WISH TO CHECK )
       READ(1,16)UNAME
   16  FORMAT(10A4)
       JN=0
       DO 1000 I=1,200
C      LIBARY SUBROUTINE COMP USED TO COMPARE THE FIRST EIGHT
C      CHARACTERS FOR EQUALITY IF THE NAME MATCHES
C      SUBROUTINE WRITE IS CALLED TO PRINT THE MATCH ON THE TERMINAL
       IF(IFORM(I,1).EQ.-1) GO TO 150
       II=12
       CALL COMP(II,NAME(I,1),1,UNAME(1),1)
       IF(II.NE.4) GO TO 1000
       II=12
       CALL COMP(II,NAME(I,2),1,UNAME(2),1)
       IF(II.NE.4) GO TO 1000
       IF(JN.GT.0) GO TO 18
       WRITE(6,20)
   20  FORMAT(//,37H THE FOLLOWING INFORMATION IS ON FILE)
   18  CALL WRITE(I)
       JN=JN+1
 1000  CONTINUE
  150  I=I-1
       WRITE(6,17)I
   17  FORMAT(//,1X,I3,19H COMPOUNDS SEARCHED,//)
       RETURN
       END
```

```
C      WRITE PRINTS THE INFORMATION OBTAINED BY THE MATCH
C      ROUTINE
       SUBROUTINE WRITE(I)
       INTEGER NAME,FILEMS,FILEUV
       COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
      1FILEUV(200),FILESP(200),D(200),NAME(200,10),ITYPE(200),
      2NN(200),NI(200),DMS(200),DIR(200)
       WRITE(6,80)(NAME(I,J),J=1,10)
       WRITE(6,81)(IFORM(I,J),J=1,7)
       WRITE(6,82)SMASS(I)
       WRITE(6,90)(FILEMS(I,J),J=1,8)
       WRITE(6,100)(FILEIR(I,J),J=1,6)
       WRITE(6,110)FILEUV(I)
       WRITE(6,120)FILESP(I)
C      TYPE READS THE VALUE IN THE FILE DESIGNATED TO A
C      PARTICULAR DRUG FAMILY AND WRITES THE CORRESPONDING DRUG
C      TYPE ON THE TERMINAL
       CALL TYPE(I)
    80 FORMAT(//,1X,14HCOMPOUND NAME:,10A4)
    81 FORMAT(1X,25HCHEMICAL FORMULA(BASE):,
      11HC,I2,1X,1HH,I2,1X,1HN,I1,1X,1HO,I1,1X,2HCL,I1,1X,1HS,
      2I1,1X,1HD,I1)
    82 FORMAT(1X,23HMOLECULAR WEIGHT(BASE):,F5.1)
    90 FORMAT(1X,26HMASS SPECTRAL EIGHT PEAKS:,8I4)
   100 FORMAT(1X,20HINFRA RED SIX PEAKS:,6F5.1)
   110 FORMAT(1X,24HULTRA-VIOLET LAMBDA MAX:,I4)
   120 FORMAT(1X,27HTHIN LAYER CURRY POWELL RF:,F4.2)
       RETURN
       END
```

```
C     PEAK MATCH ROUTINE SEARCH OPTION 1 IN THE MASTER
C     SEARCHES ANY COMBINATION OF THE ANALALYTICAL INFORMATION
C     ON FILE.
C     THE FILEDATA IS STORED IN COMMON AND THE UNKNOWN DATA IS
C     PEAKMS,PEAKIR,PEAKUV,SPOT,FOR MS IR UV TLC DATA RESPECTIVELY.
      SUBROUTINE ANAL
      INTEGER FILEMS,NAME,FILEUV,PEAKMS,PEAKUV,SCORE,NUM
      REAL FILEIR,FILESP,SPOT,PEAKIR
      COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
     1FILEUV(200),FILESP(200),D(200),NAME(200,10),ITYPE(200),
     2NN(200),NI(200),NMS(200),DIR(200)
      DIMENSION SCORE(200),PEAKMS(8),PEAKIR(6),NUM(16)
      WRITE(6,10)
   10 FORMAT(1H0,//,38H THE PROGRAM RETRIEVES INFORMATION ON ,/,
     149H ANY OF THE FOUR FOLLOWING ANALYTICAL TECHNIQUES ,/,
     25X,43H (1) MASS-SPECTRAL DATA ONE TO EIGHT PEAKS ,/,
     35X,37H (2) INFRA-RED DATA ONE TO SIX PEAKS ,/,
     45X,41H (3) ULTRA-VIOLET DATA ACIDIC LAMBDA MAX ,/,
     55X,37H (4) THIN LAYER DATA CURRY-POWELL RF ,/,
     644H THE PROGRAM OPERATES ON A MATCH BASIS AND  /,
     746H OUTPUTS THE COMPOUNDS IN ORDER OF BEST MATCH ,//)

    1 JN=0
      JJ=0
      KK=0
      DO 11 K=1,8
      PEAKMS(K)=0
   11 CONTINUE
      DO 12 J=1,6
      PEAKIR(J)=0
   12 CONTINUE
      PEAKUV=0
      SPOT=0
      DO 21 I=1,200
      SCORE(I)=0
   21 CONTINUE
```

```
      WRITE(6,20)
   20 FORMAT(1H0,30H DO YOU WISH TO CHECK MS DATA?,/,
     132H PLEASE TYPE 1 FOR YES 0 FOR NO )
      READ(1,30)M
      IF(M.EQ.0) GO TO 80
   35 WRITE(6,40)
   40 FORMAT(1H0,39H HOW MANY PEAKS DO YOU WISH TO COMPARE?,/,
     134H PLEASE TYPE A NUMBER FROM 1 TO 8 )
      READ(1,30)KK
      IF((KK.LT.1).OR.(KK.GT.8)) GO TO 35
      CONTINUE
      WRITE(6,60)
   60 FORMAT(38H PLEASE INSERT THE PEAKS ONE PER LINE )
      READ(1,30)(PEAKMS(K),K=1,KK)
      GO TO 90
   80 PEAKMS(1)=0
      CONTINUE
   90 WRITE(6,100)
  100 FORMAT(1H0,31H DO YOU WISH TO CHECK IR DATA? /,
     132H PLEASE TYPE 1 FOR YES 0 FOR NO )
      READ(1,30)M
      IF(M.EQ.0) GO TO 160
  115 WRITE(6,120)
  120 FORMAT(1H0,39H HOW MANY PEAKS DO YOU WISH TO COMPARE?,/,
     132H PLEASE TYPE NUMBER FROM 1 TO 6 )
  130 READ(1,30)JJ
      IF((JJ.LT.1).OR.(JJ.GT.6)) GO TO 115
C     IRCONV READS IN THE IR DATA OF THE UNKNOWN AND
C     CONVERTS WAVENUMBERS TO WAVELENGTHIF REQUIRED.
C     IT ALSO CHECKS FOR PEAKS IN UNCODED AREAS EG, NUJOL.
      CONTINUE
      CALL IRCONV(PEAKIR,JJ)
      GO TO 170
  160 PEAKIR(1)=0
      CONTINUE
  170 WRITE(6,180)
  180 FORMAT(1H0,31H DO YOU WISH TO CHECK UV DATA? /,
     132H PLEASE TYPE 1 FOR YES 0 FOR NO )
      READ(1,30)M
      IF(M.EQ.0) GO TO 210
  185 WRITE(6,190)
  190 FORMAT(1H0,37H PLEASE INSERT THE ACIDIC LAMBDA MAX )
      READ(1,30)PEAKUV
      IF((PEAKUV.GT.450).OR.(PEAKUV.LT.200)) GO TO 185
      GO TO 220
  210 PEAKUV=0
      CONTINUE
  220 WRITE(6,230)
  230 FORMAT(1H0,31H DO YOU WISH TO CHECK TLC DATA?,/,
     132H PLEASE TYPE 1 FOR YES 0 FOR NO )
      READ(1,30)M
      IF(M.EQ.0) GO TO 260
  235 WRITE(6,240)
  240 FORMAT(1H0,31H PLEASE INSERT CURRY-POWELL RF )
      READ(1,150)SPOT
      IF((SPOT.LT.0).OR.(SPOT.GT.0.99)) GO TO 235
      GO TO 270
  260 SPOT=0
      CONTINUE
  270 IF(JN.GE.1) GO TO 271
      N=0
  271 JL=0
```

```
244 C       THIS SECTION OF THE PROGRAM CARRIES OUT THE COMPARISONS
245 C       OF FILEDATA AGAINST THE UNKNOWNS
246 C       THE INDIVIDUAL COMPARISONS FOR EACH TECHNIQUE ARE CARRIED
247 C       OUT IN THE FOUR SUBROUTINES,MS.IR,UV,TLC.
248 C       THE VALUE IN SCORE IS CALCULATED FROM THE COMBINED MATCH
249 C       OF ALL THE TECHNIQUES ON THE BASIS:-
250 C                              MS=8(FOR SUCESSFUL MATCH)
251 C                              IR=4
252 C                              UV=2
253 C                             TLC=1
254 C       THE VALUE IN THE ARRAY D IS ORTAINED AS THE RANKING
255 C       ORDER FACTOR CALCULATED FOR MS AND IR WITHIN
256 C       THE SUBROUTTIES MS AND IR.
257         DO 1000 I=1,200
258         IF(JN.EQ.1) GO TO 1500
259         IF(IFORM(I,1).EQ.-1) GO TO 600
260  1500   CALL MS(PEAKMS,I,KK,NL,D(I))
261         SCORE(I)=NL
262         CALL IR(PEAKIR,I,JJ,NLL)
263         SCORE(I)=SCORE(I)+NLL
264         IF(SCORE(I).EQ.12) D(I)=DMS(I)+DIR(I)
265         IF(SCORE(I).EQ.8) D(I)=DMS(I)
266         IF(SCORE(I).EQ.4) D(I)=DIR(I)
267         IF(SCORE(I).LT.4) D(I)=1000
268         CALL UV(PEAKUV,I,NLLL)
269         SCORE(I)=SCORE(I)+NLLL
270         CALL TLC(SPOT,I,NLLLL)
271         SCORE(I)=SCORE(I)+NLLLL
272   560   CONTINUE
273         IF(JN.EQ.1) GO TO 1000
274         N=N+1
275  1000   CONTINUE
276 C       TERMINATOR FOR SCORE ARRAY=100.
277   600   SCORE(I)=100
278         D(I)=100
279         LK=0
280         LKK=0
281         DMIN=0
282         LK=0
283         DMS(I)=100
284         DIR(I)=100
285         NK(I)=100
286         NI(I)=100
```

```
      INUMB=16
      DO 800 JK=1,16
      NUM(JK)=INUMB-1
      INUMB=NUM(JK)
  800 CONTINUE
C     THE FOLLOWING THRLE LOOPS ARE RESPONSIBLE FOR SIFTING
C     THROUGH THE VALUES OF SCORE INORDER TO PRINT THE COMPOUND
C     WITH THE HIGHEST SCORE FIRST ON THE TERMINAL.
C     IF THERE ARE COMPOUNDS WITH EQUAL SCORE THE COMPOUND WITH THE
C     LOWEST D VALUE,IE THE HIGHEST RANK ORDER IS PRINTED FIRST.
      DO 850 JK=1,16
      IF((NUM(JK).EQ.7).AND.(KK.EQ.0)) GO TO 899
      IF((NUM(JK).EQ.7).AND.(LK.EQ.0)) CALL MSMISMATCH(I,KK)
      IF((NUM(JK).EQ.7).AND.(OMIN.GE.2)) CALL MSMISMATCH(I,KK)
      IF((NUM(JK).EQ.3).AND.(JJ.EQ.0)) GO TO 899
      IF((NUM(JK).EQ.3).AND.(LKK.EQ.0)) CALL IRMISMATCH(I,JJ)
      IF((NUM(JK).EQ.3).AND.(OMIN.GE.2)) CALL IRMISMATCH(I,JJ)
  899 DO 805 IJ=1,8
      DO 900 I=1,200
      IF(JK.EQ.16) GO TO 2000
      IF(SCORE(I).EQ.100) GO TO 805
      IF(SCORE(I).EQ.NUM(JK)) GO TO 950
  900 CONTINUE
      IF(JK.GE.13) GO TO 850
  805 CONTINUE
  850 CONTINUE
      GO TO 2000
  950 IF(JL.GE.10) GO TO 2000
      IF(SCORE(I).LT.4) GO TO 2020
      IF((D(I).GE.IJ-1).AND.(D(I).LT.IJ)) GO TO 2020
      GO TO 900
 2020 GO TO (951,953,955,957,959,961,
     1963,965,967,969,971,973,975,977,979),JK
```

```
C      FIFTEEN WRITE POSSIBILITIES ARE PRODUCED BY THE
C      MATCHING METHOD.A STAR SYSTEM IS USED TO GIVE A RAPID VISUAL
C      INDICATION OF THE BEST MATCH AVAILABLE.TOGETHER WITH THE
C      PRINTED D VALUE.
  951 WRITE(6,952)
  952 FORMAT(1H0,//,43H THE FOLLOWING COMPOUND MATCHES FOR MS,IR,UV,TLC
     16H DATA ,15H***************./)
  849 LK=0
      LKK=0
      WRITE(6,980)(NAME(I,J),J=1,10)
      WRITE(6,986)(IFORM(I,J),J=1,7)
      WRITE(6,987)SMASS(I)
      IF(DMIN.EQ.0).AND.(LK.EQ.0)) DMIN=D(I)
      IF(D(I).LT.DMIN) DMIN=D(I)
      JL=JL+1
      IF(SCORE(I).LT.8) GO TO 852
  851 WRITE(6,981)(FILEMS(I,J),J=1,8)
      LK=LK+1
      SCORE(I)=SCORE(I)-8
  852 IF(SCORE(I).LT.4) GO TO 854
  853 WRITE(6,982)(FILEIR(I,J),J=1,6)
      LKK=LKK+1
      SCORE(I)=SCORE(I)-4
  854 IF(SCORE(I).LT.2) GO TO 856
  855 WRITE(6,983)FILEUV(I)
      SCORE(I)=SCORE(I)-2
  856 IF(SCORE(I).LT.1) GO TO 860
  857 WRITE(6,984)FILESP(I)
  860 SCORE(I)=0
      IF((LK.LE.0).AND.(LKK.LE.0)) GO TO 861
      WRITE(6,995)D(I)
  861 CALL TYPE(I)
      GO TO 900
  953 WRITE(6,954)
  954 FORMAT(1H0,//,41H THE FOLLOWING MATCHES FOR MS,IR,UV DATA ,
     113X,14H**************,/)
      GO TO 849
  955 WRITE(6,956)
  956 FORMAT(1H0,//,42H THE FOLLOWING MATCHES FOR MS,IR,TLC DATA ,
     112X,15H***************,/)
      GO TO 849
  957 WRITE(6,958)
  958 FORMAT(1H0,//,37H THE FOLLOWING MATCHES FOR MS,IR DATA ,
     117X,12H************,/)
      GO TO 849
  965 WRITE(6,966)
  966 FORMAT(1H0,//,35H THE FOLLOWING MATCHES FOR MS ONLY ,
     119X,8H********,/)
      GO TO 849
  967 WRITE(6,968)
  968 FORMAT(1H0,//,42H THE FOLLOWING MATCHES FOR IR,UV,TLC DATA ,
     112X,7H*******,/)
      GO TO 849
  959 WRITE(6,960)
  960 FORMAT(1H0,//,41H THE FOLLOWING MATCHES FOR MS,UV,TLC DATA ,
     113X,11H***********,/)
      GO TO 849
  961 WRITE(6,962)
  962 FORMAT(1H0,//,42H THE FOLLOWING MATCHES FOR MS AND UV DATA ,
     112X,10H**********,/)
      GO TO 849
```

```
381   963 WRITE(6,964)
382   964 FORMAT(1H0,//,43H THE FOLLOWING MATCHES FOR MS AND TLC DATA ,
383      111X,9H*********,/)
384         GO TO 849
385   969 WRITE(6,970)
386   970 FORMAT(1H0,//,42H THE FOLLOWING MATCHES FOR IR AND UV DATA ,
387      112X,6H******,/)
388         GO TO 849
389   971 WRITE(6,972)
390   972 FORMAT(1H0,//,43H THE FOLLOWING MATCHES FOR IR AND TLC DATA ,
391      111X,5H*****,/)
392         GO TO 849
393   973 WRITE(6,974)
394   974 FORMAT(1H0,//,35H THE FOLLOWING MATCHES FOR IR ONLY ,
395      119X,4H****,/)
396         GO TO 849
397   975 WRITE(6,976)
398   976 FORMAT(1H0,//,43H THE FOLLOWING MATCHES FOR UV AND TLC DATA ,
399      111X,3H***,/)
400         GO TO 849
401   977 WRITE(6,978)
402   978 FORMAT(1H0,//,35H THE FOLLOWING MATCHES FOR UV ONLY ,
403      119X,2H**,/)
404         GO TO 849
405   979 WRITE(6,985)
406   985 FORMAT(1H0,//,36H THE FOLLOWING MATCHES FOR TLC ONLY ,
407      118X,1H*,/)
408         GO TO 849
409    30 FORMAT(I0)
410   150 FORMAT(F0.0)
411   980 FORMAT(16H COMPOUND NAME :,10A4)
412   986 FORMAT(24H CHEMICAL FORMULA(BASE):,
413      1HC,I2,1X,1HH,I2,1X,1HF,I1,1X,1HO,I1,1X,2HCL,I1,1X,
414      2HS,I1,1X,1HP,I1)
415   987 FORMAT(24H MOLECULAR WEIGHT(BASE):,F5.1)
416   981 FORMAT(22H MASS-SPECTRA EIGHT PEAKS :,814)
417   982 FORMAT(22H INFRA-RED SIX PEAKS :,6F5.1)
418   983 FORMAT(26H ULTRA-VIOLET LAMBDA MAX :,I4)
419   984 FORMAT(18H CURRY-POWELL DF :,F4.2)
420   995 FORMAT(9H D VALUE=,F5.2)
421  2000 CONTINUE
422         NM=N
423         IF(JN.EQ.0) WRITE(6,2001)N
424         IF(JN.GE.1) WRITE(6,2001)NM
425  2001 FORMAT(1H0,//,I6,20H COMPOUNDS SEARCHED ,//)
426         WRITE(6,2010)
427  2010 FORMAT(1H0,39H DO YOU WISH TO CHECK ANOTHER COMPOUND ,/,
428      12?H INSERT 1 FOR YES 0 FOR NO )
429         READ(1,30)JN
430         IF(JN.EQ.1) GO TO 1
431         CONTINUE
432         RETURN
433         END
```

```
C      MS COMPARES THE UNKNOWN MASS SPECTRUM WITH THAT IN THE
C      FILE.
       SUBROUTINE MS(PEAKMS,I,KK,NL)
       INTEGER PEAKMS,PEAKUV,FILEMS,FILEUV
       DIMENSION PEAKMS(8)
       COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
      1FILEUV(200),FILESP(200),D(200),NAME(200,10),ITYPE(200),
      2NN(200),NI(200),DMS(200),DIR(200)
       CONTINUE
       IF(PEAKMS(1).EQ.0) GO TO 405
       D(I)=0
       NN(I)=0
       SUM=0
       DO 350 K=1,KK
       DO 400 J=1,8
       IF(IABS(FILEMS(I,J)-PEAKMS(K)).EQ.0) GO TO 410
  400  CONTINUE
  350  CONTINUE
C      IF THE COMPOUND MATCHES FOR THE NUMBER OF PEAKS
C      REQUIRED(KK),THE SCORE VALUE NL IS SET TO 8,IF NOT NL
C      IS SET TO 0.
C      THE RANKING ORDER FACTOR IS CALCULATED AS THE SUM OF THE
C      SQUARES OF THE DIFFERENCES BETWEEN THE POSITIONS
C      OF THE MATCHING PEAKS J AND K.
C      THIS VALUE IS THEN DEVIDED BY THE NUMBER OF PEAKS COMPARED
C      AND STORED IN THE ARRAY D.
  405  NL=0
       DMS(I)=SUM/NN(I)
       GO TO 430
  410  NN(I)=NN(I)+1
       A=J-K
       A=A**2
       SUM=SUM+A
       IF(NN(I).EQ.KK) GO TO 420
       GO TO 350
  420  NL=8
       DMS(I)=SUM/NN(I)
  430  CONTINUE
       RETURN
       END
```

```
C       IR COMPARES THE UNKNOWN IR SPECTRUM WITH THAT IN THE
C       FILE IN AN EXACTLY SIMILAR MANNER TO THAT FOR MS.
        SUBROUTINE IR(PEAKIR,I,JJ,NLL)
        INTEGER PEAKMS,PEAKUV,FILEMS,FILEUV
        DIMENSION PEAKIR(6)
        COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
       1FILEUV(200),FILESP(200),D(200),NAME(200,10),ITYPE(200),
       2NN(200),NI(200),DMS(200),DIR(200)
        IF(PEAKIR(1).EQ.0) GO TO 460
        DIR(I)=0
        NI(I)=0
        SUM=0
        DO 440 K=1,JJ
        DO 450 J=1,6
        IF(ABS(FILEIR(I,J)-PEAKIR(K)).LE.0.2) GO TO 480
   450  CONTINUE
   440  CONTINUE
C       THE SCORE IS SET TO 4 FOR THE COMPLETE MATCH OF JJ PEAKS
C       OR 0 FOR NO MATCH.
   460  NLL=0
        DIR(I)=SUM/NI(I)
        GO TO 500
   480  NI(I)=NI(I)+1
C       THE RANKING ORDER FACTOR D IS CALCULATED AS FOR MS.
        A=J-K
        A=A**2
        SUM=SUM+A
        IF(NI(I).EQ.JJ) GO TO 490
        GO TO 440
   490  NLL=4
        DIR(I)=SUM/NI(I)
   500  CONTINUE
        RETURN
        END
```

```
      SUBROUTINE MSMISMATCH(I,KK)
      INTEGER FILEMS,FILEUV
      COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
     1FILEUV(200),FILESP(200),D(200),NAME(200,10),ITYPE(200),
     2NN(200),NI(200),DMS(200),DIR(200)
      WRITE(6,700)
  700 FORMAT(1H0,20HMSMISMATCH OPERATING)
      LK=KK-1
      DO 1000 ID=1,5
  901 DO 903 I=1,200
      IF(NN(I).EQ.100) GO TO 999
      IF(NN(I).EQ.LK) GO TO 905
  903 CONTINUE
 1000 CONTINUE
  999 LK=LK-1
      IF(LK.EQ.KK-2) GO TO 899
      GO TO 901
  905 IF((DMS(I).GE.ID-1).AND.(DMS(I).LE.ID)) GO TO 800
      GO TO 903
  800 WRITE(6,810)(FILEMS(I,J),J=1,8),(NAME(I,J),J=1,10)
  810 FORMAT(1H0,//,34H THE FOLLOWING MATCHES FOR MS DATA,/,8I4,1X,10A4)
  820 WRITE(6,830)NN(I),KK,DMS(I)
  830 FORMAT(1H0,I2,1X,12HPEAKS OUT OF,I2,5X,8HD VALUE=,F5.2)
      GO TO 903
  899 RETURN
      END
```

```
      SUBROUTINE IRMISMATCH(I,JJ)
      INTEGER FILEMS,FILEUV
      COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
     1FILEUV(200),FILESP(200),D(200),NAME(200,10),ITYPE(200),
     2NN(200),NI(200),DMS(200),DIR(200)
      WRITE(6,700)
  700 FORMAT(1H0,20HIRMISMATCH OPERATING)
      LKK=JJ-1
      DO 1000 ID=1,3
  901 DO 903 I=1,200
      IF(NI(I).EQ.100) GO TO 999
      IF(NI(I).EQ.LKK) GO TO 905
  903 CONTINUE
 1000 CONTINUE
  999 LKK=LKK-1
      IF(LKK.EQ.JJ-2) GO TO 899
      GO TO 901
  905 IF((DIR(I).GE.ID-1).AND.(DIR(I).LT.ID)) GO TO 800
      GO TO 903
  800 WRITE(6,810)(FILEIR(I,J),J=1,6),(NAME(I,J),J=1,10)
  810 FORMAT(1H0,//,34H THE FOLLOWING MATCHES FOR IR DATA,/,
     16F5.1,1X,10A4)
  820 WRITE(6,830)NI(I),JJ,DIR(I)
  830 FORMAT(1H0,I2,1X,12HPEAKS OUT OF,I2,5X,8HD VALUE=,F5.2)
      GO TO 903
  899 RETURN
      END
```

```
560 C       UV COMPARES THE UNKNOWN UV SPECTRUM WITH THAT IN THE FILE.
561         SUBROUTINE UV(PEAKUV,I,NLLL)
562         INTEGER PEAKMS,PEAKUV,FILEMS,FILEUV
563         COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
564        1FILEUV(200),FILESP(200),D(200),NAME(200,10),ITYPE(200),
565        2NN(200),NI(200),DMS(200),DIR(200)
566         IF(PEAKUV.EQ.0) GO TO 510
567         CONTINUE
568         IF(IABS(FILEUV(I)-PEAKUV).LE.4) GO TO 520
569 C       THE SCORE IS SET TO > FOR A MATCH WITHIN THE WINDOW
570 C       OR 0 FOR NO MATCH.
571     510 NLLL=0
572         GO TO 530
573     520 NLLL=2
574     530 CONTINUE
575         RETURN
576         END
```

```
577 C       TLC COMPARES THE UNKNOWN RF WITH THAT IN THE FILE.
578         SUBROUTINE TLC(SPOT,I,NLLLL)
579         INTEGER PEAKMS,PEAKUV,FILEMS,FILEUV
580         COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
581        1FILEUV(200),FILESP(200),D(200),NAME(200,10),ITYPE(200),
582        2NN(200),NI(200),DMS(200),DIR(200)
583         IF(SPOT.EQ.0) GO TO 540
584         IF(ABS(FILESP(I)-SPOT).LE.0.15) GO TO 550
585 C       SCORE IS SET TO 1 FOR MATCH WITHIN THE WINDOW 0
586 C       FOR NO MATCH.
587     540 NLLLL=0
588         GO TO 560
589     550 NLLLL=1
590     560 CONTINUE
591         RETURN
592         END
```

```
593 C       TYPE IS RESPONSIBLE FOR PRINTING THE DRUG TYPE
594 C       CORRESPONDING TO A PARTICULAR NUMERICAL VALUE ASSOCIATED
595 C       WITH THE COMPOUND ON FILE.
596 C       FIVE NUMBERS ARE USED TO INDICATE FIVE DRUG TYPES
597 C       MORE CAN ADDED IF REQUIRED.
598         SUBROUTINE TYPE(I)
599         INTEGER FILEMS,FILEUV,NAME
600         COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
601        1FILEUV(200),FILESP(200),D(200),NAME(200,10),ITYPE(200),
602        2NN(200),NI(200),DMS(200),DIR(200)
603         IF(ITYPE(I).EQ.1) GO TO 10
604         IF(ITYPE(I).EQ.2) GO TO 30
605         IF(ITYPE(I).EQ.3) GO TO 20
606         IF(ITYPE(I).EQ.4) GO TO 40
607         IF(ITYPE(I).EQ.5) GO TO 50
608         GO TO 150
609      10 WRITE(6,300)
610     300 FORMAT(1H0,21HDRUG TYPE = MORPHINE )
611         GO TO 150
612      20 WRITE(6,310)
613     310 FORMAT(1H0,24HDRUG TYPE = AMPHETAMINE )
614         GO TO 150
615      40 WRITE(6,320)
616     320 FORMAT(1H0,22HDRUG TYPE = METHADONE )
617         GO TO 150
618      30 WRITE(6,330)
619     330 FORMAT(1H0,22HDRUG TYPE = PETHIDINE )
620         GO TO 150
621      50 WRITE(6,340)
622     340 FORMAT(1H0,25HDRUG TYPE = HALLUCINOGEN )
623     150 CONTINUE
624         RETURN
625         END
```

```
626 C      MASS SEARCH OPTION 3 IN MASTER,SEARCHES FOR MOLECULAR
627 C      WEIGHT,
628        SUBROUTINE MASS
629        INTEGER FILEMS,FILEUV,NAME
630        REAL SMASS,MASS,FILEIR,FILESP
631        COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
632       1FILEUV(200),FILESP(200),D(200),NAME(200,10),ITYPE(200),
633       2NN(200),NI(200),DMS(200),DIR(200)
634      1 WRITE(6,10)
635     10 FORMAT(1H0,29H PLEASE INSERT THE MOL WEIGHT)
636        READ(1,20)UMASS
637     20 FORMAT(F0.0)
638        IF((UMASS.LT.0.0).OR.(UMASS.GT.800.0)) GO TO 1
639        JN=0
640        DO 1000 I=1,200
641        IF(IFORM(I,1).EQ.-1) GO TO 150
642        IF(ABS(SMASS(I)-UMASS).NE.0.0)  GO TO 1000
643        IF(JN.GT.0) GO TO 18
644        WRITE(6,25)
645     25 FORMAT(//,32H THE FOLLOWING INFORMATION IS ON FILE)
646 C      WRITE USED TO PRINT INFORMATION ON MATCHING COMPOUND.
647     18 CALL WRITE(I)
648        JN=JN+1
649   1000 CONTINUE
650    150 I=I-1
651        WRITE(6,17)I
652     17 FORMAT(//,1X,I3,19H COMPOUNDS SEARCHED,//)
653        RETURN
654        END
```

```
655 C       FORM SEARCH OPTION 4 IN MASTER.MOLECULAR FORMULA SEARCH,
656 C       OR PARTIAL MOLECULAR FORMULA SEARCH.
657         SUBROUTINE FORM
658         INTEGER FILEMS,FILEUV,NAME,C,H,N,O,CL,S,P
659         REAL FILEIR,FILESP
660         COMMON IFORM(200,7),SMASS(200),FILEMS(200,8),FILEIR(200,6),
661        1FILEUV(200),FILESP(200),O(200),NAME(200,10),ITYPE(200),
662        2NN(200),NI(200),DMS(200),DIR(200)
663         DIMENSION NFORM(7),C(3),H(3),N(3),O(3),CL(3),S(3),P(3)
664         DATA C(1)/12HCARBONS=     /,H(1)/12HHYDROGEN=    /,
665        1N(1)/12HNITROGEN=    /,
666        2O(1)/12HOXYGEN=      /,CL(1)/12HCHLORINE=    /,
667        3S(1)/12HSULPHUR=     /,P(1)/12HPHOSPHOROUS=/
668         KK=0
669         WRITE(6,10)(C(K),K=1,3)
670      10 FORMAT(1HO,45H PLEASE INSERT THE FORMULA YOU WISH TO CHECK,/,
671        11X,3A4)
672         READ(1,20)NFORM(1)
673      20 FORMAT(I0)
674         KK=KK+1
675         WRITE(6,30)(H(K),K=1,3)
676      30 FORMAT(1HO,3A4,28H TYPE -1 IF FORMULA COMPLETE)
677         READ(1,20)NFORM(2)
678         IF(NFORM(2).EQ.-1) GO TO 50
679         KK=KK+1
680         WRITE(6,30)(N(K),K=1,3)
681         READ(1,20)NFORM(3)
682         IF(NFORM(3).EQ.-1) GO TO 50
683         KK=KK+1
684         WRITE(6,30)(O(K),K=1,3)
685         READ(1,20)NFORM(4)
686         IF(NFORM(4).EQ.-1) GO TO 50
687         KK=KK+1
688         WRITE(6,30)(CL(K),K=1,3)
689         READ(1,20)NFORM(5)
690         IF(NFORM(5).EQ.-1) GO TO 50
691         KK=KK+1
692         WRITE(6,30)(S(K),K=1,3)
693         READ(1,20)NFORM(6)
694         IF(NFORM(6).EQ.-1) GO TO 50
695         KK=KK+1
696         WRITE(6,30)(P(K),K=1,3)
697         READ(1,20)NFORM(7)
698         KK=KK+1
```

```
699      50 JN=0
700  C      THE FOLLOWING LOOPS CARRY OUT THE COMPARISONS ON A
701  C      SIEVE PRINCIPLE.
702  C      ANY VALUE WHICH DOES NOT MEET THE REQUIREMENTS IS THROWN OUT
703  C      AND ALL THOSE WHICH MEET THE REQUIREMENTS REMAIN  TO EXIT
704  C      AS SUCESSFUL MATCHES FROM THE LOOPS.
705         DO 100 I=1,200
706         DO 200 J=1,KK
707         IF(IFORM(I,1).EQ.-1) GO TO 150
708         IF(NFORM(J).EQ.0) GO TO 200
709         IF(IFORM(I,J).NE.NFORM(J)) GO TO 100
710    200  CONTINUE
711         IF(JN.GT.0) GO TO 18
712         WRITE(6,25)
713      25 FORMAT(//,32H THE FOLLOWING INFORMATION IS ON FILE)
714  C      WRITE USED TO PRINT INFORMATION ON MATCHING COMPOUND.
715      18 CALL WRITE(I)
716         JN=JN+1
717    100  CONTINUE
718    150  I=I-1
719         WRITE(6,17)I
720      17 FORMAT(//,1X,I5,19H COMPOUNDS SEARCHED.//)
721         RETURN
722         END
```

```
C      IRCONV READS THE IR INFORMATION AND CONVERTS ANY
C      WAVENUMBER INPUT TO WAVELENGTH,IT ALSO CHECKS FOR PEAKS
C      WITHIN THE NONCODED AREAS OF THE SPECTRUM,IE:-
C                6.7-7.5 MICRONS,NUJOL
C              LESS THAN 5 MICRONS
C           GREATER THAN 15 MICRONS.
C      ANY INPUT GREATER THAN 15 MICRONS IS TREATED AS WAVENUMBER AND
C      CONVERTED ACCORDINGLY.
       SUBROUTINE IRCONV(PEAKIR,JJ)
       DIMENSION PEAKIR(6)
       WRITE(6,100)
  100  FORMAT(38H PLEASE INSERT THE PEAKS ONE PER LINE )
       DO 92 K=1,JJ
   91  READ(1,10)PEAKIR(K)
   10  FORMAT(F6.0)
       IF(PEAKIR(K) .GT. 15.0) GO TO 11
       GO TO 111
   11  PEAKIR(K)=10000.0/PEAKIR(K)
  111  CONTINUE
       IF((PEAKIR(K) .GT. 6.7) .AND. (PEAKIR(K) .LT. 7.5)) GO TO 12
       IF((PEAKIR(K) .LT. 5.0) .OR. (PEAKIR(K) .GT. 15.0)) GO TO 12
       GO TO 92
   12  WRITE(6,13)
   13  FORMAT(1HO,35H PEAK POSITION ERROR PLEASE RETYPE )
       GO TO 91
   92  CONTINUE
       RETURN
       END
       FINISH
****
```

APPENDIX 3

Coded Analytical Data of Compounds Listed in the M.D.A. 1971

3.1 Molecular Weights in increasing order of size

3.2 Molecular Formulae in increasing order of size

3.3 Mass Spectra "Eight Peak Index" Recorded on Micromass 12B Spectrometer at C.R.E.

3.4 Infra-Red "Six Peak Index" Recorded as potassium bromide discs on P.E. 137 Spectrophotometer

3.5 Coded Ultra-Violet Spectra in increasing order of acidic λ_{MAX}

3.6 Thin-Layer Chromatography Data in increasing order of Curry-Powell Rf,

The following controlled substances were not included within the data collection because of the difficulties involved with analyses by the 4 stated methods, Cannabinol derivatives (including T.H.C.), Cannabis and Cannabis resin, Coca leaf, Opium and Poppy straw. Samples and standard methods of analysis for all of these are available at C.R.E.

The analytical data of the drugs Fencamfamin, Pemoline, Phenmetrazine and Prolintane have been recorded and included within the original (1972) collection but have since been removed from the M.D.A.

The 4 drugs, Bromo-S.T.P., Difenoxin, Drotebanol (all Schedule 2 Part B) and Propiram (Schedule 2 Part C) have recently been included within the Act. Samples and analytical data for these, although not included within this collection, are available at C.R.E. The drug Nicodicodine has been transferred from Schedule 2 Part B to Part C.

The following coded analytical data is still required:-

(i) Mass Spectra, Acetorphine, Bezitramide, Metopon, Phenomorphan, Phenoperidine and Norpethidine.

(ii) Infra-Red Spectra, Acetorphine, Bezitramide, Dimenoxadole, Etorphine, Phenoperidine and Methylphenidate.

(iii) Ultra-Violet Spectra, Bezitramide, Dimenoxadole, Dioxaphetyl butyrate, Lysergamide, Lysergide, Metazocine, Methyl dihydromorphine, Proheptazine and Norcodeine.

(iv) Thin-Layer Chromatography, Betacetylmethadol, Bezitramide, Bufotenine, Cannabinol, N,N-Diethyltryptamine, N,N-Dimethyltryptamine and Norpethidine.

Work is currently in progress at C.R.E. to complete the data collection.

3.1 MOLECULAR WEIGHTS

135.0 Amphetamine

135.0 Dexamphetamine

149.0 Methylamphetamine

149.0 Phentermine

163.0 Mephentermine

176.0 Pemoline

177.0 Phenmetrazine

183.5 Chlorphentermine

188.0 N,N-Dimethyltryptamine

191.0 Phendimetrazine

200.0 Pethidine int A

204.0 Bufotenine

204.0 Psilocin

209.0 S.T.P.

211.0 Mescaline

213.0 Ethylmorphine

213.0 Norpethidine

215.0 Pethidine int C

216.0 N,N-Diethyltryptamine

217.0 Prolintane

231.0 Metazocine

232.0 Methylphenidate

234.0 Methadone int

239.0 Benzphetamine

243.0 Norlevorphanol

247.0 Ketobemidone

247.0 Pethidine

250.0 Methaqualone

257.0 Levorphanol

257.0 Racemorphan

261.0 Alphaprodine

261.0 Betaprodine

261.0 Properidine

263.0 Dimethylthiambutene

263.0 Hydroxypethidine

267.0 Lysergamide

271.0 Desomorphine

271.0 Normorphine

271.0 Racemethorphan

274.0 Phenampromide

275.0 Alphameprodine

275.0 Betameprodine

275.0 Proheptazine

275.0 Trimeperidine

282.0 Methyldesorphine

284.0 Psilocybin

285.0 Hydromorphone

285.0 Morphine

285.0 Norcodeine

287.0 Allylprodine

287.0 Dihydromorphine

289.0 Benzoyl ecgonine

291.0 Diethylthiambutene

299.0 Codeine

299.0 Hydrocodone

299.0 Methyldihydromorphine

299.0 Metopon

301.0 Dihydrocodeine

301.0 Oxymorphone

303.0 Cocaine

303.0 Hydromorphinol

309.0 Isomethadone

309.0 Methadone

311.0 Alphamethadol

311.0 Betamethadol

311.0 Cannabinol

311.0 Dimepheptanol

311.0 Thebaine

313.0 Ethylmorphine

315.0 Oxycodone

321.0 Etoxeridine

321.0 Phenazocine

323.0 Lysergide (LSD 25)

324.0 Diampromide

327.0 Dimenoxadole

335.0 Norpipanone

336.0 Fentanyl

339.0 Moramide int

339.0 Noracymethadol

341.0 Thebacon

343.0 Acetyldihydrocodeine

346.0 Morpheridine

347.0 Phenomorphan

349.0 Dipipanone

351.0 Phenadoxone

352.0 Anileridine

353.0 Alphacetylmethadol

353.0 Betacetylmethadol

353.0 Dioxaphetyl butyrate

353.0 Methadyl acetate

361.0 Furethidine

361.0 Levophenacylmorphan

366.0 Piminodine

367.0 Benzethidine

367.0 Phenoperidine

369.0 Diampromide

375.0 Benzylmorphine

386.5 Clonitazene

392.0 Levomoramide

392.0 Racemoramide

392.0 Dextromoramide

396.0 Etonitazene

398.0 Pholcodine

404.0 Nicocodine

406.0 Nicodicodine

411.0 Ethylmethylthiambutene

411.0 Etorphine

430.0 Piritramide

452.0 Diphenoxylate

492.0 Bezitramide

495.0 Nicomorphine

585.0 Myrophine

3.2 MOLECULAR FORMULAE

C	H	N	O	Cl	S	P	Name
9	8	2	2				Pemoline
9	13	1					Amphetamine
9	13	1					Dexamphetamine
10	14	1		1			Chlorphentermine
10	15	1					Methylamphetamine
10	15	1					Phentermine
11	15	1	1				Phenmetrazine
11	17	1					Mephentermine
11	17	1	3				Mescaline
12	16	2					N,N-Dimethyltryptamine
12	16	2	1				Bufotenine
12	16	2	1				Psilocin
12	17	1	1				Phendimetrazine
12	17	2	4			1	Psilocybin
12	19	1	2				S.T.P.
13	11	1	2				Norpethidine
13	16	2					Pethidine int A
13	17	1	2				Pethidine int C
14	17	1					Dimethylthiambutene
14	18	1	2				Methylphenidate
14	20	2					N,N-Dimethyltryptamine
15	23	1					Prolintane
15	21	1	1				Metazocine
15	21	1	2				Ketobemidone
15	21	1	2				Pethidine

C	H	N	O	Cl	S	P	Name
15	21	1	3				Hydroxypethidine
16	14	2	1				Methaqualone
16	17	1	3				Normorphine
16	17	3	1				Lysergamide
16	19	1	4				Benzoyl ecgonine
16	21	1					Diethylthiambutene
16	21	1	1				Norlevorphanol
16	23	1	2				Alphaprodine
16	23	1	2				Betaprodine
16	23	1	2				Properidine
17	19	1	3				Hydromorphone
17	19	1	3				Morphine
17	19	1	3				Norcodeine
17	19	1	4				Oxymorphone
17	21	1					Benzphetamine
17	21	1	2				Desomorphine
17	21	1	3				Dihydromorphine
17	21	1	4				Cocaine
17	21	1	4				Hydromorphinol
17	23	1	1				Levorphanol
17	23	1	1				Racemorphan
17	25	1	2				Alphameprodine
17	25	1	2				Betameprodine
17	25	1	2				Proheptazine
17	25	1	2				Trimeperidine
18	20	1	2				Methyl desorphine

C	H	N	O	Cl	S	P	Name
18	21	1	1				Pipradrol
18	21	1	3				Codeine
18	21	1	3				Methyl dihydromorphine
18	21	1	3				Metopon
18	21	1	3				Hydrocodone
18	21	1	4				Oxycodone
18	25	1	1				Racemethorphan
18	25	1	2				Allylprodine
18	27	1	4				Etoxeridine
19	21	1	3				Thebaine
19	22	2					Methadone int
19	23	1	3				Ethylmorphine
20	23	1	4				Thebacon
20	23	4	2	1			Clonitazene
20	25	1	1				Normethadone
20	25	1	3				Dimenoxadole
20	25	1	4				Acetyldihydrocodeine
20	25	3	1				Lysergide (L.S.D.)
20	30	2	3				Morpheridine
21	23	1	5				Diamorphine
21	25	1	3				Moramide int
21	27		2				Cannabinol
21	27	1	1				Isomethadone
21	27	1	1				Methadone
21	28	2	1				Diapromide
21	29	1	1				Alphamethadol

C	H	N	O	Cl	S	P	Name
21	29	1	1				Betamethadol
21	29	1	1				Dimepheptanol
21	31	1	4				Furethidine
22	27	1	1				Phenazocine
22	27	1	3				Dioxaphetyl butyrate
22	28	2	1				Fentanyl
22	28	2	2				Anileridine
22	28	4	3				Etonitazene
22	29	1	2				Noracymethadol
23	29	1	1				Norpipanone
23	29	1	2				Phenadoxone
23	29	1	3				Benzethidine
23	29	1	3				Phenoperidine
23	30	2	2				Piminodine
23	30	2	4				Pholcodine
23	31	1	2				Alphacetylmethadol
23	31	1	2				Betacetylmethadol
23	31	1	2				Methadyl acetate
24	24	2	4				Nicocodeine
24	25	1	3				Benzylmorphine
24	26	2	4				Nicodicodine
24	27	1	2				Levophenacylmorphan
24	29	1	1				Phenomorphan
24	31	1	1				Dipipanone
25	32	2	2				Dextromoramide
25	32	2	2				Levomoramide

C	H	N	O	Cl	S	P	Name
25	32	2	2				Racemoramide
25	33	1	4				Ethylmethylthiambutene
25	33	1	4				Etorphine
27	35	1	5				Acetorphine
29	25	3	5				Nicomorphine
30	32	2	2				Diphenoxylate
31	32	4	2				Bezitramide
38	51	1	4				Myrophine

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5.8,	5.7,	7.8,	9.0,	14.1,	9.6	Alphameprodine HCL
5.8,	6.1,	13.2,	6.4,	7.8,	6.5	Methaqualone HCL
5.8,	6.6,	7.8,	9.0,	9.7,	10.5	Oxycodone
5.8,	6.6,	9.7,	7.9,	10.7,	10.2	Oxycodone HCL
5.8,	6.6,	8.9,	7.9,	9.1,	8.3	Anileridine
5.8,	7.7,	7.8,	10.3,	9.8,	12.2	Hydromorphone HCL
5.8,	7.8,	8.7,	8.2,	8.4,	6.2	Hydroxypethidine
5.8,	8.7,	9.0,	8.0,	9.3,	9.8	Nicomorphine HCL
5.8,	7.8,	9.8,	9.2,	8.8,	8.2	Metopon
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5.8,	7.9,	9.0,	9.5,	13.7,	6.6	Nicocodeine
5.8,	8.0,	7.8,	9.7,	6.6,	13.2	Hydromorphone
5.8,	8.1,	8.2,	8.8,	10.6,	10.5	Oxymorphone
5.8,	8.1,	8.2,	9.1,	8.5,	13.8	Morpheridine HCL
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5.8,	8.1,	14.2,	9.8,	13.8,	13.1	Methadyl acetate
5.8,	8.1,	14.2,	13.8,	9.8,	6.3	Noracymethadol HCL
5.8,	8.2,	8.7,	8.5,	7.7,	9.1	Pethidine HCL
5.8,	8.2,	8.9,	8.5,	9.4,	14.3	Etoxeridine HCL
5.8,	8.2,	13.6,	9.8,	8.7,	14.2	Benzethidine HCL
5.8,	8.3,	9.1,	14.2,	13.1,	9.9	Dioxaphetyl butyrate

5.8,	8.3,	8.9,	6.6,	8.1,	14.4	Anileridine di HCL
5.8,	8.5,	8.4,	9.6,	14.3,	13.2	Allylprodine
5.8,	8.5,	8.6,	8.4,	14.3,	9.6	Alphameprodine HCL
5.8,	8.5,	8.8,	14.4,	9.5,	9.7	Alphaprodine
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5.8,	8.6,	8.4,	9.7,	9.2,	8.2	Alphaprodine HCL
5.8,	8.6,	8.4,	9.7,	14.3,	9.2	Betaprodine HCL
5.8,	8.6,	8.8,	8.5,	9.3,	14.1	Trimeperidine HCL
5.8,	8.7,	9.0,	8.5,	8.0,	9.1	Myrophine
5.8,	8.8,	9.5,	8.5,	14.4,	8.2	Betaprodine
5.8,	8.9,	8.5,	8.3,	9.5,	7.7	Etoxeridine
5.8,	8.9,	8.5,	8.3,	9.3,	14.4	Furethidine
5.8,	9.0,	8.3,	7.8,	9.2,	8.8	Properidine
5.8,	9.0,	8.5,	8.3,	7.7,	14.4	Morpheridine
5.8,	9.0,	8.5,	14.4,	8.3,	10.5	Benzethidine
5.8,	10.4,	8.5,	8.9,	8.2,	6.6	Diphenoxylate
5.8,	14.2,	13.0,	9.0,	9.2,	8.8	Methadone
5.8,	14.4,	8.2,	8.8,	13.2,	14.1	Diphenoxylate HCL
5.9,	6.3,	8.0,	12.9,	7.8,	14.3	Ketobemidone
5.9,	8.2,	8.7,	7.7,	9.8,	14.4	Norpethidine HCL
5.9,	8.8,	14.3,	14.1,	11.6,	8.8	Levomoramide
5.9,	9.2,	14.1,	14.3,	8.0,	9.0	Phenadoxone HCL
5.9,	14.0,	9.0,	13.2,	10.3,	10.5	Dipipanone HCL
5.9,	14.0,	13.2,	6.2,	10.2,	9.1	Isomethadone
5.9,	14.2,	13.0,	9.1,	9.3,	8.9	Methadone HCL
5.9,	14.3,	6.6,	9.0,	9.2,	13.3	Dipipanone
5.9,	14.3,	13.2,	9.0,	10.2		Normethadone HCL

5.9,	14.3,	13.4,	13.3,	6.6,	9.2	Piritramide
6.0,	6.1,	13.3,	6.2,	9.5,	7.7	Lysergamide
6.0,	6.2,	12.9,	13.1,	7.9,	7.6	Methaqualone
6.0,	6.3,	14.4,	7.9,	8.5,	8.8	Diampromide
6.0,	6.0,	6.3,	8.9,	7.9,	14.2	Phenampromide
6.0,	8.0,	6.2,	8.2,	7.9,	8.8	Norlevorphanol
6.0,	14.2,	13.2,	14.0,	14.9,	10.4	Isomethadone HCL
6.0,	14.3,	6.3,	7.9,	8.5,	8.6	Diampromide
6.0,	14.3,	6.6,	7.9,	7.8,	8.1	Fentanyl
6.0,	14.3,	13.2,	9.2,	8.4,	6.3	Pirintramide
6.1,	9.0,	14.3,	11.7,	14.0,	8.9	Levomoramide
6.1,	13.9,	7.9,	7.8,	6.6,	6.2	Phenampromide HCL
6.1,	14.2,	9.0,	13.2,	14.0,	6.2	Racemoramide
6.2,	7.7,	9.1,	8.3,	8.0,	9.4	Lysergide (L.S.D.)
6.2,	8.0,	7.7,	14.0,	8.3,	8.9	Dextromoramide Tartrate
6.3,	5.9,	7.8,	8.2,	10.2,	10.6	Ketobemidone HCL
6.3,	7.9,	13.6,	14.2,	12.4,	6.0	Pethidine int C
6.3,	9.7,	6.5,	9.0,	8.3,	8.8	Cannabinol
6.4,	13.6,	7.8,	8.1,	12.4,	10.8	Pethidine int C HCL
6.6,	7.9,	9.0,	9.4,	8.9	12.7	Codeine
6.6,	7.9,	9.7,	8.0,	8.7,	9.5	Dihydrocodeine
6.6,	8.1,	13.5,	7.7,	6.2,	8.4	Etonitazene
6.6,	8.1,	14.5,	6.2,	7.9,	6.3	Phenazocine
6.6,	8.2,	7.8,	7.6,	14.3,	13.3	Phenomorphan
6.6,	8.8,	8.6,	9.1,	6.1,	6.0	Pholcodine
6.6,	9.4,	9.6,	7.9,	8.8,	8.4	Ethylmorphine
7.6,	6.6,	13.6,	12.5,	9.2,	12.0	Clonitazene

7.6,	8.0,	12.6,	9.4,	9.7,	9.0	Normorphine
7.8,	5.8,	9.0,	13.6,	8.1,	8.0	Cocaine HCL
7.8,	6.0,	8.6,	7.6,	6.4,	6.3	Fentanyl
7.8,	7.7,	7.6,	5.7,	8.7,	8.1	Hydrocodone Acid Tartrate
7.8,	9.5,	12.5,	12.7,	8.9,	8.4	Norcodeine
7.8,	9.6,	6.6,	9.8,	13.3,	9.5	Benzylmorphine
7.9,	5.8,	6.2,	13.9,	9.0,	9.8	Benzoyl ecgonine
7.9,	9.1,	5.8,	6.7,	13.5,	9.5	Nicodicodine
8.0,	7.0,	9.4,	8.8,	8.3,	14.7	Dihydrocodeine Tartrate
8.0,	8.9,	12.4,	10.6,	12.0,	9.2	Morphine
8.0,	10.6,	10.4,	9.2,	13.4,	12.5	Dihydromorphine
8.0,	12.0,	6.6,	12.4,	12.6,	6.1	Bufotenine Oxalate
8.1,	5.8,	8.3,	5.7,	9.7,	8.5	Diamorphine HCL
8.1,	5.8,	8.6,	9.8,	13.7,	7.6	Norpethidine HCL
8.1,	5.8,	14.2,	6.6,	9.9,	9.7	Alphacetylmethadol
8.1,	5.8,	14.2,	6.6,	9.9,	9.7	Methadyl acetate
8.1,	5.8,	14.3,	9.8	13.9	9.1	Betacetylmethadol HCL
8.1,	6.2,	12.6,	10.5,	8.9,	9.2	Morphine-N-Oxide
8.1,	6.3,	7.9,	13.2,	7.7,	6.2	Metazocine
8.1,	6.6,	7.9,	13.3,	6.2,	7.2	Norlevorphanol
8.1,	6.6,	9.6,	8.0,	6.2,	11.8	Racemthorphan
8.1,	6.6,	13.3,	7.8,	6.3,	7.6	Norlevorphanol
8.1,	7.7,	9.6,	9.4,	7.9,	9.9	Racemethorphan HBr
8.1,	7.8,	6.3,	6.6,	6.2,	7.9	Racemorphan
8.1,	8.2,	13.3,	6.6,	7.9,	6.2	Levophenacylmorphan
8.1,	8.7,	11.0,	6.2,	7.8,	9.7	Thebaine HCL

8.2,	5.8,	7.9,	8.9,	11.1,	8.7	Thebacon HCL
8.2,	7.8,	5.8,	12.7,	6.7,	9.3	Acetyldihydrocodeine Base.
8.2,	8.1,	14.2,	13.2,	7.9,	7.7	Phenazocine HBr
8.2,	8.4,	5.8,	5.7,	8.4,	9.5	Diamorphine
8.2,	9.6,	6.6,	11.5,	9.2,	8.5	S.T.P. HCL
8.2,	9.6,	6.6,	14.6,	11.5,	8.5	S.T.P. Base
8.2,	11.6,	11.0,	7.6,	12.6,	9.0	Methyl desorphine Base
8.2,	14.3,	6.0,	6.5,	8.8,	7.8	Pemoline Base
8.3,	8.7,	9.2,	6.0,	13.0,	9.5	Levophenacylmorphan Methane Sulphonate
8.4,	6.6,	9.5,	9.7,	13.6,	12.8	Clonitazene HCL
8.5,	8.3,	8.7,	5.8,	6.3,	9.7	Piminodine Esylate
8.7,	5.8,	8.5,	14.5,	9.3,	13.3	Betaprodine HCL
8.8,	14.2,	13.4,	6.6,	6.3,	6.2	Amphetamine Sulphate
8.8,	14.2,	13.4,	6.6,	6.3,	6.2	Dexamphetamine Sulphate
8.9,	6.3,	8.1,	6.6,	9.9,	10.1	Mescaline
8.9,	8.1,	6.3,	10.0,	6.6,	12.2	Mescaline Sulphate
8.9,	9.1,	9.2,	13.2,	14.3,	10.0	Phendimetrazine Base
8.9,	10.3,	9.0,	7.9,	9.5,	9.1	Pholcodine
9.0,	5.9,	14.3,	13.1,	6.6,	8.0	Phenadoxone
9.0,	7.6,	6.6,	9.2,	10.2,	9.7	Hydromorphinol
9.0,	7.7,	7.9,	8.2,	9.4,	8.7	Phendimetrazine Bitartrate
9.0,	9.3,	12.7,	7.6,	8.5,	10.6	Morphine Sulphate
9.0,	14.0,	14.3,	6.3,	13.0,	9.7	Mephentermine
9.1,	5.8,	5.9,	7.9,	13.7,	8.2	Cocaine
9.1,	6.3,	5.8,	7.9,	8.8,	8.1	Oxymorphone

9.1,	7.6,	9.4,	7.9,	9.5,	10.7	Morphine Methobromide
9.2,	14.3,	13.2,	10.4,	9.0,	10.1	Phenmetrazine HCL
9.4,	7.8,	9.0,	12.6,	10.7,	8.0	Codeine
9.4,	7.9,	9.6,	8.9,	8.5,	12.5	Ethylmorphine HCL
9.4,	10.9,	8.5,	8.1,	11.5,	12.5	Psilocybin
9.5,	10.6,	9.0,	10.4,	8.0,	12.7	Codeine Phosphate
9.6,	8.1,	7.7,	7.8,	9.3,	12.1	Levomoramide Tartrate
9.6,	9.7,	8.4,	6.6,	12.5,	13.1	Benzylmorphine HCL
9.6,	12.0,	9.4,	8.0,	8.1,	13.7	Psilocin
10.7,	10.4,	10.5,	12.6,	9.4,	13.5	Dihydromorphine HCL
11.5,	8.1,	8.7,	13.4,	11.1,	9.7	Methyl desorphine HCL
12.0,	8.0,	8.2,	9.6,	9.5,	13.8	Psilocin
12.3,	9.2,	9.9,	11.8,	7.8,	13.3	Chlorphentermine HCL
12.7,	7.6,	9.3,	9.0,	8.9,	10.6	Morphine HCL
12.7,	7.8,	9.5,	8.9,	8.4,	7.9	Norcodeine
12.9,	14.1,	13.4,	8.8,	9.9,	6.2	Prolintane
13.2,	14.3,	7.9,	8.9,	8.7,	10.1	Pethidine int A
13.3,	8.0,	8.6,	10.7,	7.6,	8.8	Desomorphine
13.4,	14.1,	14.4,	6.3,	7.7,	10.1	Pipradrol HCL
13.4,	14.3,	9.5,	6.3,	9.3,	9.6	Methylamphetamine HCL
13.5,	9.0,	9.4,	9.2,	8.1,	13.8	N,N-Diethyltryptamine
13.5,	9.9,	8.1,	9.6,	9.1,	9.3	N,N-Dimethyltrypt-amine
13.6,	8.1,	9.1,	9.6,	9.9,	12.4	N,N-Dimethyltrypt-amine
13.6,	14.0,	8.0,	9.3,	11.3,	11.6	Ethylmethylthiam-butene HCL

13.6,	14.3,	13.0,	13.2,	9.2,	9.0	Benzphetamine HCL
13.8,	14.2,	11.7,	12.8,	6.2,	8.4	Phentermine
13.9,	13.6,	11.6,	9.1,	9.5,	8.8	Dimethylthiam-butene HCL
14.0,	5.9,	8.3,	9.0,	14.9,	8.1	Moramide int HCL
14.0,	5.9,	8.8,	6.2,	9.0,	12.9	Dipipanone HCL
14.0,	13.5,	11.7,	8.0,	12.0,	6.2	Diethylthiam-butene HCL
14.1,	12.8,	8.8,	13.0,	6.6,	8.8	Alphamethadol
14.2,	9.0,	13.1,	9.5,	10.2,	9.9	Betamethadol

3.5 U.V. λ_{MAX}

251 Levophenacylmorphan

254 Fentanyl

256 Norpethidine

256 Pethidine int A

256 Pemoline

256 Phenmetrazine

256 Phendimetrazine

256 Phenoperidine

256 Norpethidine

257 Allyprodine

257 Alphameprodine

257 Alphamethadol

257 Amphetamine

257 Alphaprodine

257 Betameprodine

257 Betamethadol

257 Benzethidine

257 Betaprodine

257 Cocaine

257 Dexamphetamine

257 Diampromide

257 Diphenoxylate

257 Methylamphetamine

257 Methylphenidate

257 Moramide int

257 Pethidine

257 Pethidine int C

257 Phenampromide

257 Phenoperidine

257 Piminodine

257 Piritramide

257 Properidine

257 Trimeperidine

258 Anileridine

258 Betaprodine

258 Benzphetamine

258 Etoxeridine

258 Furethidine

258 Mephentermine

258 Methadone int

258 Noracymethadol

258 Norpipanone

258 Phentermine

258 Pipadrol

258 Prolintane

258 Racemoramide

259 Alphacetylmethadol

259 Betacetylmethadol

259 Dipipanone

259 Dimepheptanol

259 Isomethadone

259 Levomoramide

259 Methadone

279 Phenomorphan

280 Hydrocodone

280 Metopon

280 Norlevorphanol

280 Oxycodone

281 Hydromorphone

281 Oxymorphone

281 Thebacon

282 Benzylmorphine

282 Dihydrocodeine

282 Etonitazene

283 Acetorphine

283 Clonitazene

283 Dihydromorphine

283 Methyl desorphine

283 Myrophine

283 Pholcodine

283 Thebaine

284 Acetyldihydrocodeine

284 Cannabinol

284 Codeine

284 Hydromorphinol

284 Morphine

284 Morphine-N-Oxide

285 Ethylmorphine

285 Normorphine

287 Etorphine

3.6 T.L.C. Rf.

0.02 Pholcodine

0.06 Psilocybin

0.08 Hydromorphinol

0.09 Oxymorphone

0.11 Lysergamide

0.12 Hydrocodone

0.12 Normorphine

0.14 Morphine

0.14 Morphine-N-Oxide

0.15 Hydromorphone

0.16 Bufotenine

0.16 Codeine

0.16 Dihydromorphine

0.16 Oxycodone

0.18 Norcodeine

0.20 Dihydrocodeine

0.22 Hydrocodone

0.22 Morpheridine

0.24 Metopon

0.25 Mescaline

0.25 Methyl dihydromorphine

0.25 Nicomorphine

0.30 Anileridine

0.30 Betaprodine

0.30 Nicodicodine

0.31 Nicocodine

0.31 Psilocin

0.32 Thebaine

0.33 Diampromide

0.34 Acetyldihydrocodeine

0.35 Ethylmorphine

0.35 Desomorphine

0.36 Pethidine int C

0.36 Thebacon

0.38 Cocaine

0.38 Pethidine int A

0.38 Piritramide

0.39 Ketobemidone

0.40 Benzoyl ecgonine

0.40 Benzylmorphine

0.44 Methyl desorphine

0.47 Lysergide (L.S.D.)

0.48 Hydroxypethidine

0.48 Metazocine

0.48 Phendimetrazine

0.49 Phenmetrazine

0.50 Ketobemidone

0.50 Properidine

0.50 Racemethorphan

0.51 Amphetamine

0.51 Dexamphetamine

0.51 Methylamphetamine

0.52 S.T.P.

0.54 Etoxeridine

0.54 Pethidine

0.56 Proheptazine

0.58 Alphaprodine

0.59 Racemorphan

0.60 Dimethylthiambutene

0.60 Levomoramide

0.60 Levorphanol

0.60 Moramide int

0.60 Norlevorphanol

0.60 Phentermine

0.61 Betameprodine

0.61 Dextromoramide

0.61 Racemoramide

0.62 Dimenoxadole

0.62 Mephentermine

0.63 Etorphine

0.63 Methylphenidate

0.65 Chlorphentermine

0.65 Trimeperidine

0.66 Methadone int

0.66 Racemethorphan

0.67 Diethylthiambutene

0.67 Normethoadone

0.68 Acetorphine

0.68 Clonitazene

0.68 Phenampromide

0.68 Phenomorphan

0.70 Furethidine

0.70 Norpipanone

0.70 Pipradrol

0.71 Ethylmethylthiambutene

0.72 Etonitazene

0.73 Isomethadone

0.73 Pemoline

0.74 Alphamethadol

0.74 Betamethadol

0.74 Dimepheptanol

0.74 Methadone

0.75 Allylprodine

0.75 Alphacetylmethadol

0.75 Alphameprodine

0.75 Benzphetamine

0.75 Dioxaphetyl butyrate

0.75 Methadyl acetate

0.76 Diampromide

0.76 Prolintane

0.77 Phenadoxone

0.78 Levophenacylmorphan

0.79 Noracymethadol

0.80 Benzethidine

0.83 Myrophine

0.83 Piminodine

0.85 Dipipanone

0.86 Fentanyl

0.86 Phenazocine

0.90 Diphenoxylate

0.91 Benzethidine

0.94 Methaqualone

3.7 FULL MONOGRAPHS

SCHEDULE 2 PART 1 CLASS A

No. 1 Acetorphine

C27 H35 N1 05 MW = 453.0

UV = 283

TLC = 0.68

TYPE = Morphine

No. 2 Allylprodine

C18 H25 N1 02 MW = 287.0

MS = 172, 214, 42, 57, 110, 91, 173, 44

IR = 5.8, 8.5, 8.4, 9.6, 14.3, 13.2

UV = 257

TLC = 0.75

TYPE = Pethidine

No. 3 Alphacetylmethadol

C23 H31 N1 02 MW = 353.0

Di-HCL

MS = 72, 43, 73, 46, 91, 71, 42, 225

IR = 5.8, 8.1, 14.2, 9.8, 13.8, 13.1

Base

IR = 8.1, 5.8, 14.2, 6.6, 9.9, 9.7

UV = 259

TLC = 0.75

TYPE = Methadone

No. 4 Betacetylmethadol

C23 H31 N1 02 MW = 353.0

Di-HCL

MS = 72, 43, 44, 91, 278

IR = 8.1, 5.8, 14.3, 9.8, 13.9, 9.1

UV = 259

TYPE = Methadone

No. 5 Alphameprodine

C17 H25 N1 02 MW = 275.0

HCL

MS = 97, 172, 91, 105, 57, 42, 77, 201

IR = 5.8, 8.5, 8.6, 8.4, 14.3, 9.6

Base

IR = 5.7, 8.5, 8.6, 8.7, 8.4, 9.6

UV = 257

TLC = 0.75

TYPE = Pethidine

No. 6 Betameprodine

C17 H25 N1 02 MW = 275.0

HCL

MS = 97, 172, 91, 105, 57, 42, 77, 201

IR = 5.8, 8.5, 8.6, 8.7, 8.4, 14.3

Base

IR = 5.7, 8.7, 8.5, 14.4, 9.5, 9.3

UV = 257

TLC = 0.61

TYPE = Pethidine

No. 7 Alphamethadol (Dimepheptanol)

C21 H29 N1 01 MW = 311

Base

MS = 72, 56, 91, 129, 105, 130, 73, 57

IR = 14.1, 12.8, 8.8, 13.0, 6.6, 8.8

HCL

IR = 14.2, 13.0, 10.2, 9.0, 9.2, 9.4

UV = 257

TLC = 0.74

TYPE = Methadone

No. 8 Betamethadol

C21 H29 N1 01 MW = 311.0

Base

MS = 72, 73, 91, 58, 253, 193, 42, 115

IR = 14.2, 9.0, 13.1, 9.5, 10.2, 9.9

UV = 257

TLC = 0.74

TYPE = Methadone

No. 9 Alphaprodine

C16 H23 N1 02 MW = 261.0

HCL

MS = 172, 187, 144, 84, 42, 57, 188, 44

IR = 5.8, 8.6, 8.4, 9.7, 9.2, 8.2

Base

IR = 5.8, 8.5, 8.8, 14.4, 9.5, 9.7

UV = 257

TLC = 0.58

TYPE = Pethidine

No. 10 Betaprodine

C16 H23 N1 02 MW = 261.0

HCL

MS = 172, 187, 84, 42, 57, 188, 44

IR = 8.7, 5.8, 8.5, 14.5, 9.8, 13.3

IR = 5.8, 8.6, 8.4, 9.7, 14.3, 9.2

Base

IR = 5.8, 8.8, 9.5, 8.5, 14.4, 8.2

UV = 258

TLC = 0.30

TYPE = Pethidine

No. 11 Anileridine

C22 H28 N2 02 MW = 352.0

Base

MS = 246, 42, 247, 120, 172, 80, 218, 106

IR = 5.8, 6.6, 8.9, 7.9, 9.1, 8.3

Di-HCL

IR = 5.8, 8.3, 8.9, 6.6, 8.1, 14.4

UV = 258

TLC = 0.30

TYPE = Pethidine

No. 12 Benzethidine

C23 H29 N1 03 MW = 367.0

HCL

MS = 246, 91, 42, 233, 162, 57, 56, 149

IR = 5.8, 8.2, 13.6, 9.8, 8.7, 14.2

Base

IR = 5.8, 9.0, 8.5, 14.4, 8.3, 10.5

UV = 257

TLC = 0.91

TYPE = Pethidine

No. 13 Benzylmorphine

C24 H25 N1 02 MW = 375

HCL

MS = 284, 91, 375, 81, 42, 285, 175, 44

IR = 9.6, 9.7, 8.4, 6.6, 12.5, 13.1

Base

IR = 7.8, 9.6, 6.6, 9.8, 13.3, 9.5

UV = 282

TLC = 0.40

TYPE = Morphine

No. 14 Bezitramide

C31 H32 N4 02 MW = 492.0

MS =

IR =

UV =

TLC =

No. 15 Bufotenine

C12 H16 N2 01 MW = 204.0

MS = 58, 204, 146, 59, 42, 160, 43, 159

IR = 8.0, 12.0, 6.6, 12.4, 12.6, 6.1

UV = 277

TLC = 0.16

TYPE = Hallucinogen

No. 16 Cannabinol

C21 H27 02

MS = 295, 296, 43, 310, 238, 299, 58, 41

IR = 6.3, 9.7, 6.5, 9.0, 8.3, 8.8

UV = 284

TYPE = Hallucinogen

No. 17 Clonitazene

C20 H23 N4 02 CL1 MW = 386.5

Base

MS = 86, 57, 43, 71, 55, 69, 58, (41)

IR = 7.6, 6.6, 13.6, 12.5, 9.2, 12.0

HCL

IR = 8.4, 6.6, 9.5, 9.7, 13.6, 12.8

UV = 283

TLC = 0.68

No. 18 Cocaine

C17 H21 N1 04 MW = 303.0

HCL

MS = 82, 182, 44, 77, 83, 105, 94, 96

IR = 7.8, 5.8, 9.0, 13.6, 8.1, 8.0

IR = 5.8, 5.7, 7.8, 9.0, 14.1, 9.6

Base

IR = 9.1, 5.8, 5.9, 7.9, 13.7, 8.2

UV = 257

TLC = 0.38

No. 19 Desomorphine

C17 H21 N1 02 MW = 271.0

Base

MS = 271, 214, 44, 270, 228, 272, 42, 148

IR = 13.3, 8.0, 8.6, 10.7, 7.6, 8.8

UV = 277

TLC = 0.35

TYPE = Morphine

No. 20 Dextromoramide

C25 H32 N2 02 MW = 392.0

Tartrate

MS = 100, 265, 128, 56, 44, 55, 266, 42

IR = 6.2, 8.0, 7.7, 14.0, 8.3, 8.9

UV = 261

TLC = 0.61

TYPE = Methadone

No. 21 Diamorphine

C21 H23 N1 05 MW = 369.0

HCL

MS = 327, 369, 43, 268, 310, 42, 215, 128

IR = 8.1, 5.8, 8.3, 5.7, 9.7, 8.5

Base

IR = 8.2, 8.4, 5.8, 5.7, 8,4, 9.5

UV = 278

TLC = 0.33

TYPE = Morphine

No. 22 Diampromide

C21 H28 01 MW = 324.0

Base

MS = 162, 105, 44, 163, 57, 190, 106, 58

IR = 6.0, 6.3, 14.4, 7.9, 8.5, 8.8

IR = 6.0, 14.3, 6.3, 7.9, 8.5, 8.6

UV = 257

TLC = 0.76

TYPE = Methadone

No. 23 Diethylthiambutene

C16 H21 N1 S2 MW = 291.0

HCL

MS = 276, 219, 111, 277, 278, 42, 100, 97

IR = 14.0, 13.5, 11.7, 8.0, 12.0, 6.2

Base

IR = 14.4, 11.8, 8.1, 9.3, 13.3

UV = 288

TLC = 0.67

TYPE = Methadone

No. 24 Dihydrocodinone-o-carboxymethyl oxime

No Sample No Analytical Data

No. 25 Dihydromorphine

C17 H21 N1 03 MW = 287.0

Base

MS = 287, 70, 44, 42, 163, 59, 288, 286

IR = 8.0, 10.6, 10.4, 9.2, 13.4, 12.5

HCL

IR = 10.7, 10.4, 10.5, 12.6, 9.4, 13.5

UV = 283

TLC = 0.16

TYPE = Morphine

No. 26 Dimenoxadole

C20 H25 N1 03 MW = 327.0

Base

MS = 58, 105, 57, 43, 71, 55, (41,) 167

TLC = 0.62

TYPE = Methadone

No. 27 Dimepheptanol (See Alphamethadol)

No. 28 Dimethylthiambutene

C14 H17 N1 S2 MW = 263.0

HCL

MS = 248, 97, 219, 111, 72, 249, 56, 263

IR = 13.9, 13.6, 11.6, 9.1, 9.5, 8.8

UV = 288

TLC = 0.60

TYPE = Methadone

No. 29 Dioxaphetyl butyrate

C22 H27 N1 03 MW = 353.0

Base

MS = 100, 42, 56, 101, 114, 353, 165, 91

IR = 5.8, 8.3, 9.1, 14.2, 13.1, 9.9

TLC = 0.75

TYPE = Methadone

No. 30 Diphenoxylate

C30 H32 N2 02 MW = 452.0

HCL

MS = 246, 375, 42, 247, 91, 376, 156, 184

IR = 5.8, 14.4, 8.2, 8.8, 13.2, 14.1

Base

IR = 5.8, 10.4, 8.5, 8.9, 8.2, 6.6

UV = 257

TLC = 0.90

TYPE = Pethidine

No. 31 Dipipanone

C24 H31 N1 01 MW = 349.0

HCL

MS = 112, 113, 56, 57, 110, 91, 55, 42

IR = 14.0, 5.9, 8.8, 6.2, 9.0, 12.9

IR = 5.9, 14.0, 9.0, 13.2, 10.3, 10.5

Base

IR = 5.9, 14.3, 6.6, 9.0, 9.2, 13.3

UV = 259

TLC = 0.85

TYPE = Methadone

No. 32 Benzoyl ecgonine

$C_{16}H_{19}N_1O_4$ MW = 289

MS = 82, 124, 105, 77, 168, 122, 42, 83

IR = 7.9, 5.8, 6.2, 13.9, 9.0, 9.8

UV = 275

TLC = 0.40

No. 33 Ethylmethylthiambutene

C25 H33 N1 04 MW = 411.0

HCL

MS = 262, 219, 111, 97, 263, 56, 218, 42

IR = 13.6, 14.0, 8.0, 9.5, 11.3, 11.6

UV = 268

TLC = 0.71

TYPE = Methadone

No. 34 Etonitazene

C22 H28 N4 03 MW = 396.0

MS = 86, 162, 58, 87, 107, 105

IR = 6.6, 8.1, 13.5, 7.7, 6.2, 8.4

UV = 282

TLC = 0.72

No. 35 Etorphine

C25 H33 N1 04 MW = 411.0

MS = 44, 215, 324, 164, 45, 216, 162, 58

IR =

UV = 287

TLC = 0.63

TYPE = Morphine

No. 36 Etoxeridine

C18 H27 N1 04 MW = 321.0

HCL

MS = 246, 247, 42, 45, 91, 56, 219, 248

IR = 5.8, 8.2, 8.9, 8.5, 9.4, 14.3

Base

IR = 5.8, 8.9, 8.5, 8.3, 9.5, 7.7

UV = 258

TLC = 0.54

No. 37 Fentanyl

C22 H28 N2 01 MW = 336.0

MS = 121, 152, 93, 65, 122, 63, 153, 64

IR = 6.0, 14.3, 6.6, 7.9, 7.8, 8.1

IR = 7.8, 6.0, 8.6, 7.6, 6.4, 6.3

UV = 254

TLC = 0.86

TYPE = Pethidine

No. 38 Furethidine

C21 H31 N1 04 MW = 361.0

MS = 246, 247, 42, 71, 43, 56, 232

IR = 5.8, 8.9, 8.5, 8.3, 9.3, 14.4

UV = 258

TLC = 0.70

TYPE = Pethidine

No. 39 Hydrocodone

C18 H21 N1 03 MW = 299.0

Acid Tartrate

MS = 299, 44, 242, 59, 96, 42, 76, 243

IR = 7.8, 7.7, 7.6, 5.7, 8.7, 8.1

Base

IR = 5.8, 7.9, 6.6, 10.4, 9.5, 12.5

UV = 280

TLC = 0.22

TYPE = Morphine

No. 40 Hydromorphinol

C17 H21 N1 04 MW = 303.0

MS = 303, 70, 58, 44, 57, 42, 216, 286

IR = 9.0, 7.6, 6.6, 9.2, 10.2, 9.7

UV = 284

TLC = 0.08

TYPE = Morphine

No. 41 Hydromorphone

C17 H19 N1 03 MW = 285.0

Base

MS = 277, 214, 229, 228, 42, 96, 286, 70

IR = 5.8, 8.0, 7.8, 9.7, 6.6, 13.2

HCL

IR = 5.8, 7.7, 7.8, 10.3, 9.8, 12.2

UV = 281

TLC = 0.15

TYPE = Morphine

No. 42 Hydroxypethidine

C15 H21 N1 03 MW = 263.0

HCL

MS = 71, 140, 70, 263, 262, 189, 57, 42

IR = 5.8, 8.1, 8.5, 6.3, 10.5, 7.9

Base

IR = 5.8,7.8, 8.7, 8.2, 8.4, 6.2

UV = 275

TLC = 0.48

TYPE = Pethidine

No. 43 Isomethadone

C21 H27 N1 01 MW = 309

Base

MS = 58, 43, 128, 127, 59

IR = 5.9, 14.0, 13.2, 6.2, 10.2, 9.1

HI

MS = 58, 128, 127, 59, 193, 179, 178, 115

IR = 6.0, 14.2, 13.2, 14.0, 14.9, 10.4

UV = 293

TLC = 0.73

TYPE = Methadone

No. 44 Ketobemidone

C15 H21 N1 02 MW = 247.0

HCL

MS = 70, 44, 71, 57, 247, 190, 119, 191

IR = 6.3, 5.9, 7.8, 8.2, 10.2, 10.6

Base

IR = 5.9, 6.3, 8.0, 12.9, 7.8, 14.3

UV = 279

TLC = 0.50

TYPE = Pethidine

No. 45 Levomoramide

C25 H32 N2 02 MW = 392.0

Tartrate

MS = 100, 265, 128, 266, 56, 129, 55, 101

IR = 9.6, 8.1, 7.7, 7.8, 9.3, 12.1

Base

MS = 100, 128, 265, 55, 44, 42, 56, 129

IR = 6.1, 9.0, 14.3, 11.7, 14.0, 8.9

UV = 259

TLC = 0.61

TYPE = Methadone

No. 46 Levophenacylmorphan

C24 H27 N1 02 MW = 361.0

Methane Sulphonate

MS = 43, 58, 256, 45, 51, 55, 44, 56

IR = 8.3, 8.7, 9.2, 6.0, 13.0, 9.5

Base

IR = 8.1, 8.2, 13.3, 6.6, 7.9, 6.2

UV = 251

TLC = 0.78

TYPE = Morphine

No. 47 Levorphanol

C17 H23 N1 01 MW = 257.0

Tartrate

MS = 59, 257, 256, 150, 80, 42, 82, 200

IR = 7.7, 8.0, 8.2, 8.8, 9.4, 14.8

Base

IR = 8.1, 6.6, 13.3, 7.8, 6.3, 7.6

UV = 279

TLC = 0.60

TYPE = Morphine

No. 48 Lysergamide

C16 H17 N3 01 MW = 267.0

MS = 227, 44, 54, 196, 72, 222, 181, 45

IR = 6.0, 6.1, 13.3, 6.2, 9.5, 7.7

TLC = 0.11

TYPE = Hallucinogen

No. 49 Lysergide (LSD 25)

C20 H25 N3 01 MW = 323.0

IR = 6.2, 7.7, 9.1, 8.3, 8.0, 9.4

TLC = 0.47

TYPE = Hallucinogen

No. 50 Mescaline

C11 H17 N1 03 MW = 211.0

Sulphate

MS = 182, 181, 149, 44, 167, 211, (40), (41)

IR = 8.9, 8.1, 6.3, 10.0, 6.6, 12.2

Base

IR = 8.9, 6.3, 8.1, 6.6, 9.9, 10.1

UV = 268

TLC = 0.25

TYPE = Amphetamine

No. 51 Metazocine

C15 H21 N1 01 MW = 231.0

MS = 231, 216, 84, 124, 59, 42, 72, 74

IR = 8.1, 6.3, 7.9, 13.2, 7.7, 6.2

TLC = 0.48

TYPE = Morphine

No. 52 Methadone

C21 H27 N1 01 MW = 309.0

HCL

MS = 72, 73, 58, 57, 223, 165, 70, 56

IR = 5.9, 14., 13.0, 9.1, 9.3, 8.9

Base

IR = 5.8, 14.2, 13.0, 9.0, 9.2, 8.8

UV = 291

TLC = 0.74

TYPE = Methadone

No. 53 Methadyl acetate (See Alphacetylmethadol)

No. 54 Methyl desorphine

C18 H20 N1 02 MW = 282.0

HCL

MS = 283, 282, 160, 42, 284, 268, 110, 44

IR = 11.5, 8.1, 8.7, 13.4, 11.1, 9.7

Base

IR = 8.2, 11.6, 11.0, 7.6, 12.6, 9.0

UV = 283

TLC = 0.44

TYPE = Morphine

No. 55 Methyl dihydromorphine

C18 H21 N1 03 MW = 299.0

MS = 57, 43, 149, 58, 55, (41,) 69, 71

TLC = 0.25

TYPE = Morphine

No. 56 Metopon

C18 H21 N1 03 MW = 299.0

IR = 5.8, 7.8, 9.8, 9.2, 8.8, 8.2

UV = 280

TLC = 0.24

TYPE = Morphine

No. 57 Morpheridine

C20 H30 N2 03 MW = 346.0

HCL

MS = 246, 100, 42, 82, 91, 56, 232, (41)

IR = 5.8, 8.1, 9.1, 8.5, 13.8

Base

IR = 5.8, 9.0, 8.5, 8.3, 7.7, 14.4

UV = 257

TLC = 0.22

TYPE = Pethidine

No. 58 Morphine

C17 H19 N1 03 MW = 285.0

Sulphate

MS = 285, 42, 70, 162, 44, 284, 124, 59

IR = 9.0, 9.3, 12.7, 7.6, 8.5, 10.6

HCL

IR = 12.7, 7.6, 9.3, 9.0, 8.9, 10.6

Base

IR = 8.0, 8.9, 12.4, 10.6, 12.0, 9.2

UV = 280

TLC = 0.14

No. 59 Morphine methobromide

MS = 45, 58, 73, 285, 72, 80, 82, 42

IR = 9.1, 7.6, 9.4, 7.9, 9.5, 10.7

No. 60 Morphine-N-oxide

MS = 58, 285, 72, 42, 71, 59, 186, 44

IR = 8.1, 6.2, 12.6, 10.5, 8.9, 9.2

No. 61 Myrophine

C38 H51 N1 04 MW = 585.0

MS = 91, 43, 57, (41,) 73, 55, 60, 81

IR = 5.8, 8.7, 9.0, 8.5, 8.0, 9.1

UV = 283

TLC = 0.83

TYPE = Morphine

No. 62 Nicodicodine

C24 H26 N2 04 MW = 406.0

MS = 106, 78, 70, 59, 42, 284, 300, 44

IR = 7.9, 9.1, 5.8, 6.7, 13.5, 9.5

UV = 261

TLC = 0.30

TYPE = Morphine

No. 63 Nicomorphine

C29 H25 N3 05 MW = 495.0

HCL

MS = 172, 106, 42, 57, 78, 44, 214, 149

IR = 5.8, 7.8, 9.0, 8.0, 9.3, 9.8

IR = 5.8, 7.8, 9.7, 8.9, 13.6, 9.3

UV = 261

TLC = 0.25

TYPE = Morphine

No. 64 Noracymethadol

C22 H29 N1 02 MW = 339.0

HCL

MS = 58, 134, 43, 99, 59, 91, 44, 150

IR = 5.8, 8.1, 14.2, 13.8, 9.8, 6.3

UV = 258

TLC = 0.79

TYPE = Methadone

No. 65 Norlevorphanol

C16 H21 N1 01 MW = 243.0

MS = 45, 243, 136, 200, 159, 157, 198, 242

IR = 8.1, 6.6, 7.9, 13.3, 6.2, 7.2

IR = 6.0, 8.0, 6.2, 8.2, 7.9, 8.8

UV = 280

TLC = 0.60

TYPE = Morphine

No. 66 Normethadone

C20 H25 N1 01 MW = 295.0

HCL

MS = 58, 72, 71, 42, 59, 165, 91, 179

IR = 5.9, 14.3, 13.2, 9.0, 10.2

Base

IR = 14.3, 5.9, 6.3, 9.7, 8.9, 13.2

UV = 292

TLC = 0.67

TYPE = Methadone

No. 67 Normorphine

C16 H17 N1 03 MW = 271.0

MS = 271, 81, 150, 148, 45, 110, 42, 82

IR = 7.6, 8.0, 12.6, 9.4, 9.7, 9.0

UV = 285

TLC = 0.12

TYPE = Morphine

No. 68 Norpipanone

C23 H29 N1 01 MW = 335.0

HCL

MS = 98, 111, 44, (41,) 55, 99, 42, 149

IR = 14.3, 5.9, 13.2, 8.8, 9.1, 12.8

Base

IR = 14.3, 13.7, 5.9, 8.9, 13.2, 9.8

UV = 258

TLC = 0.70

TYPE = Methadone

No. 69 Oxycodone

C18 H21 N1 04 MW = 315.0

Base

MS = 315, 230, 70, 44, 316, 42, 140, 258

IR = 5.8, 6.6, 7.8, 9.0, 9.7, 10.5

HCL

IR = 5.8, 6.6, 9.7, 7.9, 10.7, 10.2

UV = 280

TLC = 0.16

TYPE = Morphine

No. 70 Oxymorphone

C17 H19 N1 04 MW = 301

MS = 44, 42, 301, 115, 70, 216, 91, 43

IR = 5.8, 8.1, 8.2, 8.8, 10.6, 10.5

IR = 9.1, 6.3, 5.8, 7.9, 8.8, 8.1

UV = 281

TLC = 0.09

TYPE = Morphine

No. 71 Pethidine

C15 H21 N1 02 MW = 247.0

HCL

MS = 71, 70, 57, 42, 44, 43, 247, 172

IR = 5.8, 8.2, 8.7, 8.5, 7.7, 9.1

IR = 5.8, 8.2, 8.6, 8.5, 7.6, 14.3

UV = 257

TLC = 0.54

No. 72 Phenadoxone

C23 H29 N1 02 MW = 351.0

HCL

MS = 162, 105, 57, 163, 114, 190, 44, 77

IR = 5.9, 9.2, 14.1, 14.3, 8.0, 9.0

Base

IR = 9.0, 5.9, 14.3, 13.1, 6.6, 8.0

UV = 292

TLC = 0.77

TYPE = Methadone

No. 73 Phenampromide

C17 H26 N2 01 MW = 274.0

Base

MS = 98, 125, 99, 42, 120, 55, 57

IR = 6.0, 6.6, 6.3, 8.9, 7.9, 14.2

HCL

IR = 6.1, 13.9, 7.9, 7.8, 6.6, 6.2

UV = 257

TLC = 0.68

TYPE = Methadone

No. 74 Phenazocine

C22 H27 N1 01 MW = 321.0

HBr

MS = 230, 58, 231, 44, 42, 105, 173, 56

IR = 8.2, 8.1, 14.2, 13.2, 7.9, 7.7

Base

IR = 6.6, 8.1, 14.5, 6.2, 7.9, 6.3

UV = 278

TLC = 0.86

TYPE = Morphine

No. 75 Phenomorphan

C24 H29 N1 01 MW = 347.0

IR = 6.6, 8.2, 7.8, 7.6, 14.3, 13.3

UV = 279

TLC = 0.68

TYPE = Morphine

No. 76 Phenoperidine

C23 H29 N1 03 MW = 367.0

UV = 256

TLC = 0.90

TYPE = Pethidine

No. 77 Piminodine

C23 H30 N2 02 MW = 366.0

Ethane Sulphonate

MS = 246, 366, 42, 106, 133, 247, 57, 260

IR = 8.5, 8.3, 8.7, 5.8, 6.3, 9.7

UV = 257

TLC = 0.83

TYPE = Pethidine

No. 78 Piritramide

C27 H34 N4 01 MW = 430.0

MS = 386, 138, 42, 387, 162, 110, 301, 91

IR = 5.9, 14.3, 13.4, 13.3, 6.6, 9.3

IR = 6.0, 14.3, 13.2, 9.2, 8.4, 6.3

UV = 257

TLC = 0.47

TYPE = Methadone

No. 79 Proheptazine

C17 H25 N1 02 MW = 275.0

MS = 58, 202, 57, 201, 42, 84, 44, 186

IR = 5.7, 8.5, 8.4, 14.3, 13.3, 8.2

TLC = 0.56

TYPE = Pethidine

No. 80 Properidine

C16 H23 N1 02 MW = 261.0

MS = 71, 70, 218, 57, 42, 44, 43, 174

IR = 5.8, 9.0, 8.3, 7.8, 9.2, 8.8

UV = 257

TLC = 0.50

TYPE = Pethidine

No. 81 Psilocin

C12 H16 N20 1 MW = 204.0

MS = 58, 204, 59, 42, 146, 160, 130, 77

IR = 9.6, 12.0, 9.4, 8.0, 8.1, 13.7

IR = 12.0, 8.0, 8.2, 9.6, 9.5, 13.8

UV = 266

TLC = 0.31

TYPE = Hallucinogen

No. 82 Psilocybin

C12 H17 N2 04 MW = 284.0

MS = 58, 204, 42, 59, 57, 44, 146, (41)

IR = 9.4, 10.9, 8.5, 8.1, 11.5, 12.5

UV = 268

TLC = 0.06

TYPE = Hallucinogen

No. 83 Racemethorphan

C18 H25 N1 01 MW = 271.0

HBr

MS = 59, 271, 58, 150, 270, 214, 42, 80

IR = 8.1, 7.7, 9.6, 9.4, 7.9, 9.9

Base

IR = 8.1, 6.6, 9.6, 8.0, 6.2, 11.8

UV = 277

TLC = 0.50

TYPE = Morphine

No. 84 Racemoramide

C18 H25 N1 01 MW = 392.0

IR = 6.1, 14.2, 9.0, 13.2, 14.0, 6.2

UV = 258

TLC = 0.61

TYPE = Methadone

No. 85 Racemorphan

C17 H23 N1 01 MW = 257.0

HBr

MS = 44, 43, 257, 59, 150, 200

Base

IR = 8.1, 7.8, 6.3, 6.6, 6.2, 7.9

UV = 278

TLC = 0.59

TYPE = Morphine

No. 86 Thebacon

C20 H23 N1 04 MW = 341.0

HCL

MS = 341, 298, 43, 42, 342, 284, 242, 299

IR = 8.2, 5.8, 7.9, 8.9, 11.1, 8.7

UV = 281

TLC = 0.36

TYPE = Morphine

No. 87 Thebaine

C19 H21 N1 03 MW = 311.0

HCL

MS = 311, 44, 255, 296, 310, 312, 42, 253

IR = 8.1, 8.7, 11.0, 6.2, 7.8, 9.7

UV = 283

TLC = 0.32

TYPE = Morphine

No. 88 Trimeperidine

C17 H25 N1 02 MW = 275.0

MS = 186, 201, 42, 202, 187, 56, 57, 71

IR = 5.8, 8.6, 8.8, 8.5, 9.3, 14.1

UV = 257

TLC = 0.65

TYPE = Pethidine

No. 89 Methadone intermediate

C19 H22 N2 MW = 234.0

MS = 58, 72, 42, 165, 192, 71, 59, 73

IR = 14.3, 13.2, 13.0, 9.6, 13.4, 8.6

UV = 258

TLC = 0.66

No. 90 Pethidine intermediate A

C13 H16 N2 MW = 200.0

MS = 57, 42, 43, 70, 71, 200, 199, 44

IR = 13.2, 14.3, 7.9, 8.9, 8.7, 10.1

UV = 256

TLC = 0.38

No. 91 N,N-Diethyltryptamine

C14 H20 N2 MW = 216.0

MS = 86, 58

IR = 13.5, 9.0, 9.4, 9.2, 8.1, 13.8

UV = 278

TYPE = Hallucinogen

No. 92 N,N-Dimethyltryptamine

C12 H16 N2 MW = 188.0

MS = 58, 188, 130, 59, 42, 77, 115, 143

IR = 13.5, 9.9, 8.1, 9.6, 9.1, 9.3

IR = 13.6, 8.1, 9.1, 9.6, 9.9, 12.4

UV = 277

TYPE = Hallucinogen

No. 93 S.T.P.

C12 H19 N1 02 MW = 209.0

HCL

MS = 44, 163, 91, 42, 71, 65, 43, 151

IR = 8.2, 9.6, 6.6, 11.5, 8.2, 8.5

Base

IR = 8.2, 9.6, 6.6, 14.6, 11.5, 8.5

UV = 288

TLC = 0.57

TYPE = Amphetamine

No. 94 Pethidine intermediate C

C13 H17 N1 02 MW = 215.0

HCL

MS = 42, 43, 44, 57, 70, 71, 103, 91

IR = 6.4, 13.6, 7.8, 8.1, 12.4, 10.8

Base

IR = 6.3, 7.9, 13.6, 14.2, 12.4, 6.0

UV = 257

TLC = 0.36

No. 95 Moramide intermediate

C21 H25 N1 03 MW = 339.0

MS = 100, 56, 101, 42, 165, 91, 115, 70

IR = 14.0, 5.9, 8.3, 9.0, 14.9, 8.1

UV = 257

TLC = 0.60

TYPE = Methadone

No. 96 Norpethidine

C13 H11 N1 02 MW = 213.0

HCL

IR = 8.1, 5.8, 8.6, 9.8, 13.7, 7.6

IR = 5.9, 8.2, 8.7, 7.7, 9.8, 14.4

UV = 256

TYPE = Pethidine

SCHEDULE 2 PART 2 CLASS B

No. 97 Acetyldihydrocodeine

C20 H25 N1 04 MW = 343.0

MS = 343, 284, 344, 300, 43, 70, 59, 226

IR = 8.2, 7.8, 5.8, 12.7, 6.7, 9.3

UV = 284

TLC = 0.34

TYPE = Morphine

No. 98 Amphetamine

C9 H13 N1 MW = 135.0

Sulphate

MS = 44, 103, 91, 65, 42, 104, 45, 102

IR = 8.8, 14.2, 13.4, 6.6, 6.3, 6.2

Base

IR = 14.2, 13.5, 6.2, 9.2, 12.1, 11.6

UV = 257

TLC = 0.51

No. 99 Codeine

C18 H21 N1 03 MW = 299.0

Phosphate

MS = 299, 81, 42, 229, 162, 124, 300, 44

IR = 9.5, 10.6, 9.0, 10.4, 8.0, 12.7

Base

IR = 6.6, 7.9, 9.0, 9.4, 8.9, 12.7

IR = 9.4, 7.8, 9.0, 12.6, 10.7, 8.0

UV = 284

TLC = 0.16

TYPE = Morphine

No. 100 Dexamphetamine (See Amphetamine)

No. 104 Methylphenidate

C14 H18 N1 02 MW = 232.0

HCL

MS = 84, 91, 55, 150, 146, 56, 85, 83

UV = 257

TLC = 0.63

TYPE = Amphetamine

No. 105 Nicocodeine

C24 H24 N2 04 MW = 404.0

MS = 282, 106, 78, 229, 267, 42, 124, 283

IR = 5.8, 7.9, 9.0, 9.5, 13.7, 6.6

IR = 5.8, 7.8, 7.9, 8.9, 8.0, 9.0

UV = 261

TLC = 0.31

TYPE = Morphine

No. 106 Norcodeine

C17 H19 N1 03 MW = 285.0

MS = 285, 81, 262, 148, 286, 214, 164, 110

IR = 7.8, 9.5, 12.5, 12.7, 8.9, 8.4

IR = 12.7, 7.8, 9.5, 8.9, 8.4, 7.9

TLC = 0.18

TYPE = Morphine

No. 101 Dihydrocodeine

C18 H23 N1 03 MW = 301.0

Tartrate

MS = 301, 44, 70, 164, 59, 42, 244, 302

IR = 8.0, 7.0, 9.4, 8.8, 8.3, 14.7

Base

IR = 6.6, 7.9, 9.7, 8.0, 8.7, 9.5

UV = 282

TLC = 0.20

TYPE = Morphine

No. 102 Ethylmorphine

C19 H23 N1 03 MW = 313.0

HCL

MS = 313, 243, 162, 124, 59, 42, 112

IR = 9.4, 7.9, 9.6, 8.9, 8.5, 12.5

Base

IR = 6.6, 9.4, 9.6, 7.9, 8.8, 8.4

UV = 285

TLC = 0.35

TYPE = Morphine

No. 103 Methylamphetamine

C10 H15 N1 MW = 149.0

HCL

MS = 58, 91, 56, 59, 42, 65, 134

IR = 13.4, 14.3, 9.5, 6.3, 9.3, 9.6

UV = 257

TLC = 0.51

TYPE = Amphetamine

No. 107 Phenmetrazine

C11 H15 N1 01 MW = 177.0

HCL

MS = 71, 42, 56, 43, 44, 177, 117, 51

IR = 9.2, 14.3, 13.2, 10.4, 9.0, 10.1

UV = 256

TLC = 0.49

No. 108 Pholcodine

C23 H30 N2 04

MS = 100, 114, 42, 56, 115, 70, 101, 55

IR = 6.6, 8.8, 8.6, 9.1, 6.1, 6.0

IR = 8.9, 10.3, 9.0, 7.9, 9.5, 9.5

UV = 283

TLC = 0.02

TYPE = Morphine

SCHEDULE 2 PART 2 CLASS C

No. 109 Benzphetamine

C17 H21 N1 MW = 239.0

MS = 91, 148, 149, 92, 65, 56, 42, 120

IR = 13.6, 14.3, 13.0, 13.2, 9.2, 9.0

UV = 258

TLC = 0.75

TYPE = Amphetamine

No. 110 Chlorphentermine

C10 H14 N1 MW = 183.5

HCL

MS = 58, 42, (41,) 125, 59, 168, 89, 63

IR = 12.3, 9.2, 9.9, 11.8, 7.8, 8.6

IR = 12.3, 9.2, 9.9, 11.8, 7.8, 13.3

UV = 267

TLC = 0.65

TYPE = Amphetamine

No. 111 Mephentermine

C11 H17 N1 MW = 163.0

MS = 72, 91, 73, 56, 148, (41,) 57, 42

IR = 9.0, 14.0, 14.3, 6.3, 13.0, 9.7

UV = 258

TLC = 0.62

TYPE = Amphetamine

No. 112 Methaqualone

C16 H14 N2 01 MW = 250.0

HCL

MS = 235, 250, 91, 233, 236, 65, 76, 251

IR = 5.8, 6.1, 13.2, 6.4, 7.8, 6.5

Base

IR = 6.0, 6.2, 12.9, 13.1, 7.9, 7.6

UV = 269

TLC = 0.94

No. 113 Pemoline

C9 H8 N2 02 MW = 176.0

MS = 107, 176, 90, 42, 105, 89, 77, 70

IR = 8.2, 14.3, 6.0, 6.5, 8.8, 7.8

UV = 256

TLC = 0.73

No. 114 Phendimetrazine

C12 H17 N1 01 MW = 191.0

Bitartrate

MS = 57, 42, 85, 44, 56, 77, 51, 70

IR = 9.0, 7.7, 7.9, 8.2, 9.4, 8.7

Base

IR = 8.9, 9.1, 9.2, 13.2, 14.3, 10.0

UV = 256

TLC = 0.48

No. 115 Phentermine

C10 H15 N1 MW = 149.0

MS = 58, 91, 59, 44, 42, 134, 65, 57

IR = 13.8, 14.2, 11.7, 12.8, 6.2, 8.4

UV = 258

TLC = 0.60

TYPE = Amphetamine

No. 116 Pipradrol

C18 H21 N1 O1 MW = 267.0

MS = 84, 56, 85, 77, 105, 55, 42, 51

IR = 13.4, 14.1, 14.4, 6.3, 7.7, 10.0

UV = 258

TLC = 0.70

No. 117 Prolintane

C15 H23 N1 MW = 217.0

MS = 126, 91, 127, 174, 55, 42, 97

IR = 12.9, 14.1, 13.4, 8.8, 9.9, 6.2

UV = 258

TLC = 0.76

TYPE = Amphetamine

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