4-1-1962

Mass spectra correlations and the appearance potentials of the major tobacco alkaloids

William Frederick Kuhn

Recommended Citation

Kuhn, William Frederick, "Mass spectra correlations and the appearance potentials of the major tobacco alkaloids" (1962). *Master's Theses.* Paper 185.

MASS SPECTRA CORRELATIONS

AND THE APPEARANCE POTENTIALS

OF THE MAJOR

TOBACCO ALKALOIDS

BY

WILLIAM FREDERICK KUHN

A THESIS
SUBMITTED TO THE GRADUATE FACULTY
OF THE UNIVERSITY OF RICHMOND
IN CANDIDACY
FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY

APPROVED:

E. S. Grable

W. Allan Powell

Jean ...e Pierce

Wm E. Trout

J. ... Worsham, Jr.

... Campbell

JUNE, 1962

DEDICATION

To Norma and our children; Jeffrey, Timothy,

Diane, and Gregory.

TABLE OF CONTENTS

INTRODUCTION

The main objectives of this investigation were three-fold: (1) to design and fabricate a heated inlet system for the mass spectrometer; (2) to obtain the mass spectra of the major tobacco alkaloids under normal operating conditions; and (3) to determine the ionization potentials of the alkaloids as well as the appearance potentials of some of the major fragment ions derived from the alkaloids.

The mass spectrometer is designed to analyze only materials in the vapor state. Since some materials do not exert sufficient vapor pressure at room temperature under reduced pressure to be analyzed directly, it is necessary to heat these materials before the analysis is possible. The tobacco alkaloids are among the many organic compounds which cannot be analyzed mass spectrometrically at room temperature and at a pressure of 1×10^{-6} mm. of Hg. or higher. Since this is the case, a suitable heated inlet must be improvised in order to vaporize the alkaloids. From the mass spectrum

of the alkaloid, it is then possible to arrive at a positive
identification of the material if it is present in a sample
of unknown composition.

The ionization potential of a molecule is simply an
additional physical constant similar to a boiling point,
melting point, etc. Generally speaking, it cannot be used
as a direct method of identification, but it can serve as an
additional parameter for substantiating the proposed structure
of a compound. The appearance potential of a fragment ion
may lend itself useful in determining such entities as bond
energy and heat of formation.

HISTORICAL

I. Theory of Operation of the Mass Spectrometer

The Consolidated Electrodynamics Corporation (CEC) model
21-103C mass spectrometer is comprised of three basic units.
These units are the inlet chassis, the analyzer assembly, and
the control panel. The mass spectrometer is an electronic
and high-vacuum instrument capable of quantitative and qualitative
analysis of mixtures of materials in the vapor state.

The inlet chassis contains the components necessary for
introduction of the unknown material as well as various control
panels for standardization of the pressures in the inlet and
exhaust systems of the instrument.

The analyzer assembly is the heart of the instrument. In
this assembly ion formation, bond rupture, acceleration, and
separation of the ions occur.

The control panel contains the components necessary for
stabilization of the magnet field, temperature control of the
ion source and other necessary power supplies. A thorough

description of the component parts of the CEC 21-103C mass spectrometer may be found in Mr. Varsel's thesis (227).

The mass spectrometer is based on the sorting of components according to the molecular weight or mass-to-charge ratios, and then recording these separate components. The principle of operation is illustrated in the attached figure. (a) A sample of the unknown substance is stored in a container at relatively low pressures. (b) The neutral molecules are then introduced through the inlet system, a series of special valves. (c) This conglomerate mixture of molecules passes through a gold leak, a small opening in gold foil. The gold leak passes only a limited number of molecules-practically a molecular flow. (d) In the ionization chamber, the Isatron, a higher vacuum is maintained. In the Isatron, the neutral molecules are bombarded with a stream of electrons from a heated filament. This bombardment results in the formation of positive ions, negative ions, and neutral particles. Of the ions formed, only the positive ions are of interest. (e) The positive ions leave the Isatron through a narrow slit. They are then accelerated to a high velocity by a strong electrostatic field, and pass through a second slit. The purpose of the slit is to electrostatically concentrate the ion beam as it passes through the accelerating region. (f) A magnetic field, parallel to the slits, diverts the fast-moving ions into circular paths,

Figure 1

3-LITER VOLUME

MICROMANOMETER
BRIDGE AMPLIFIER

MICROMANOMETER

LEAK ASSEMBLY

CONNECTOR

ISATRON

d e f

SAMPLE

a

INLET SYSTEM

b

c

HEATER ASSEMBLY

ISATRON MOUNT

CONNECTOR

ANALYZER ASSEMBLY

GALVANOMETERS

h

i

AMPLIFIER

ELECTROMETER
TUBE

LAMP

COLLECTOR ASSEMBLY

g

j RECORDING OSCILLOGRAPH
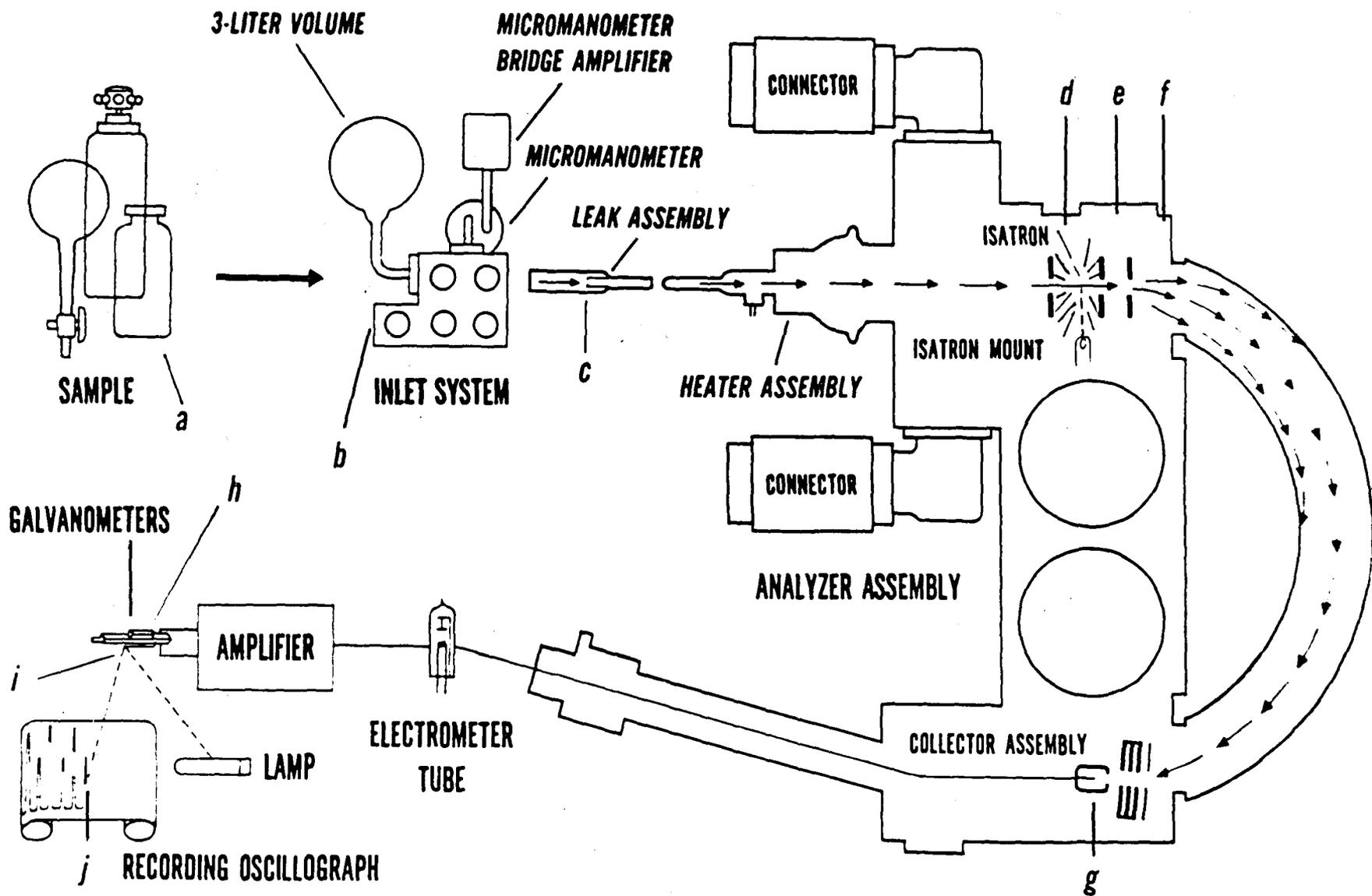
the radii of which are proportional to the mass-to-charge ratio and the velocity of the ion. Thus, the single ion beam is divided into individual beams, the lighter particles curving the most. (g) Ions of a given mass pass through the resolving slits and strike a collector located at 180° from their starting point. The charges given up to the collector by the ions are amplified by an electrometer. (h) The results, having been translated into an electric signal, are then fed to a bank of five galvanometers. Each galvanometer is set for a different sensitivity, hence initial sample pressures seldom need adjustment for adequate detection. (i) A tiny beam of light reflected from each galvanometer mirror is photographed on a moving roll of sensitive paper in the oscillograph. (j) Thus, the complete mass spectrum is obtained by focussing the separated ion beams successively on the collector by varying the ion-accelerating voltage.

II. High Temperature Mass Spectrometry

A.   Instrumentation and Techniques

High temperature mass spectrometry began in 1950 when
O'Neal and Wier (183) described a suitable introduction system
for vaporizing non-volatile organic compounds. Hence, the
field of high molecular weight mass spectrometry is only
twelve years old. Although a number of minor improvements
have been made since this initial report, the equipment and
techniques presently employed in high-temperature mass spect-
rometry are mainly those described by O'Neal and Wier.

The introduction of high boiling or high melting com-
pounds is more difficult than is the introduction of compounds
volatile at room temperature. Special problems of sample
introduction are encountered. A mercury orifice system may
be used at room temperature, but mercury is unsuitable for
use in heated systems because of its high vapor pressure
(0.1 mm at 82°C) and toxicity. It must be replaced by a liquid
of a much higher boiling point. For most purposes, gallium
metal or an alloy of gallium is a suitable substitute for
mercury. Gallium is a liquid between 30°C and 1983°C. It
resembles aluminum in its chemical properties including that
of forming a surface coating of oxide when heated in air.
Constant dipping of a pipette through this oxide surface leads
to a steady loss of the gallium because the oxide tends to stick

to the glass of the pipette. Fritted discs covered with gallium are likely to become blocked for the same reason. Periodical "shutdowns" are necessary to replace the discs. The usable period of time for such an introductory system is about 6-8 weeks. This period of operation can be extended by the application of CH_3SiCH_2Cl to the porous disc before the gallium is added to prevent the wetting of the glass by the gallium. Gallium expands on solidification and therefore, may burst its containing vessel if allowed to solidify.

The use of a gallium covered disc as a method of sample introduction was first described by O'Neal and Wier (183). Their sample system was made of glass and included a gallium tap capable of closing against a pressure differential of the order of a millimeter of mercury. A piece of soft iron, controlled by an external bar magnet, was lowered into one arm of the gallium filled tube which caused the level of the molten metal to rise in the other arm to isolate the sample reservoir from the pumps.

Development of an inlet system designed to reduce sorption effects at room temperature was described by Brown, Melpolder, and Young (39). They employed a parallel inlet system that could be heated to 300°C. The composition of a wax and wax distillate was obtained by analysis of the original material and of separated fractions. Melpolder, Brown, Washall, Doherty and Young (170) reported on the efficiency of thermal diffusion

or the separation of light lubricating oils into specific
hydrocarbon types. Their high temperature inlet system was
similar to that of Brown, Melpolder, and Young (170) except
that molten tin was used in the cut-off tap. Tin does not
wet glass and in this respect is more suitable than gallium.
Lumpkin and Johnson (146) reported on high temperature studies
using an inlet system differing from that of O'Neal's only
in the design of the isolating gallium valve. They used an
inverted cap that could be raised or lowered by an external
magnet to open and close the valve. Gallium sealed the valve
when closed.

An alternative design of the gallium tap was described
by Beynon and Nicholson (18). In their design a small glass
bell-jar was lowered into the gallium to form the seal.
The glass bell-jar was attached to a soft iron bar and could
be raised or lowered with a permanent magnet. Another type
of vacuum valve operable at elevated temperature was described
by Axelrod (7) which employed molten indium and was claimed to
overcome some of the disadvantages of similar valves described
in the literature. This valve, essentially, had the same virtues
as the one described by Páty and Schürer (188). The only new
feature of this valve was the use of indium to form the top
sealant rather than gallium. The seal is made by immersing a
glass enclosed soft iron bar into the molten indium to displace
enough indium to form a satisfactory seal.

The use of molten metals as sealants for high vacuum valves has not been limited to gallium or indium. Tin has been used satisfactorily by Balanaru (31) and Haaland (105). The main difference between the Haaland valve and those already discussed is that it is not operated by the use of magnets. This valve is opened and closed by melting the tin and raising or lowering a cold drawn steel cylinder with a metal bellows mechanism to transfer motion into the vacuum.

An all-glass high vacuum valve was designed and used by the Esso Research and Engineering Company. This valve eliminated sealants such as gallium, indium, tin or mercury. The valve employed 35/20 spherical joints which were meticulously lapped to insure a vacuum seal. The male member was made an integral part of the valve body and the female joint was attached to a mild steel bar. The valve was opened and closed by means of an magnetically operated cap. A manually operated all-glass valve, similar to the one described above, was designed by the Atlantic Refining Company. The magnetically operated cap was replaced by a glass bellows which was attached to the female portion of the lapped joint. This valve was unsatisfactory in our application because it lacked durability. In our first attempt to design a heated inlet system, we had incorporated an electro-magnetically-operated, indium-sealed, isolation valve. This valve was satisfactory but the indium adhered to the movable portion of the valve and with repeated usage, the weight of the movable

portion increased; thus more current was required to open the valve.

The use of gallium covered disk is restricted to the introduction of liquid samples. Solids may be introduced if they can be kept molten long enough to be drawn into the micropipette and introduced into the instrument through the disk. A heated pipette is also necessary for the analysis of very viscous liquids. It has been shown that only the relatively volatile liquids can flow quantitatively out of the pipette and through the disk. An alternative method for the introduction of samples with high melting points is to dissolve the sample in a suitable solvent and introduce the solution through the disk. The solvent must be removed from the instrument prior to the analysis of the sample to increase the partial pressure of sample. To do this, the sample system must be cooled after introduction of the solution to a temperature low enough so that the solvent can be pumped off, leaving the solute in the sample reservoir. Such a method is complicated and time consuming, and any volatile components in the sample will be removed whenever the solvent is removed. Furthermore, the gallium-covered disk must be cooled to enable the solution to be introduced. If the temperature of the gallium is above the boiling point of the solution, much of the liquid will be lost due to evaporation. Thus, quantitative transfer of the sample is difficult. In addition, sample fractionation may occur.

A suitable method for the introduction of either solid or liquid samples into a heated inlet system at a temperature up to 200°C was described by Caldecourt (47). The system contains a massive metal block which includes a valve for isolating the system from the pumps, a lead to the mass spectrometer and one to the sample reservoir. The sample is weighed into a small teflon bucket of the same diameter as the sealing slug. The sample bucket and another sealing slug are pushed down onto the sealing plug and into the entry port. The original sealing plug and the sample bucket fall through into the sample reservoir and the final slug seals the entry port. The sample reservoir must be replaced periodically to remove the teflon slugs. A similar method for introducing materials into a heat inlet, without the use of a gallium sinter, is to inject the sample through a silicone rubber septum which is attached to the evacuated sample reservoir. This method also requires shutting down the instrument to replace the perforated septum.

A gallium-covered orifice for introduction of samples into a heated inlet system was described by Genge (98). The total sample is injected through the orifice to avoid sample fractionation. The gallium can be recycled through the orifice after purification to remove contaminats from the original cycle.

Solids could be introduced from a demountable connection by the use of a suitable valve to close off the sample system

against atmospheric pressure. This necessitates the use of
a metal valve, and large areas of metal within the heated
sample must be avoided or, at best, kept to a minimum. One
of the main problems encountered in high temperature inlet
systems is the possibility of thermal decomposition which
exists with many organic compounds. It is this instability,
rather than limitations imposed by physical failure of con-
struction materials, which sets the upper temperature limit
of examination in a heated inlet system. Thermal degradation
is catalyzed by hot metal surfaces. Because of this possibility
of thermal degradation,efforts have been made in the past to
keep the area of metal surface in heated inlet systems to a
minimum. This catalytic effect is marginal for most compounds
in contact with stainless steel at temperatures to 200°C
and systems equipped with stainless steel valves are now in
use.

A suitable system which incorporates metal bellows valves
was designed by Metropolitan-Vickers Electrical Company and
described by Beynon (12). A weighed amount of sample can be
introduced into a glass bulb attached to a gold gasketed metal
union. The sample system can be evacuated at low temperature
and then, by placing a furnace around the bulb, the sample can
be vaporized rapidly through the metal system into the glass
reservoir. All metal surfaces on the reservoir side are covered

with an enamel which will withstand the repeated thermal
variations associated with the operation of the system. The
only metal surface to which the sample vapor is exposed is
the tip of the needle-valve and a small area surrounding it.

Even less volatile materials have been analyzed by placing
the sample in a small furnace within the ionization chamber and
evaporating it directly into the electron beam. An additional
method is to situate the furnace just outside the ionization
chamber so that a molecular beam of sample material flows into
this enclosure. Such techniques have been widely employed in
the examination of metals and inorganic compounds. Organic
materials can be examined only at comparatively low temperatures
where thermal decomposition is minimized. In some cases
thermal decomposition products can be used to characterize
high molecular weight compounds. Organic compounds which are
vaporized directly into the ionization chamber may condense and
form insulating layers on the walls of the chamber. These
layers adversely effect the performance of the instrument and
necessitate frequent cleaning. Most organic compounds can be
vaporized at temperatures below that of the ionization chamber.
Thus, this problem is not generally encountered.

Most of the heated inlet systems in use at this time have
been developed by the individual spectroscopists as the need
arose for such systems. These systems were necessary to extend

the capabilities of the mass spectrometer. Consolidated
Electrodynamics Corporation has designed and constructed a
heated inlet system which is an accessory item for the model
21-103C mass spectrometer. The safe operating temperature of
this inlet is 250°C and the introduction of the sample is
accomplished by introduction through a heated, gallium-
covered, sintered disk external to the oven. The disadvantages
of a fritted disk, pointed out previously, is that the sample
may be fractioned on the disk. Young and Laurene (243) have
modified the CEC standard heated inlet system for the analysis
of solids. The solid sample is placed in a tube equipped with
a 12/30 male joint. This tube is then fitted into the stainless
steel 12/30 female joint of the inlet system where the gallium
frit assembly is ordinarily attached. The stainless steel
joint must contain the teflon sealing ring normally used with
the gallium frit assembly. The sample is vaporized by an
external heater. Micro-Tek Instruments, Inc. also has con-
structed a standard inlet system for the analysis of gases,
liquids and solids. This inlet system is reportedly operable
from ambient to 800°F (427°C).

Some relatively nonvolatile organic compounds have been
analyzed by evaporization from a furnace located near the
electron beam. For example, de Mayo and Reed (166) have used
this technique to determine the molecular weights of the higher
terpenoids and the steroids. A difficulty in plotting the complete

spectrum of a compound by this technique is that of insuring
a high sensitivity and, at the same time, a constant rate of
evaporation. The rate can be maintained constant if the sample
on the inside walls of a Knudsen cell and the vapor evaporating
from the large surface is allowed to diffuse through a small
orifice into the ionizing electron beam. However, this latter
technique results in a low sensitivity. Further difficulties
occur if the method, surface ionization, is used for the
examination of mixtures of a wide range of vapor pressures,
since the sensitivity for any component of the mixture will be
a function of its vapor pressure. Nevertheless, the method
is useful in giving qualitative information on the species
present. It has been used to study the products of thermal
degradation of polymers such as polystyrene (32). Bradt
and Mohler have also used this technique to study the mass
spectra of polyvinylchloride, polymethylene, crepe rubber,
polyphenyl and poly-p-xylylene polymers (33). Hydrocarbon
fragments of masses greater than 1000 have been observed in
these latter measurements. The method has also been used for
studying the effects of heat on coal and coal extracts (119).
A study of the molecular weight distribution in fluorinated
polyphenyls has also been made by this technique (34). These
compounds are thermally stable and can be evaporated at high
temperatures out of a furnace which is directly attached to

the ionization chamber. In such an experiment, complete evaporation of all species present is not accomplished, and the composition of the vapor at any instant is not the same as that of the unevaporated sample. The vapor is more abundant in the more volatile components.

The method can only be quantitative if the ion currents characteristic of the various species present are integrated over the time in which the entire sample evaporates. Sensitivities for the various components present can be obtained in similar experiments in which pure samples of each are completely evaporated. Bradt and Mohler (38) have successfully used this technique to analyze a mixture of tri-, tetra-, penta-, hexa-, and octa-phenyl.

In some applications it may be necessary to heat a solid sample to a high temperature to release relatively volatile compounds contained in it. For example, Landsberg, Escher, and Dawkins (135) incorporated a vacuum oven in their sample inlet system to investigate the outgassing of metals.

Samples which cannot be vaporized into the mass spectrometer ion source, such as polymers and other compounds of very high molecular weight, may be examined indirectly by a method described by Zemany (246). In this method, the pyrolysis products are analyzed and these are related to the original molecule (136). It was found that very rapid high temperature pyrolysis usually gives the simplest products. In the case of a linear homopolymer,

the monomer comprises the bulk of the volatile material obtained
by high temperature pyrolysis. If the polymeric material is
pyrolyzed slowly at lower temperatures, the mixture of products
is generally more complex. Polystyrene, for example, when
pyrolyzed slowly gives off large amounts of benzene and iso-
propylbenzene; whereas, if it is decomposed rapidly at elevated
temperature, styrene is the main product.

In some cases, pyrolysis at lower temperatures is advant-
ageous. For example, 6:6 nylon, when decomposed at about 300°C,
evolves cyclopentanone. Only nylons made from adipic acid give
this product. If the nylon is pyrolyzed rapidly at elevated
temperatures, the major products are carbon monoxide, water
and methane (13). These compounds are too small to give much
useful information about the composition of the parent substance.

One of the major problems in the analysis of high molecular
weight samples is that of charging a known quantity of material
into the instrument for calibration purposes. Hood (123) and
Crable and Coggeshall (62) independently suggested a method to
eliminate this difficulty. The basis of the method is that
the total ionization per mole of hydrocarbon and hydrocarbon-like
compounds is an additive function of the atomic ionization cross
sections of the constituent atoms. Molar volume relationships
for these compounds are such that, for high molecular weight
materials, the total ion intensity is about proportional to the

liquid volume introduced into the mass spectrometer. The
spectra, normalized by dividing the peak heights by the total
ionization (summation of all peak heights), are roughly
standardized with respect to both liquid sample volume and
instrument sensitivity. More precise standardization may
be obtained by including a term involving the molar volume
of the compound. This standardization scheme obviates
charging a known quantity of material to obtain calibration
data. The disadvantage of this technique is that the ion
current for each peak must be determined and this procedure
is time consuming. Lampe, Franklin, and Field (139)
described a method to record the total ion current directly
and Lumpkin, and Beauxis (150) described a method which
allowed direct instrumental determination of the total ionization.

B. Analytical Applications

This is a brief review of the published work in the field
of high molecular weight mass spectrometry which includes mainly
the analysis of organic compounds which can be vaporized at
about 300°-350°C.

The initial work in this field was performed by O'Neal
and Weir (183). They presented the mass spectra of sixteen
n-alkane, isoalkane, cyclokane, and aromatic hydrocarbons. This
development has proved to be one of the major advances in
analytical mass spectrometry.

Brown, Melpolder, and Young (39) studied the composition
of a wax and a wax distillate by analyses of the original

material and of the separated fractions. Melpolder, Brown, Washall, Doherty, and Young (169) reported an analytical study of the efficiency of thermal diffusion for the separation of light lubricating oils into specific hydrocarbon types.

Lumpkin and Johnson (146) utilized a combination of separation techniques, ultraviolet, and mass spectrometry to identify hydrocarbon and sulfur compound types in aromatic portions of a heavy gas oil. The oil contained C_{18} to C_{35} compounds with maximum concentrations in the C_{27} to C_{28} region.

Sauer, Melpolder, and Brown (205) used a heated introduction system to examine the non-basic nitrogen compounds in catalytically cracked and virgin heating oils. These compounds included carbazoles, indoles, pyrroles, quinolines, and pyridines and they were determined at concentrations of the order of 0.001 to 1 per cent of the total.

Shaerer, Busso, Smith, and Skinner (207) discussed the use of mass spectral analyses to guide the final purification step in the isolation of n-paraffins from wax fractions. Edwards (72, 73) determined the hydrocarbon types in a variety of petroleum waxes and wax fractions. He related structures to the spectra from these waxes. Andre and O'Neal (2) determined the hydrocarbon types in seven medium-viscosity lube oils from various crudes and correlated the molecular structures with the viscosity index.

According to Hood, Clerc, and O'Neal (120, 121), spectral evidence points to a new and simple picture of the structural

composition of petroleum. They reported that the molecular structure was essentially one of long straight chains with the possibility of ring systems or short branches occuring at one of both ends of the chain. Furthermore, polyaromatics generally appeared to have all of their aromatic rings in a single condensed nucleus. Clerc, Hood, and O'Neal (51) established a method for the quantitative analysis of a saturated hydrocarbon fraction from petroleum according to the following compound types: alkanes, non-condensed cycloalkanes, condensed cycloalkanes, substituted benzene impurities, and naphthalene impurities. The relative abundances of the cyclopentyl and cyclohexyl rings were also determined.

Melpolder, Brown, Washall, Doherty and Headington (170) described a procedure for type-analysis of high-boiling paraffin fractions from petroleum. The components were categorized as paraffins, mono-and/or non-condensed polycyclo-paraffins, condensed di-to nona-cycloparaffins, free phenyl impurities, free indans and/or tetralins, and free naphthyls.

Lumpkin (147) described a compound-type analysis of saturated petroleum materials in which the components are determined as paraffins, non-condensed naphthenes, and condensed naphthenes containing two through six condensed rings per molecule.

Turner, Brown, and Harrison (226) determined the composition

of various paraffin waxes and correlated composition with some physical properties of the waxes. Their method was suitable for determining the distribution by molecular weight of the n-paraffins, isoparaffins, and cycloparaffins contained in mixtures of saturated compounds.

Brown, Skahan, Cirillo, and Melpolder (40) presented quantitative methods for the analyses of propylene polymers, alkylated benzenes, and petroleum waxes. Calibration data were included which should enable other laboratories to use these methods directly.

A procedure for the semi-quantitative analysis of the sulfur and aromatic compound types found in petroleum was described by Hastings, Johnson, and Lampkin (112). The method was used to determine the total benzenes, naphthene-benzenes, dinaphthenebenzenes, naphthalenes, acenaphthalenes, acenaphthylenes, phenanthrenes, pyrenes, chrysenes, and benzothiophenes.

A new mass spectrometric method to determine the alcohols and water in complex mixtures obtained by the Fischer-Tropsch synthesis was reported by Langer, Friedel, Wender, and Sharkey (137). The direct determination of alcohols in the presence of hydrocarbons is difficult because of the similarities in the spectra. This difficulty was overcome by treating the mixture with hexamethyldisilazane to convert the alcohols to their respective trimethylsilyl ethers which have characteristic spectra that are free of interferences from hydrocarbon ion fragments.

Brown, Young, and Nicolaides (41) analyzed the high
molecular weight alcohols separated from hair oils. They
identified the C_{16} to C_{27} straight chain alcohols.

Bergstrom, Ryhage, and Stenhagen (22, 23) described their
analytical work on the carnauba acid and the solid hydrocarbon
fractions of tall oil. Normal paraffins in the C_{22}-C_{26} range
and a C_{26} ethylene hydrocarbon were detected. Hallgren,
Stenhagen, and Ryhage (108) as well as Nilsson, Ryhage, and
Von Sydow (179) reported quantitative mass spectrometric
analyses of mixtures of saturated and unsaturated fatty acids
and of long-chain hydrocarbons in alcohols. Hallgren, Ryhage,
and Stenhagen (109) compared the fragmentation patterns of
methyloleate, methyl linoleate, and methyl linolenate with
patterns of the methyl esters of the saturated long-chain
acids. They concluded that it was not possible to establish
the position of the double bonds in unsaturated fatty acids
by direct mass spectrometric analysis. Dinh-Nguyen, Rhyage,
and Stenhagen (68) later determined the double bond locations
in cis-petroselinic, oleic, and elaidic acids. Their method
involved the formation of dideutero stearates whose spectra
were then compared with that of methyl stearate. Ryhage and
Stenhagen (202) reported the spectra of some saturated long-
chain esters of ethanol and higher alcohols. These authors
also published spectra of twenty-five methyl esters of monoalkyl-
substituted acids with ethyl or longer side chains and included

the spectra of methyl esters of di- and polyalkyl-substituted
acids. In another article, Ryhage and Stenhagen (203) reported
the spectra of the dimethyl esters of dibasic acids containing
up to twenty-two carbon atoms and found these spectra were
quite different from those of the monomethyl esters. Rhyage
and Stenhagen (204) also presented the spectra of the methyl
esters of oxo-, hydroxy-, methoxy, and epoxy acids.

The methyl esters of the resin acids were determined by
Genge (99) through the use of fragment peaks in the higher
mass portion of the spectra. Sharkey, Shultz and Friedel (208)
used fragment and rearrangement peaks for the identification
of esters. In addition, Kourey, Tuffley, and Yarborough (133)
determined the hydroformylation products of ethyl sorbate from
the spectra of the diesters of the four to seven carbon dibasic
acids. In a paper on aromatic esters, Emery (74) correlated
spectra with structure. Seven homologous series of esters
involving both aliphatic esters of aromatic acids and aromatic
esters of aliphatic esters were studied. The seven series were
the benzyl, beta-phenylethyl, cinnamyl, benzoate, cinnamate,
salicylate, and phthalate esters.

Gilpin (101) identified the three classes of aliphatic
amides. Fragmentation and rearrangement processes, typifying
the three classes, were noted for the spectra of thirty-five
compounds. Using mass spectral data, McLafferty (151)

identified some aliphatic ethers.

Dineen, Cook, and Jensen (67) combined chemical and physical methods of analysis, including mass spectrometry, to tentatively identify the types of nitrogen compounds in shale-oil. The authors suggested that alkyl pyridines, cyclo-alkanopyridines, pyrroles, indoles, quinolines, tetrahydro-carbazoles, and tetrahydroacridine type compounds were present.

Holden and Robb (119) volatilized coal at the entrance to the ionization chamber. They found that cracking occurs if aliphatic compounds, alkylbenzenes, naphthalenes, and higher aromatics were vaporized between 200 and 370°C. However, the corresponding series of substituted phenols and naphthols were detected at these temperatures.

The feasibility of using the mass spectrometer to study steroids was demonstrated by Reed (197). The spectra of several typical steroids were given, together with a description of how these were used to ascertain the size of the side chains and other structural factors. Friedland and co-workers (89) were able to obtain much structural information from the characteristic fragmentation patterns of steroids. Thermal instability of the steroids was reduced by holding the inlet temperature at 200°C. A mass spectrometric procedure involving the external pyrolysis of the sample was also discussed. O'Neal and Hood (185) described the detection of steroid-like four

ring saturates and monoaromatics from the mass spectral data.

Ardenne and Tummler (5) and Ardenne (4) used the technique of electron addition mass spectrometry in their studies. Low energy electrons were added to high molecular weight compounds to give characteristic negative ion spectra.

Asselineau, Ryhage, and Stenhagen (6) reported the mass spectra of several methyl esters of the C_{20}-C_{23} carboxylic acids and showed that the structure of mycoerosic acid is 2,4,6-trimethyl nonacosanic acid. Beynon, Lester, and Williams (19) showed the particular type of rearrangements which occur when carbon monoxide is eliminated from oxygenated compounds. A detailed study of the fragmentation of anthraquinone was presented. Fragmentations of some nitrogen-containing compounds such as nitroanilines and of some aromatic ethers and ketones were also discussed. Biemann, Gapp, and Siebl (28) studied the characteristic patterns from the fragmentation of polyamino acids derived from peptides. Biemann and Sibel (29) investigated the spectra of epimeric cyclic alcohols and noted that the parent ion abundances differed distinctly even though the spectra were similar in other mass regions.

Friedel and Sharkey (88) discussed the spectra of acetals. They observed that acetals, because of their characteristic patterns, are easily detected in the presence of alcohols and aldehydes.

Gilpin and McLafferty (101) and McLafferty (152) related the spectra of aldehydes and ethers to their respective structures. Quale (192) observed that tri-aryl phosphates dissociate in a manner comparable to the aromatic hydrocarbons. He found, however, that alkyl and alkyl-aryl phosphates undergo considerable rearrangement and many peaks in their spectra occur at one or two mass units higher than would be expected from normal fragmentation. Friedman, Irsa and Wilkinson (90) studied the mass spectra of cyclopentodienyl metal compounds of boron, chromium, iron, cobalt, nickel, rhenium, ruthenium, manganese, and magnesium.

Ryhage, Stenhagen, and Von Sydow (200, 201) established the position of the methoxy groups in phthiocerol and reported the spectra of some other high molecular weight glycols.

Sharkey, Shultz and Friedel (209) described the effect of alkyl substitution on the spectra of aliphatic ketones. They derived empirical rules which related fragmentation and rearrangement peaks to molecular structures.

Wacks and Dibeler (231) studied the fragmentation and ionization processes for anthracene, naphthalene, benzene, and phenanthrene under electron impact. They suggested a completely empirical method of group equivalents which provides a rapid means of computing the first ionization potentials of aromatic compounds.

The spectra of aromatic acids and esters were discussed by McLafferty and Gohlke (153). They showed that the formation of major ions can involve cleavages at the carbonyl group or at the oxygen-alkyl bond.

Finan and Reed (82) applied mass spectrometry to the study of polysaccharides. They found that the dissociation of laminarion from mass 28 to mass 700 occurred in two main series and that step-wise polymer fragmentation was indicated.

Beyon and Williams (21) studied the fragmentation processes in anthraquinones and related compounds with the aid of high resolution mass spectrometry. Spectra of twenty-one substituted anthraquinones, three other quinones, and two cyclic ketones were presented.

Coggeshall (54) studied the spectra of the n-paraffins from C_6 to C_{30} to find quantitative relations predicted by any theory of ion formation by electron impact. He observed that the details of the fragmentation process depended on the type of molecular skeleton and only secondarily on the size of the molecule.

The mass spectra of some aromatic hydrocarbons were presented by Reed (196). Structures were correlated with the fragmentation patterns. The investigation included analyses of coal and coal extracts.

In a study of deuterated biphenyls, Burr, Scarborough,

and Shudde (45) noted a decrease in the total ionization with increasing number of deuterium atoms. Monoisotopic patterns and group ionization by carbon number were given.

Pyridine and quinoline-type compounds in concentrates from petroleum fractions were determined by LaLau (134). This method employed peak intensity summations of the parent and parent minus one series and was based on total ionization concepts.

Carlson and co-workers (49) identified several molecular types in petroleum fractions which previously had been reported on the basis of indirect evidence or had not been reported at all. They use a double focusing high resolution mass spectrometer allowed them to take advantage of the "mass defect" of certain ions.

Levy, Doyle, Brown, and Melpolder (141) identified components of paraffin wax by combined high temperature gas chromatography and mass spectrometry. They found that the predominant hydrocarbons were n-paraffins, monomethyl paraffins, and monocycloparaffins. In another study of wax, Arabian (3) found that some fractions were composed entirely of n-alkanes and others were high in cycloalkanes. O'Connor and Norris (182) combined molecular sieve and mass spectrometry techniques to analyze petroleum distillates boiling between 100 and 650°F.

Biemann (24) and Biemann and Vetter (25) applied mass

spectrometry to the study of amino acids and peptides. The
amino acid sequences of di-to penta-peptides were determined
and the results indicated considerable potentialities for the
method. Biemann (26) used mass spectrometry to study the
carbon skeleton of sarpagine. He demonstrated that the mass
spectra of the indole alkaloids are characteristic of the
particular alicyclic carbon skeleton present. Biemann and
Friedmann-Spiteller (27) studied the mass spectra of the indole
alkaloids ibogamine, ibogaine, and tabernanthine. The usefulness
of mass spectrometry for the determination of the structures of
such compounds was illustrated.

The high resolution mass spectra of twenty-seven aliphatic
esters were obtained by Beynon, Saunders and Williams (20).
They assigned a formula to each fragment ion in the spectra.
This made it easier to identify a compound from its spectrum
and, in particular, to distinguish an ester from compounds such
as isobaric alcohols, ethers, and acids.

Frisque and co-workers (92) described a total analysis
of olefinic naphthas by combining the salient features of high
and low voltage mass spectrometry.

Levy and Stahl (140) developed correlations between the
mass spectra and molecular structures of thiols and sulfides.
In addition to differentiating the thiols from the sulfides
solely on mass spectral data, it was possible to further classify

the thiol as primary, secondary, or tertiary.

The analyses of multicomponent methyl-and phenylchlorosilane solutions was described by Hirt (117). He demonstrated that the analyses of chlorosilane mixtures are satisfactorily performed by mass spectrometric techniques based on pressure sensitivities.

Howard and Ferguson (125) discussed the resolution of cyclopentanes and cyclohexanes in gasoline by mass spectrometry. The relative amounts of alkyl cyclopentanes and alkyl cyclohexanes were determined from a single mass spectrometric analysis of the petroleum mixture.

Catalytic dehydrogenation and mass spectrometry were employed by Cousins, Clancy and Crable (61) to differentiate naphthenes containing cyclohexyl and cyclopentyl rings. The method was based upon the dehydrogenation of naphthenes containing cyclohexyl rings to the corresponding aromatics, while the naphthenes containing only cyclopentyl rings were unaffected.

McLafferty (154, 155) correlated the mass spectra with structures of some aliphatic and aromatic halogenated compounds. In both classes of compounds, he showed that the molecular ion (parent) abundance is in the order I>Br>Cl>F. He also observed that the parent ion for halogenated aromatic compounds are generally abundant. McLafferty (156) also correlated the spectra of eighteen aliphatic nitriles and demonstrated that the mass spectrometer is uniquely applicable to the identification of these compounds.

Aczel and Lumpkin (1) correlated the mass spectra of seven methyl benzoates and nine benzyl benzoate-type esters with structures of these compounds. The major spectral features depended primarily on the nature of the oxygenated functional groups and the positions of the methyl groups substituted on the ring.

Bendoraitis, Brown, and Hepner (10) employed the combined techniques of gas liquid chromatography and mass, infrared, and proton magnetic resonance spectroscopy to isolate and identify 2, 6, 10, 14- tetra methylpentadecane (prinstane).

A comprehensive paper on the instrumentation and techniques of low voltage mass spectrometry was given by Lumpkin (148). He included the low voltage sensitivities of a large number of aromatic and olefinic compounds. The use of the low voltage method as illustrated by the analyses of low molecular weight polypropylenes and some aromatic fractions from gas oils. Gordon, Moore, and Muller (103) identified the aromatic compound types present in heavily cracked gas oil fractions from ultraviolet spectra and boht high- and low-voltage mass spectra. Low voltage methods were used by Sharkey, Wood, and Friedel (212) to obtain the molecular weight distribution and to identify structural types present in high-boiling neutral and phenolic portions of coal-hydrogenation oil. They found phenols, indanols, naphthols, and acenaphthols. Kearne, Maranowski, and Crable (127)

applied the low-voltage technique to the analyses of C_{12} to C_{20} aromatics and correlated parent peak sensitivity with the degree of alkyl substitution on the nucleus. These authors (128) also combined standard and low-voltage mass spectrometry with fluorescent indicator adsorption to determine the composition of C_{12} to C_{20} petroleum products. The variation of low-voltage aromatic sensitivities was used to obtain the average number of substitutions per benzene ring. Sharkey and co-workers (210) and Sharkey, Robinson, and Friedel (211) determined the compounds present in the aromatic and saturated fractions of coal hydrogenation products. They also analyzed a phenolic fraction using low-voltage spectra before and after making the trimethylsilyl ether derivatives.

Crable, Kearns, and Norris (63) described a means for predicting low voltage sensitivities of aromatic compounds based on the number of condensed aromatic rings in the nucleus and the relative electron-accepting or the electron-donating properties of the substituent groups. Sensitivity data for a large number of compounds were tabulated.

The application of mass spectrometry to the analysis of organic compounds has been generally limited to materials of molecular weight less than 600. However, Bradt and Mohler (34) used the mass spectrometer to demonstrate the existence of the polymers of p-dibromotetrafluorobenzene and p-diiodotetra-fluorobenzene with molecular weights up to about 1000 and 1750,

respectively. Molecule (parent) ions were predominant in the mass spectra of the polymers; therefore, the identification of the components of such a mixture was greatly simplified. No fragmentation of the polymer chains was caused by electron impact or thermal decomposition. Bradt and Mohler (33) studied polymeric structure from the mass spectra of the thermal degradation products. The samples were pyrolyzed in the mass spectrometer.

To assist in the determination of compounds formed by the radiation of diphenyl, Bradt and Mohler (35) obtained the spectra of several polyphenyls. The mass spectra of pure tetraphenyl, hexaphenyl, and octaphenyl were obtained by evaporating each compound from a furnace directly into the ionization chamber of the spectrometer. Mixtures of the polyphenyls were studied by obtaining spectra at different temperature levels. A similar procedure was used by Mohler, Bradt, and Dibeler (32) to identify the aromatic hydrocarbons filtered from smoky air. Compounds containing from three to seven fused rings were detected.

Mass spectrometry has been used in the field of geochemistry by Stevens, Bray, and Evans (217) who observed that n-paraffins with an odd-number of carbon atoms were present in greater concentration than those with an even number of carbon atoms in sediments. The odd-carbon predominance was not evident in a crude oil and a shale oil. Evans, Kenny, Meinschein, and

containing compounds, and stearic acid.

Analytical mass spectrometry and high-mass work was reviewed by Waldron (235) in a British publication. He also complied and edited (236) the proceedings of a joint conference of the Hycrocarbon Research Group, Institute of Petroleum, and ASTM Committee E-14 which was held at the University of London, September, 1958. Young, Brown, and Melpolder (244) reviewed the application of mass spectrometry to petroleum fractions, including gas oils, and in other reviews Coggeshall (53) and Young (245) discussed high-temperature mass spectrometry. At the Fourth World Petroleum Congress in Rome, O'Neal, Hood, Clerc, Andre, and Hines (184) reviewed the use of mass spectrometry in the study of high-boiling petroleum fractions.

A comprehensive discussion of analytical mass spectrometry is given in a book by Beynon (11). Much of the material is devoted to high molecular weight techniques and includes such subjects as sample handling, qualitative analysis, and quantitative analysis. A number of useful tables are included. Over 2000 references are listed.

III. Ionization Potential Measurements

The first ionization potential of a molecule is the energy difference between the ground vibrational levels of

the lowest electronic states of the molecule and the molecular ion (11). It is sometimes referred to as the adiabatic ionization potential. The measured minimum energy necessary to produce the molecular ion by a particular process may not equal the adiabatic ionization potential. This potential can generally be deduced spectroscopically by extrapolation of the positions of vibrational bands, but it may not be possible to produce the molecular ion in its ground state by electron bombardment. In such cases, the measured value will be higher than the spectroscopic value.

The conditions under which ionization occurs are described by the Franck-Condon principle. This principle is based on the premise that the positions of the relatively massive atomic nuclei within the molecule do not change while an electronic transition is occurring. If the potential energy curves representing the molecule before the transition and the molecular ion after the transition are plotted, the points on these curves representing the conditions before and after ionization will correspond to the same nuclear configuration and will be on a line parallel to the energy axis. Such a transition is known as a vertical transition. The ionization potential measured in this way is referred to as the vertical ionization potential. This potential is the minimum energy necessary to remove an electron from the molecule without a change in molecular con-figuration.

The term "appearance potential" generally applies to the formation of a fragment ion from a molecule, i.e., when ionization and dissociation occur.

Ionization efficiency curves showing the number of ions formed as a function of the energy of the impacting electrons have been obtained for a wide variety of molecular species (139, 165, 187, 225). These curves, in general, are similar. Their main characteristics are as follows: (a) an initial rapid rise from the onset to, (b) a maximum at about 50-100 electron volts followed by (c) a slow decrease or "tailing" of the efficiency curve. With large organic molecules the majority of the ions formed may not be molecular ions, but rather, fragment ions may predominate. The proportion of multiply-charged ions is smaller than for monatomic gases and reflects the increased probability of fragmentation at high electron energies. The maximum efficiency of ionization, as stated previously, usually occurs in the region of 50-100 electron volts (223). For this reason, electron energies of this magnitude are used in chemical analysis.

Ionization potentials can be used to confirm values predicted for the removal of electrons from particular molecular orbitals (107, 175, 176) and to provide data for the calculation of electronic wave functions (106).

Appearance potentials of fragment ions in conjunction with molecular ionization potentials and calorimetric data can be used to estimate various thermodynamic quantities such as

latent heats and bond strengths (174, 69, 70, 71, 131, 142, 195, 220).

Many investigators have studied the shapes of the ionization efficiency curves for particular ion species in the vicinity of the ionization potential. The general shape of the curve is an initial curved region extending over about one electron-volt followed by an approximately straight portion extending over about ten electron-volts. Early plots of fragment-ion efficiency curves varied considerably in their curvatures (130). Plots of doubly-charged molecular ions showed greater ranges of curvature than did the corresponding singly-charged ions (218). Several attempts have been made to obtain the shape of the ionization efficiency curve immediately above the threshold of ionization (9, 97, 237, 238, 241, 242).

Instrumental conditions can affect the shape of the ionization efficiency curve. Such an effect is due to the energy spread of the bombarding electrons. The energy distribution of the electrons emitted from a hot filament has been shown to be essentially Maxwellian (124, 180) and the effect of this spread in energies upon the shape of the ionization efficiency curve has been the subject of a detailed study (83, 124, 198, 218). The most accurate measurements have been when this electron energy spread has been minimized.

There are many sources of error which cannot be eliminated in the measurement of an ionization potential by mass spectrometry. These have been discussed by Waldron and Wood (234) and are briefly enumerated herein. The occurrence of a potential

gradient within the ionization chamber provides the electrons
with an additional increment of energy. Consequently, the ion
repeller voltage is kept small to minimize this effect. This
effect is virtually eliminated if the repeller plate voltage
is constant while measuring the difference between two
ionization potentials.

The electric field within the ionization chamber is due
in part to penetration of the ion accelerating field via the
slit through which the electrons emerge. To maintain a con-
stant field within the ion chamber for the examination of two
ions of different mass, magnetic scanning is preferred.

The slit leading from the ionization chamber to the
electron trap is relatively wide and the voltage on the
trap can produce a field of penetration extending to the
ionizing region. To minimize this effect, experiments are
usually conducted with the trap at the same potential as the
ionization chamber.

The temperature of the filament which produces the
electron beam affects the spread of electron energy proportionately.
This means that more high energy electrons are available and
the ionization probability curve will extend to a lower appearance
potential. The effect will be the greatest at the lowest
electron energies when the emission from the filament is
space-charge limited. This effect can be minimized by rigid
control of the filament temperature.

Contact potentials within the ionization chamber may
vary when the sample is introduced. Consequently, an
"internal" standard is used when measuring an ionization
potential. ("Internal" standard is a substance of known
ionization potential whose ionization efficiency curve can
be compared with that of the substance under investigation
while they are both in the system and under identical con-
tact potential conditions).

After all of the above effects have been eliminated, there
remains the problem of choosing the value of the desired
potential from the curve. The various methods which have
been used are critically discussed by Nicholson (178). These
methods will be discussed briefly.

One of the early methods (213) was to extrapolate the
linear portion of the ionization efficiency curve to zero
current and to accept the intercept on the voltage scale as
the ionization potential. This method assumes that a linear
relationship exists between the ion current and the electron
energy down to the onset of ionization and that the entire
"tail" is the result of the energy spread in the electron
beam. This method is now rarely used.

Smyth (214) used the "vanishing current" method to measure
the ionization potentials. In this method, the exponential
portion of the ionization efficiency curve is extrapolated to

zero ion current. The objection to the use of this method
is that the point detected in this way depends on the sample
pressure, the number of bombarding electrons and the sensitivity
of the amplifier employed. However, this objection may be over-
come by the simultaneous introduction of a rare gas; e.g., xenon,
so that the difference between the two "vanishing currents"
may be determined.

An extension of the "vanishing current" method employed by
Warren (239) is known as the "extrapolated difference" method
of determining appearance potentials. In this method, which
uses an internal standard, the ion current scales of the two
plots are adjusted to make the straight-line portions parallel
and the voltage difference between corresponding points on the
curves is extrapolated to zero.

Several other methods, which also depend on the similarity
of the shapes of the two curves being compared, are classified
by Nicholson as the "logarithmic methods". The first of these
attributable to Honig and Wannier (124), while not attempting
to eliminate the electron energy spread, accounts for it in
an analytical expression which indicates that at one electron-
volt below the ionization potential the curve will be approximately
exponential. A semi-log plot of the ionization efficiency yields
a curve whose slope is 2(3KT) at the ionization potential.
All such curves are implicitly assumed to be of identical shape.

Other methods which are similar to this have been described by
Lossing, Tickner, and Bruce (145) and Dibeler and Reese (64).

All the methods discussed give values which are usually
reliable to ±0.1 electron-volt for ions which give curves
similar in shape to those of the rare gas ions. If special
apparatus is used to produce an essentially mono-energetic
electron beam, the curves become easier to interpret since
any fine structure which is smoothed out by a spread in electron
energies is more easily observed. Nicholson (178), suggests
that accuracy in the determination of ionization potentials can
be increased by any method which can detect fine structure in
ionization efficiency curves. The early work of Nottingham (181),
using electrons homogeneous in energy, made apparent the fine
structure in the ionization efficiency curve of mercury near
the ionization potential.

Price and Sugden (191, 219) demonstrated that fine structure
in the efficiency curve is sometimes visible when photo-electrons
rather than thermal electrons are used to produce ionization.
Their apparatus did not include mass analysis. Herzog and
Marmo (116) described a radio-frequency mass spectrometer to
determine the mass of the ions formed by photoionization
techniques. Interestingly, these authors showed that only
molecule ions were formed by the photoionization process.

More recently, Clarke (50) used a 127° electrostatic

velocity selector to obtain a beam of nearly monoenergetic electrons. His experiments showed that as the spread in electron energy is reduced the efficiency curves become segmented straight lines with little curvature as the ionization potential is approached.

A different approach for obtaining the effect of a monoenergetic electron beam has been made by Fox, Hickam, Kjeldaas, and Grove (84, 85). Their approach is called the "retarding potential difference" method. Because this method gives results which more closely approximate the spectroscopic values (11), it will be described, briefly. A retarding electrode, whose potential is negative with respect to the filament, is positioned between the filament and the ionization chamber. Electrons whose energies are lower than the retarding potential cannot pass through the slit in this electrode, but those that do are accelerated towards the ionization chamber. These electrons have an energy distribution with a sharply-defined lower limit corresponding to those electrons which had only sufficient energy to pass through the retarding electrode. If now the negative voltage on the retarding electrode is increased slightly, additional electrons, contained in a narrow energy band corresponding to this voltage change, are prevented from entering the ion chamber. The reduction in ion current caused by the loss of these electrons (which are about mono-energetic) from the beam can be measured.

Marmet and Kerwin (163), have developed an improved electrostatic energy selector which produces an electron beam with an energy spread of 0.03 electron volts. They use a special metallic material, which they call "electron velvet," to eliminate those electrons that are normally reflected from the metal walls of the ionization chamber. With this device they have been able to establish some of the vibrational levels for the hydrogen molecule-ion (164).

Caldecourt (46) has developed an automatic appearance potential measuring mass spectrometer. This instrument gives an approximate record of the appearance potential of each mass-spectral peak and is useful for determining the electron accelerating potential to be used for a particular analysis by "low-voltage" mass spectrometry.

Other things being equal, the more easily an electron is removed from its field of influence (the less strongly bound) the less strongly bonding it is in a chemical sense. Attempts have been made to define the concept of bond order in terms of the ionization potential (233).

As previously stated, the ionization potentials obtained by mass spectrometry have not been as accurate or as reliable as those obtained spectroscopically because of the difficulties of interpretation. The majority of these values are different than the spectroscopic values; but they are important in numerous

applications. The more recent work with mono-energetic ionizing beams, described above, should increase the usefulness of the mass spectrometric method, especially in cases such as the study of free radicals where spectroscopic data are not available. The instruments used for these studies have been reviewed by Varsel (227).

Because of the large number of ionization potential measurements which have been made, it is impractical to describe all of these data in this thesis. Several excellent reviews have been prepared and are cited for informational purposes. The measurements of ionization potentials which were completed prior to 1930 were reviewed by Smyth (215). Field and Franklin (76) have reviewed the subsequent data in an excellent manner. Cottrell (60) has published a book which includes data not listed in Field and Franklin's treatise. An excellent review article by Neuert (177) augments the data presented in these latter two publications.

The ionization potentials measured since these publications are quite numerous. A resume of the work done is presented to acquaint the reader with these data. Frost and McDowell (93) have measured the inner ionization potentials of chlorine and iodine by the retarding potential difference (RPD) method of Fox (84). They interpreted the results in terms of the electronic structures suggested by the molecular orbital theory. Collin (56) also used an RPD source in his studies with nitromethane.

He found that two processes were responsible for the NO_2^+ formation. One of these was probably the same as that found by Weissler's group (240) in their photoionization studies. This group used a vacuum ultraviolet monochromator with a mass spectrometer to study photoionization processes in the wavelength region from 1570 to 430A.

Dibeler and Reese (66) studied the energy required to form Na^{2+} and Na^{3+} from sodium vapor. Their values are in good agreement with the spectroscopic values.

Buchel'nikova (43) used a total ionization tube with an RPD electron beam about 0.2 electron volt wide to study the capture of slow electrons by several halogenated inorganic compounds. He quotes maximum capture cross-sections and some appearance potentials. Bakulina and Ionov (8) used a mass spectrometer to determine positive ion currents, and hence the difference in ionization potentials, for two atomic species ionized simultaneously on a heated metal surface.

Ionization potentials of n-propyl and the four butyl radicals have been measured by a direct ionization technique by Lossing and co-workers (144). The ionization potentials measured by this way were considerably higher than those determined by indirect methods for the same species. Their results suggest that the indirect methods probably involve processes leading to rearrangement. These authors (143) also reported the ionization potentials of some partially halogenated

methyl radicals. Stanton (216) studied propane under electron bombardment. He examined the kinetic energy (K.E.) of the CH_3^+ and $C_2H_5^+$ fragments formed by 70 volt electrons. The absence of the $C_2H_5^+$ group of other than zero K.E. suggests that previous theories that postulate the formation of a doubly charged parent which subsequently dissociates to $CH_3^+ + C_2H_5^+$ being acquired through coulomb repulsion may be in error.

Dibeler, et al. (65) studied the appearance potentials of many ions from hydrazine, monomethyl-, 1,1-dimethyl-, 1,2-dimethyl-, trimethyl-, and tetramethyl hydrazine. Their molecular ionization potentials are in good agreement with values calculated semi-empirically from antisymmetric orbitals. They tabulated heats of formation and relevant processes for radical ions, and determined bond strengths in methyl hydrazine and some nitrogen-containing molecules.

Collin (57) measured the ionization potential of methyl-amines and ethylamines in an attempt to resolve inconsistencies in the literature. All his data lie between photoionization and previous electron impact values, and probably refer to initial formation of ions in vibrationally excited states.

Cloutier and Schiff (52) employed a modified RPD method to study nitric oxide. The potential minimum existing between the anode and the cathode of a space-charge-limited diode provided the electron retarding potential.

Koski, et al. (132) made rough estimates of the appearance potentials of fragment ions from BCl_3, BBr_3, and BI_3. They also determined the average boron-iodine bond dissociation energy.

Lampe and Field (138) determined the appearance potentials of various ions from neopentane. They deduced various ionization processes and heats of reaction from their measurements. These differed considerably from these observed by Koffel and Lad (130).

Thorburn (224) used a conventional ion source to study the positive and negative ions formed by electron impact from F_2, HF, Cl_2, and HCl. His value for the ionization potential of molecular fluorine is 0.8 electron volts higher than the spectroscopic value and is probably in error.

Collin and Lossing (58) collected previously determined values for the ionization potentials of some olefins, di-olefins, and branched paraffins, re-measured several, and measured others for which the values were not available. They resolved some anomalies which seemed to exist and attempted to correlate published ionization potentials and molecular structures.

Franklin, Lampe, and Lumpkin (87) measured the appearance potential of the $C_6H_7^+$ ion from 1,3 cyclohexadiene and from it calculated the proton affinity of benzene.

Reed and Snedden (193) reported the ionization potential

of NH·. However, the origin of the free NH radicals in this work is somewhat obscure. These same authors (194) reported values for the appearance potentials of the mono-and dichloro- and the mono- and dibromo-methyl ions. These species were produced by the pyrolysis of halogenated methanes on a heated tungsten wire. Margrave (162) measured the ionization and appearance potentials of several halogen-substituted ethylenes.

Wacks and Dibeler (229) investigated the formation of singly and doubly charged ions from benzene, naphthalene, anthracene, and phenanthrene. These authors found the ionization potentials for both the singly and doubly charged ions to be fairly well predicted by one or two theoretical or empirical methods.

Hunt and Huffman (126) have shown a satisfactory relationship between the ionization potentials and the atomic radii for rare gas atoms by assuming a complex between the impinging electron and the atom. The complex, thus formed, is subsequently broken down by collision with other electrons.

In 1960, Wacks and Dibeler (230) continued their systematic examination of the ionization potentials of aromatic hydrocarbons by studying the quadricondensed molecules of which 1,2-benzanthracene and pyrene are examples.

Herron and Dibeler (114) examined the cyanogen halides (CNCl, CNBr, and CNI). The appearance potentials of the various

fragment ions were measured and the heats of formation of the neutral CN and negative ion were derived.

Herron and Dibeler (115) also examined tetrafluoro-hydrazine and silicon tetrafluoride. The appearance potentials of the NF_2^+ ion and the F^- ion were determined.

The ionization and dissociation of some halogen molecules by electron impact were discussed by Frost and McDowell (94). The molecules examined were chlorine, bromine, iodine, iodine-monochloride, and iodine monobromide. Many ionization potentials corresponding to the different electronic states of the molecular ions $(Cl_2, Br_2,$ and $I_2)$ were reported.

Fox (86) determined the threshold ionization potential of hydrogen chloride. He reported a marked curvature in the graph of the ion abundance versus electron energy at the threshold and attributed it to the presence of the $2\pi_1$ doublet ground state of the ion.

Kelen and Bievre (129) measured the ionization and appearance potentials of the principal ions obtained from acetonitrile and its mono-, di-, and tri- fluoro and chloro derivatives.

Collin (59) described his apparatus, a Fox type for the production of monoenergetic electrons, and its application in the measurement of the ionization potentials of the excited states of the molecular ions of carbon dioxide and carbon disulfide. Spectroscopic data for these ions has been published by Tanaka,

Jursa, and LeBlanc (221, 222). The agreement between the two methods for the four excited states of the carbon dioxide ion is satisfactory. Six states of the carbon disulfide ion are also reported and tentative assignments are made.

Some ionization potentials of free radicals have been made measured by Lossing and his colleagues. They measured the ionization potentials of the cyclopentadienyl and the cycloheptratrienyl radicals (110). Harrison and Lossing (111) measured the ionization potentials of the beta-naphthylmethyl, alpha-naphthylmethyl, and diphenylmethyl radicals. Further, Pottie and Lossing (190) made similar measurements upon some cyano substituted alkyl radicals. These results support the view that the replacement of a hydrogen by a methyl group lowers the ionization potential while the introduction of a cyano group raises it by about one electron volt.

Inorganic materials are now being studied more frequently by electron impact methods. The bond-dissociation energy of dimeric sulfur vapor has been re-determined by Colin, Goldfinger and Jeunehomme (55). Goldfinger (102) used similar methods to deduce some thermodynamics properties of several elements and alloys, and some sulfides, selenides, and tellurides of the group II elements. Heats of sublimation of zinc and cadmium have been determined by Mann and Tickner (161) who used a mass spectrometer to determine the vapor pressures of these elements. Many of the mass spectrometric studies of inorganic systems,

while not directed toward this end, have provided information about the ionization potentials of gaseous inorganic species. Grimley, Burns and Inghram (104) studied the oxides of osmium. The ionization potentials of the oxides of molybdenum were measured by Burns and co-workers (44). In a similar manner, Porter and Zeller (189) determined the appearance potentials of many ions obtained from the bromide, chloride, and fluoride of aluminum. Schoonmaker (206) reported the gaseous species that resulted from the vaporization of alkali metal fluorides and hydroxides.

Among the relatively few precision studies on the metallic elements are those of Blais and Mann (30) with the vapors of copper, silver and gold. The relative ionization probabilities were studied near the threshold and they observed narrow peaks superimposed upon the ion yield, which represented the transition to the ground state ion. These peaks were correlated with energy levels, or groups of these, which are known to autoionize.

Finally, a review of some aspects of mass spectrometry was published by Momigny (173). A portion of this review discusses the determination of ionization potentials by electron impact methods.

EXPERIMENTAL

I. Reagents

The compounds listed below were used to establish the
mass spectra and the ionization and appearance potential data.
With the exception of xenon, pyridine, piperidine, and pyrroli-
dine, the mass spectra of these compounds have not been reported
previously:

Xenon, 99.9 mole per cent minimum, Matheson Company, Inc.,

Pyridine, Certified Reagent, Fisher Scientific Company,

Piperidine, Practical grade, Eastman Organic Chemicals,

Pyrrolidine, Practical grade, Eastman Organic Chemicals,

N-methylpyrrolidine, Aldrich Chemical Company, Inc.,

Nicotine, 99% pure, Diamond Black Leaf Company,

Anabasine, ca. 96% pure, Fluka A. G., Switzerland,

Nornicotine, as the dipicrate, Mann Research Laboratories, Inc.

The xenon, pyridine, piperidine, pyrrolidine, N-methyl-

pyrrolidine were analyzed mass spectrometrically without additional

purification. The spectra of these compounds demonstrated that all were sufficiently pure for this study.

The nicotine was freshly distilled in our analytical laboratory prior to the mass spectrometric analysis.

The anabasine was paper chromatographed in the laboratory. The conditions used were as follows: (a) the Whatman number one paper was treated with a 0.2 molar sodium acetate in methanol solution (pH 5.6) and allowed to dry; (b) various amounts of the anabasine were spotted on the paper along with a stock solution of pure nicotine, nornicotine, and anabasine; (c) the paper was placed in a chromatographic chamber containing tertiary amyl alcohol saturated with acetic acid-sodium acetate buffer (pH 5.6) and conditioned overnight; (d) the paper was then air dried and sprayed with a solution of p-aminobenzoic acid; and (e) it was placed in another chromatographic chamber containing cyanogen bromide vapors. An azo dye was formed for each alkaloid zone. Slight impurities, less than 5%, were detected at a 50 microgram concentration of anabasine.

The nornicotine dipicrate was dissolved in dilute sodium hydroxide solution. Anhydrous diethyl ether was added after the solubilization had taken place. The ether layer, containing the nornicotine, was separated. The ether was evaporated and the nornicotine was analyzed.

inlet described in the following statements has been in operation since February of 1960 with few difficulties attributable to malfunction of the component parts.

The oven is constructed with an inner and outer casing of 1/4 inch asbestos board with a 1.5 inch fiberglas insulation batt between the two casings. The dimensions of the outer asbestos casing are as follows: the front and the back panel are 14.00 X 15.75 inches; the two side panels are 15.75 X 18.50 inches; and the top and bottom panels are 14.0 X 19.0 inches. The dimensions of the inner asbestos casing are as follows: the front and the back panels are 10.00 X 12.25 inches; the two side panels are 12.5 X 15.0 inches; the bottom panel is 10.0 X 15.5 inches; and the top panel is 13.5 X 18.5 inches. A cabinet made of sheet aluminum encloses the insulated casings described previously.

A two-kilowatt, two-coil, rectangular heater inside the oven provides the extra capacity necessary for rapid increase of temperature. Copper tubing, 1/8 inch I.D. and mounted in close proximity to the heater carries chilled water to provide rapid cooling of the oven. The oven can be cooled, if necessary, between analyses of samples of different volatility.

The inlet system shown in Figure 2 consists basically of two Veeco stainless steel angle valves, type R5055, at the input of the system, a one-liter expansion volume, and a sample

HEATED INLET FOR MASS SPECTROMETRY
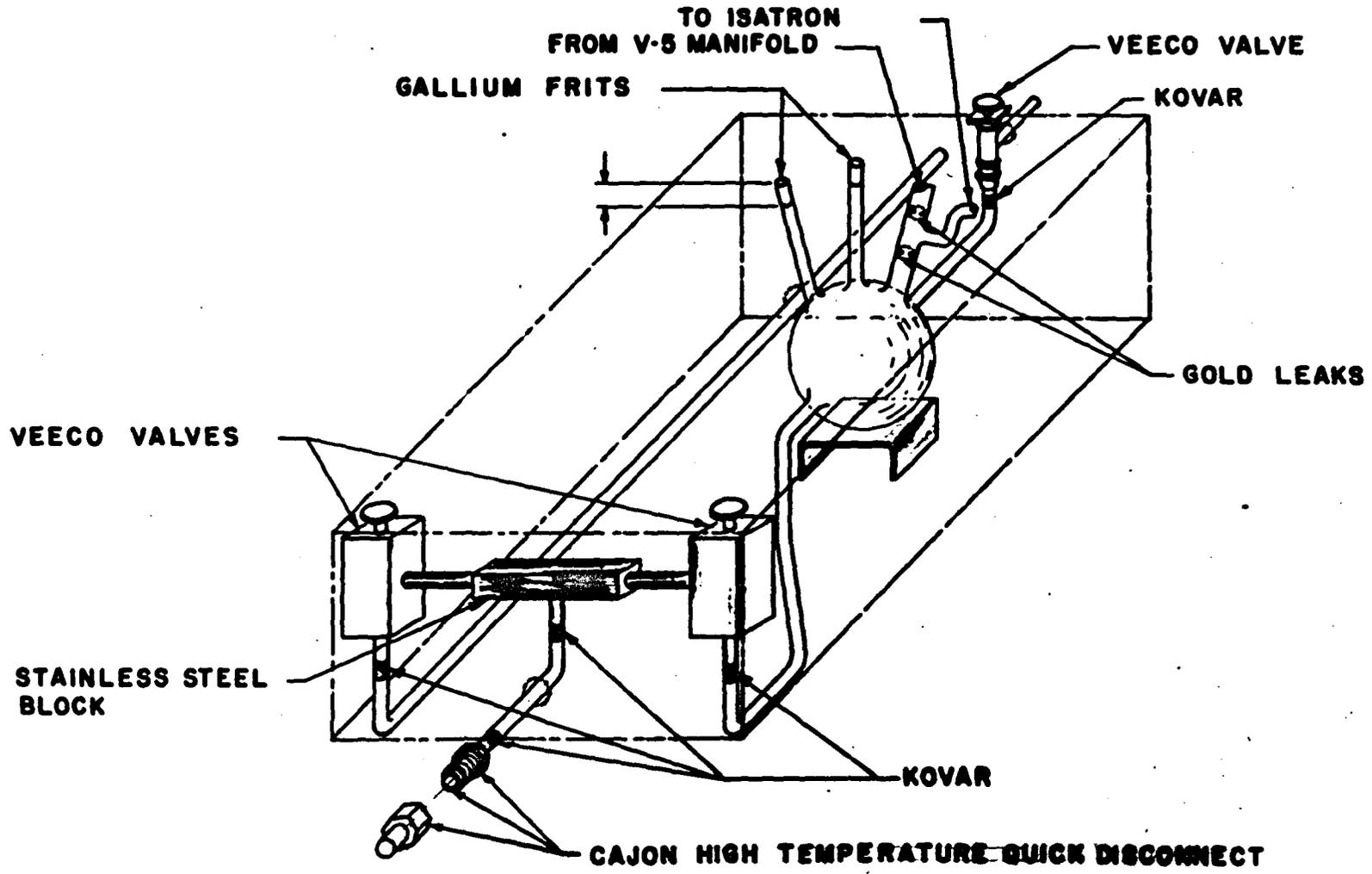
Figure 2

exhaust valve like the input valves. The entire system is evacuated through a safety valve mounted externally at the back of the oven. The output of the safety valve is fed into an oil diffusion pump and, in turn, into a Welch vacuum pump which is mounted in the cabinet base of the standard inlet chassis of the CEC-21-103 mass spectrometer.

The side arms of the input two valves are connected to a stainless steel tee (see figure). One arm of this tee protrudes through the front panel of the oven to permit introduction of solid samples. The end of this side arm is fitted with a Cajon high-vacuum coupling; the female portion of the coupling acts as the sample holder. It can be disconnected from the male portion for cleaning and for the introduction of a new sample. A silicone rubber washer, placed between the male and female portions of the coupling, provides the vacuum seal. A nichrome wire heater is wound around the coupling to provide the heat necessary to vaporize the solid sample. The vapor sample enters the 1 liter reservoir which can be heated to any desired temperature to 250°C. The coupling temperature, normally, is maintained about ten degrees centigrade below the temperature of the oven. This minimizes the effect of "background" in the heated inlet.

The leak line from the gas inlet manifold, in the standard inlet chassis, is connected to the heated inlet sample expansion volume through a glass tee. The common conductor from the tee

extends through the top of the oven and is sealed to the heated cover plate of the analyzer assembly. Two gold leaks (restricted orifices) one for the gas inlet and one for the heated inlet are sealed into the arms of the tee inside the oven. Two, gallium covered, glass frits are attached to the sample expansion volume for the introduction of high-boiling liquid samples.

Current for the oven heater is supplied from a two kilowatt Variac mounted above the oven. A Fenwal thermo-regulator is attached to the expansion volume through the top of the oven. The contacts of the thermo-regulator actuate a relay that switches between taps on the primary of the Variac to increase or decrease the heater current, as needed, to maintain the pre-set temperature of the oven. A thermocouple, attached to heated expansion volume and a pyrometer, monitors the temperature of the oven.

The advantages of this heated inlet system are as follows: (1) it is relatively inexpensive; (2) it successfully maintains a pre-set temperature; (3) it permits the vaporization of solid samples directly rather than the dissolution of the solid in an appropriate solvent which is "flashed-off" prior to the analysis of the solid; (4) it is durable in that the valves are rugged; (5) it does not cause catalytic breakdown of compounds which may come into contact with any of its component parts. It has been used to analyze minute samples of high

boiling fractions collected from gas chromatographs. The
tip of the trap is broken off and inserted into the solid
sample holder. Limited success has also been achieved with
the direct analysis of "spots" on paper chromotograms.

The entire heated inlet system was positioned between
the inlet chassis and the analyzer assembly of the mass
spectrometer. The front view of the heated inlet system
is shown in Figure 3. The rear view of this system is
shown in Figure 4.

Exhaust Pumping System. This study was performed with
a modified exhaust pumping system. The basic CEC instrument
is equipped with a mercury diffusion pump. This pump operates
satisfactorily, but it requires the use of refrigerants
(liquid nitrogen, dry ice, and chilled water). This pump was
replaced by a 8 liter/second Vac-Ion pump which was obtained
from Varian Associates.

The Vac-Ion pump operates by taking gas molecules and atoms
our of circulation by the formation of chemically stable com-
pounds and by ion burial. This is achieved by three interrelated
phenomena; ionization, sputtering, and chemical combination.
The major components of the Vac-Ion pump system are the power
supply, the permanent magnet, and the pump. The pump consists
of an enclosure containing an anode grid "sandwiched" between
two cathode plates. The operation is initiated by a suitable
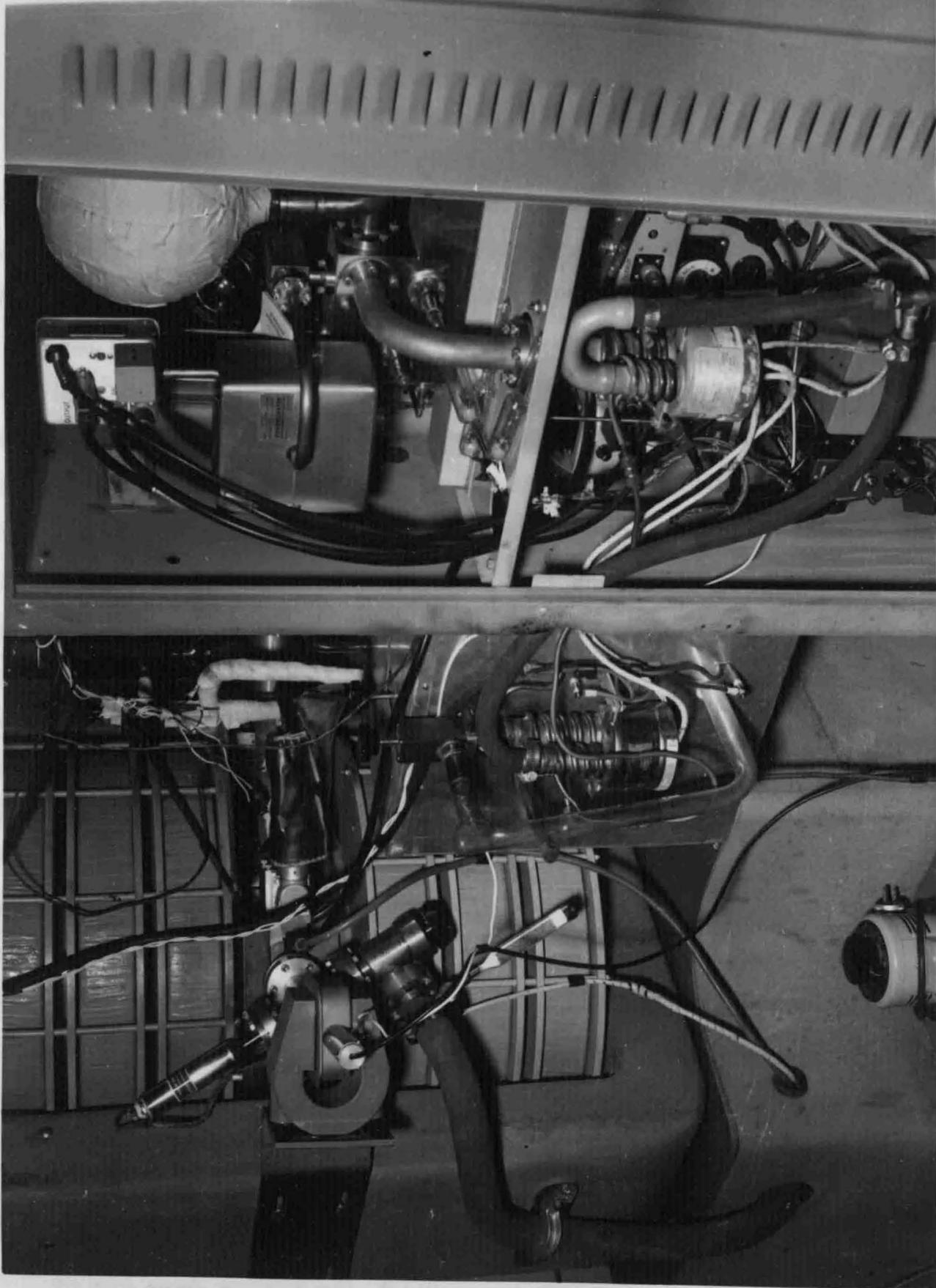
Figure 4

voltage between the anode grid and the cathode plates. Electrons, tending to flow to the anode, are forced in a spiral path by the presence of a magnetic field. This greatly increased electron path length results in a high probability of collision between free electrons and gas molecules. These collisions produce positively charged gas ions and more free electrons. These positively charged ions then bombard the titanium cathode plates and titanium atoms are sputtered out of the plate. The sputtered titanium atoms are deposited on the anode grid, forming chemically stable compounds with the active gas atoms such as oxygen and nitrogen. Chemically inert gases are also removed, probably by ion burial in the cathode and by entrapment on the anode. The operational characteristics and advantages of this pump have been more thoroughly described elsewhere (118). The Vac-Ion pump was equipped with an argon stable cathode, so that the rare gases could be pumped more efficiently. This pump has operated unattended since its installation in February of 1961.

Low Voltage Circuitry. The instrument modifications necessary to measure the ionization and appearance potentials were described by Varsel, Morrell, Resnik and Powell (228).

IV. High Voltage Mass Spectrometry

In the mass spectrometer, which operates at low pressures

(ca. 10^{-6}mm Hg), the molecules of the compound studied are bombarded in the gas phase with electrons of low energy (10 to 100 electron volts). The processes which result from the impact of electrons on organic molecules are exceedingly complex and are by no means fully understood (199, 79, 232). If an impacting electron possesses energy greater than the ionization potential of the molecule, the most common primary process which results from this collision is the removal of one electron from the molecule:

$$M + e^- \longrightarrow M^+ + 2e^- \quad ; \text{ where}$$
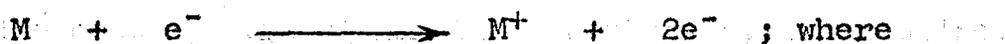
M represents the neutral molecule, e^- the impacting electron, and M^+ the molecular ion. The molecular ion may decompose into a positive ion and a neutral fragment (or free radical). This process can occur repeatedly thus leading to a stepwise multi-fragmentation. The nature of the ions and their relative abundances depend on the structure of the molecules which were bombarded. In general, two compounds that are structurally different will give different fragmentation patterns. Like the infrared spectrum, the mass spectrum can be considered as a fingerprint of the compound.

The literature contains much useful information in regard to correlations of molecular structure and mass spectra. Two recent books have been published which are concerned with this subject (159, 76). These works briefly but thoroughly summarize

all the spectra-structure correlations which have been published
to date. The compounds discussed in this regard are aliphatic
hydrocarbons, alkylbenzenes, monohydric alcohols and phenols,
ketones, aldehydes, ethers, carboxylic acids, esters amines,
amides, indoles, pyrroles, quinolines, pyridines, nitriles,
nitro-compounds and nitrites, nitrosamines, sulfur compounds,
halogenated compounds, and silicone compounds. These books
contain a wealth of information and serve as a part of an
excellent source of knowledge to the novice mass spectroscopist.

The mass spectra of nicotine, anabasine, nornicotine,
pyridine, N-methylpyrrolidine, piperidine, and pyrrolidine
were obtained with the CEC mass spectrometer at an ionizing
voltage of 70 electron-volts and a magnet current of 400
milliamperes. A search of the literature indicates that the
mass spectral patterns of nicotine, anabasine, nornicotine
and N-methylpyrrolidine have not been reported previously.
The mass spectra obtained for pyridine and piperidine compare
quite favorably with those listed in the American Petroleum
Institute tables of mass spectral data. The mass spectrum of
pyrrolidine is in agreement with that reported by Galligos and
Kiser (95).

The spectra of pyridine, piperidine, pyrrolidine, and
N-methylpyrrolidine were obtained by introducing a microliter
of the respective sample via the standard mercury orifice inlet.

The spectra of the alkaloids; nicotine, anabasine, and nor-nicotine were determined by charging a microliter of the respective alkaloid into the heated inlet via the gallium covered sintered disk similar to that of O'Neal and Weir (183). Each alkaloid was also analyzed by introduction into the heated inlet via the Cajon vacuum coupling. The purpose of these analyses was to determine if the alkaloids were pyrolyzed upon contact with the hot metal surface of the coupling. In both cases, the spectrum of the alkaloid obtained by using the gallium frit for sample introduction was identical to that obtained by using the vacuum coupling. These studies show that nicotine, nornicotine, and anabasine did not pyrolyze in the vacuum coupling.

The partial mass spectra of nicotine, nornicotine, and anabasine obtained at a potential of 70 electron-volts are shown in Figure 5. Probably structures are included to coincide with the various ions which were detected. The spectra of these three tobacco alkaloids are characterized by having abundant molecular (parent) ions. Other intense peaks occur at mass-to-charge (m/e) ratios which are attributable to the abstraction of a hydrogen atom (parent minus one), the "splitting out" of a CH_3N neutral fragment (parent minus twenty-nine), and the rupture of the bond between the pyridyl and the cyclic aminyl nuclei (parent minus seventy-eight). The mass spectral

MASS SPECTRA OF NICOTINE, ANABASINE, AND NORNICOTINE
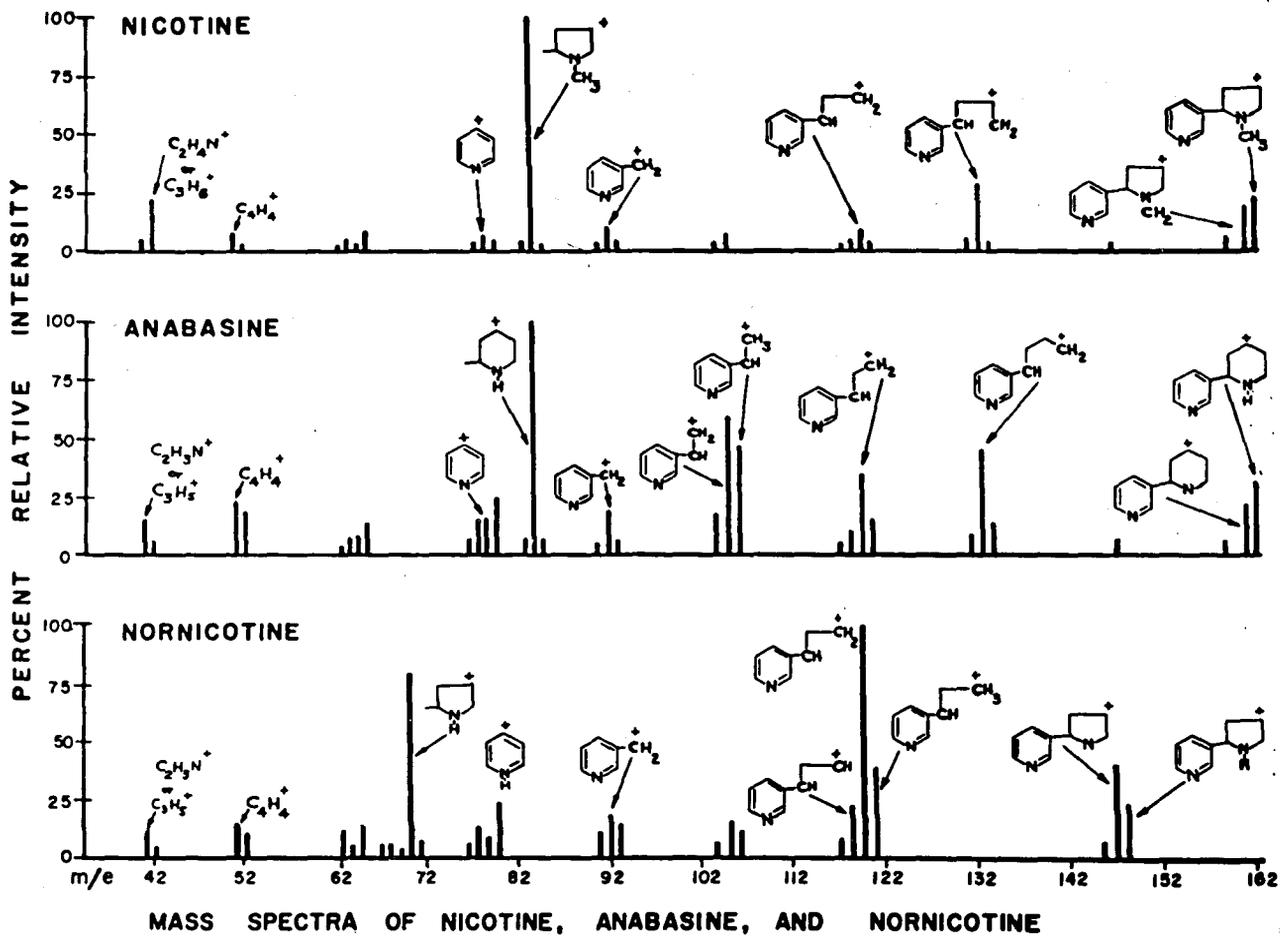
Figure 5

patterns are significantly different, thus the identification
of the individual alkaloid is relatively simple if an unknown
is suggested as being one of the three alkaloids studied in
this work. A description of the proposed mechanisms of ion
formations by electron impact for the three alkaloids will be
presented.

A.   Nicotine (3' - pyridyl - 2 - (N-methyl) - pyrrolidine)

The mass spectrum of nicotine at 70 electron volts exhibits
only six major peaks. These peaks are present at mass to charge
(m/e) ratios of 162, 161, 133, 84, 42, and 28. The m/e 162
ion is the molecular or parent ion. This ion is formed by the
removal of one electron from the neutral molecule. The process
may be illustrated as follows:
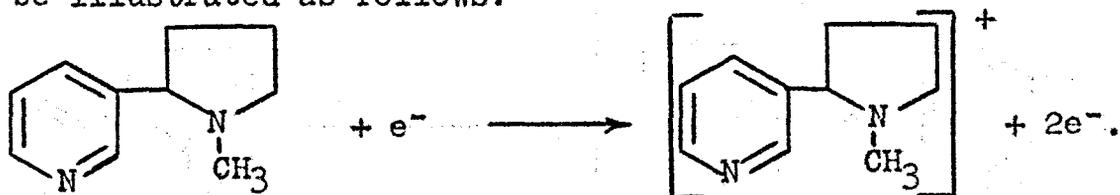
The m/e 161 ion is formed by the removal of a hydrogen atom
from the molecular ion. The hydrogen atom may come from the
pyridyl nucleus, the N-methyl group or the carbons which comprise
the cyclic saturated amine. Based on data which will be discussed
later, it is felt that the hydrogen atom is removed from the
N-methyl group. The postulated process is as follows:
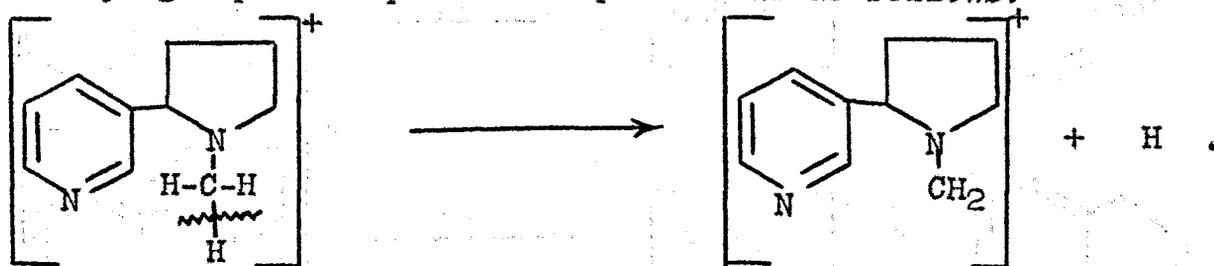
The m/e 133 ion is thought to be formed by the loss of a CH₃N neutral fragment from the molecular ion. Undoubtedly this neutral fragment is formed by bond rupture of both the carbon-nitrogen bonds of the cyclic amine. The proposed process is as follows:
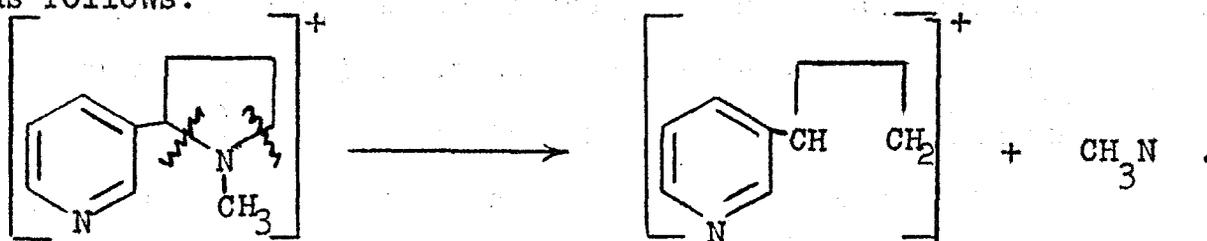
The most abundant ion (base peak) in the mass spectrum of nicotine occurs at m/e 84. This ion is undoubtedly formed by breaking the bond between the pyridyl and the N-methyl-pyrrolidinyl nuclei. The process is as follows:
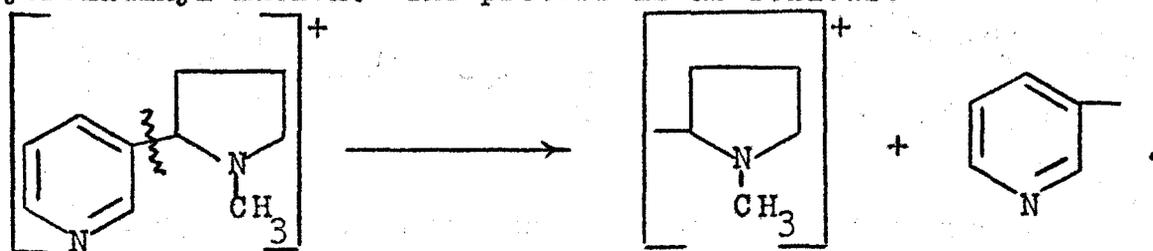
The m/e 42 ion is believed to be formed from nicotine by splitting out a C_2H_4N positive ion. However, this ion could exist empirically as C_3H_6 which could be formed by cleavage of the carbon-carbon bonds in the cyclic amine. The processes are:
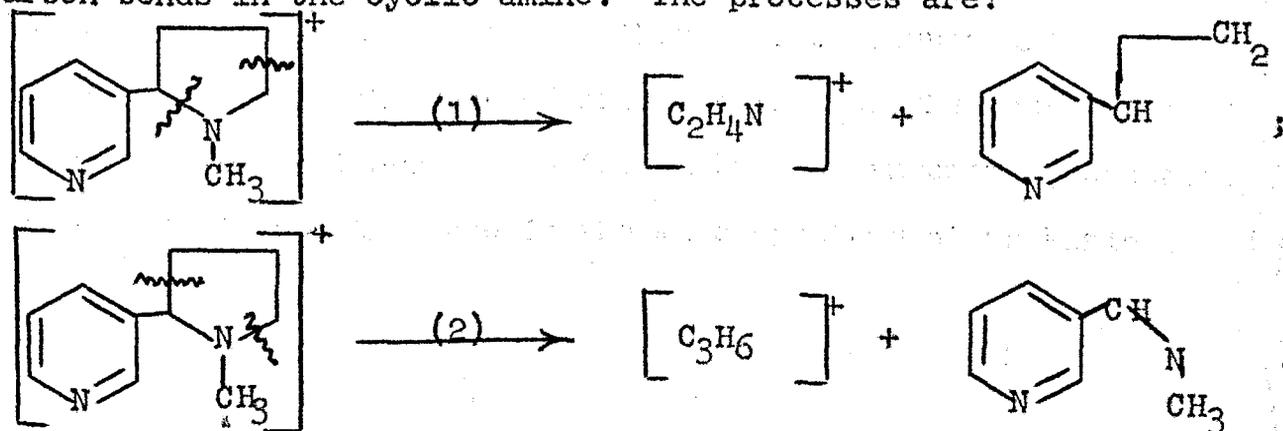
The prominence of this ion in the spectrum indicates that it is formed quite readily.

The m/e 28 ion probably results from the formation of CH_2N^+ or $C_2H_4^+$. This ion could be formed from the parent minus one ion (m/e 161) by either of the processes shown below. Although energy considerations cannot rule out either mode of formation, a high resolution mass spectrometer would be useful in elucidating the exact mass of the fragment ion.
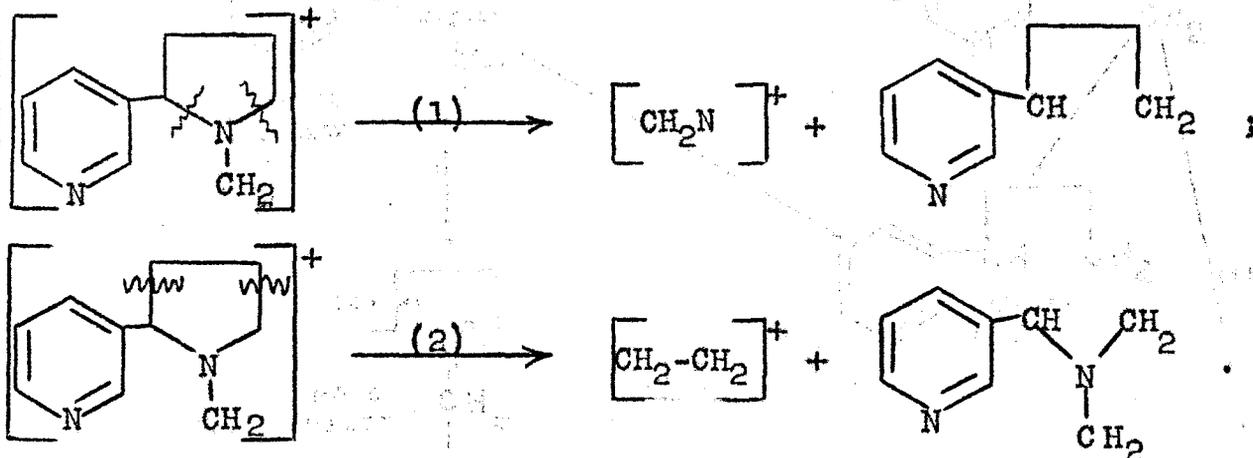
The proposed mechanisms and structures of the various fragment ions together with respective pattern coefficients are summarized in Figure 6.

B.   Anabasine (3' pyridyl-2-piperidine)

Although the empirical formulas of nicotine and anabasine are identical, the mass spectra of these two compounds are quite different. In the case of nicotine none of the most abundant ions are believed to be formed by rearrangement processes. However, this is not the case in the mass spectrum of anabasine.

FRAGMENTATION POSSIBILITIES FOR NICOTINE

Figure 6