THE FAST ATOM BOMBARDMENT MASS SPECTROMETRIC ANALYSIS
OF THE CARBAMATE PESTICIDE CARBARYL

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To my father and mother
for their love and encouragement

ABSTRACT

The carbamate pesticide, carbaryl, was quantitatively studied using fast atom bombardment mass spectrometry (FAB-MS). Mass spectra were obtained in the positive ion-mode using both 2-nitrophenyloctyl ether (NPOE) and 3-nitrobenzyl alcohol (NBA) as matrix liquids. The sample was applied by three different techniques; simple mixing, solvent mixing and surface precipitation.

Smaller volumes of matrix liquid were found to produce more favourable ion currents. Detection limits were largely independent of the matrix or application technique used. The relationship between ion current and the mass of analyte was found to be intricately related to the choice of matrix liquid.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF GRAPHS

I. INTRODUCTION

A. The Compound

   1) History

The first carbamate insecticide was synthesized by Dr. Hans Gysin while working as a reasearch chemist at the Geigy Chemical Company in Switzerland (1). The research involved the synthesis of cycloaliphatic carbamate esters which the company hoped would prove to be insect repellants. One of these compounds was dimetan, illustrated in Figure 1.1. Biological testing proved the compound to be a particularly poor repellent but an excellent insecticide when applied to houseflies and aphids.

Dr. Joseph A. Lambrech of the Union Carbide Corporation in the United States, encouraged by the work done at Geigy, synthesized the experimental compound UC7744, later given the trade name Sevin and the common name, carbaryl (2). Carbaryl differed from dimetan in that it possessed an aryl rather than an enone group and a monomethylcarbamyl moiety (Figure 1.2). A description of the pesticide first appeared in the literature in 1957 (3). By 1965, millions of pounds were being applied worldwide (4).

   2) Basic Chemical and Physical Properties

The physical and chemical properties of carbaryl make it an ideal pesticide to work with in the laboratory. It is readily available in

Figure 1:   The Structure of Two of the Earliest Carbamate
            Pesticides

1.   Dimetan
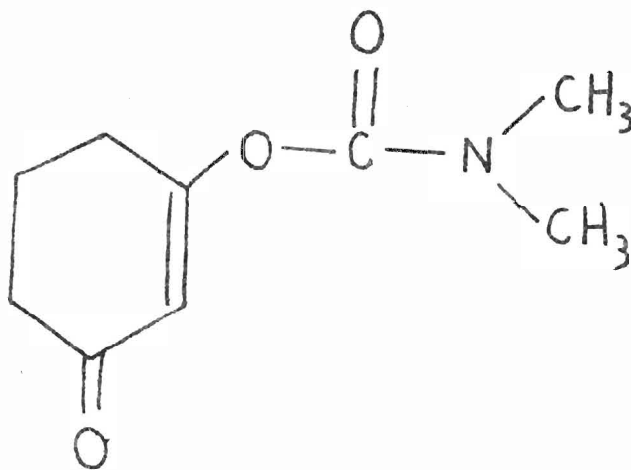
2.   Carbaryl
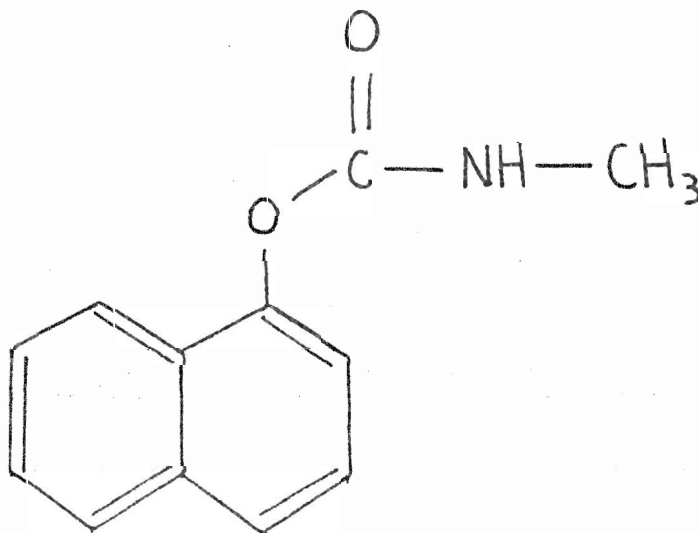
the form of a 99% pure white powder.

The compound has a melting point of 142^0C, is moderately soluble in most organic solvents, is soluble in water at 120mg/L at 30^0C, is non-corrosive, and is stable to light and acids (5). The most significant degradative pathway for carbaryl involves hydrolysis in alkaline media. This mechanism involves initial removal of a proton from the NH group by OH$^-$ to form an unstable intermediate which decomposes to form methylisocyanate and a phenoxide ion. Methylisocyanate then reacts instantaneously with water to give N-methylcarbamic acid which decomposes to methylamine and carbon dioxide (Figure 2)(4,7).

Carbaryl is manufactured by two methods: (1) by the reaction of 1-naphthol and methyl isocyanate (2) by the reaction of 1-naphthol, phosgene and methylamine (Figure 3 on page 5).

Carbaryl acts as both a residual contact and stomach insect poison. It has a low mammalian toxicity: the oral LD50 to rats is 250 mg/kg and the rabbit dermal LD50 is in excess of 2000 mg/kg (8). Minimal hazard is presented to non-target organisms with the exception of honeybees and certain plant species including apple trees (9).

3) Methods of Application for Carbaryl

A variety of formulations of carbaryl are available and include a 50% or 10% granule and 2% to 10% dust. It would be virtually impossible to list all of the uses for carbaryl but some of the more important include application to various fruit, vegatable, grain, fiber and forage crops, as well as forests, livestock, pets and poultry. Rates of application usually extend from 1/2 to 4 lb

Figure 2:   Mechanism for the Alkaline Hydrolysis of Carbaryl (6)

1.

$$\text{(ArO-C(=O)-NHCH}_3\text{)} + OH^{\ominus} \rightleftharpoons \left[\text{Ar O C(=O) N}^{\ominus}\text{CH}_3 \right] + H_2O$$

$$\updownarrow$$

$$\left[\text{Ar O C(O}^{\ominus}\text{)} = NCH_3 \right]$$

$$\downarrow$$

$$+ CH_3NCO$$

2.

$$CH_3NCO + H_2O \longrightarrow CH_3NHC(=O)OH$$

3.

$$CH_3NHC(=O)OH \longrightarrow CH_3NH_2 + CO_2$$
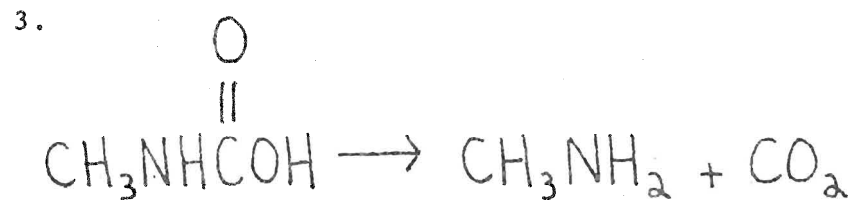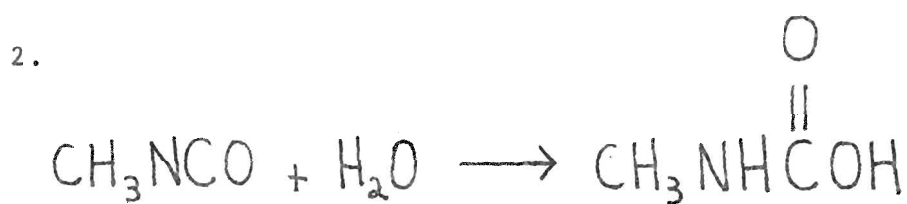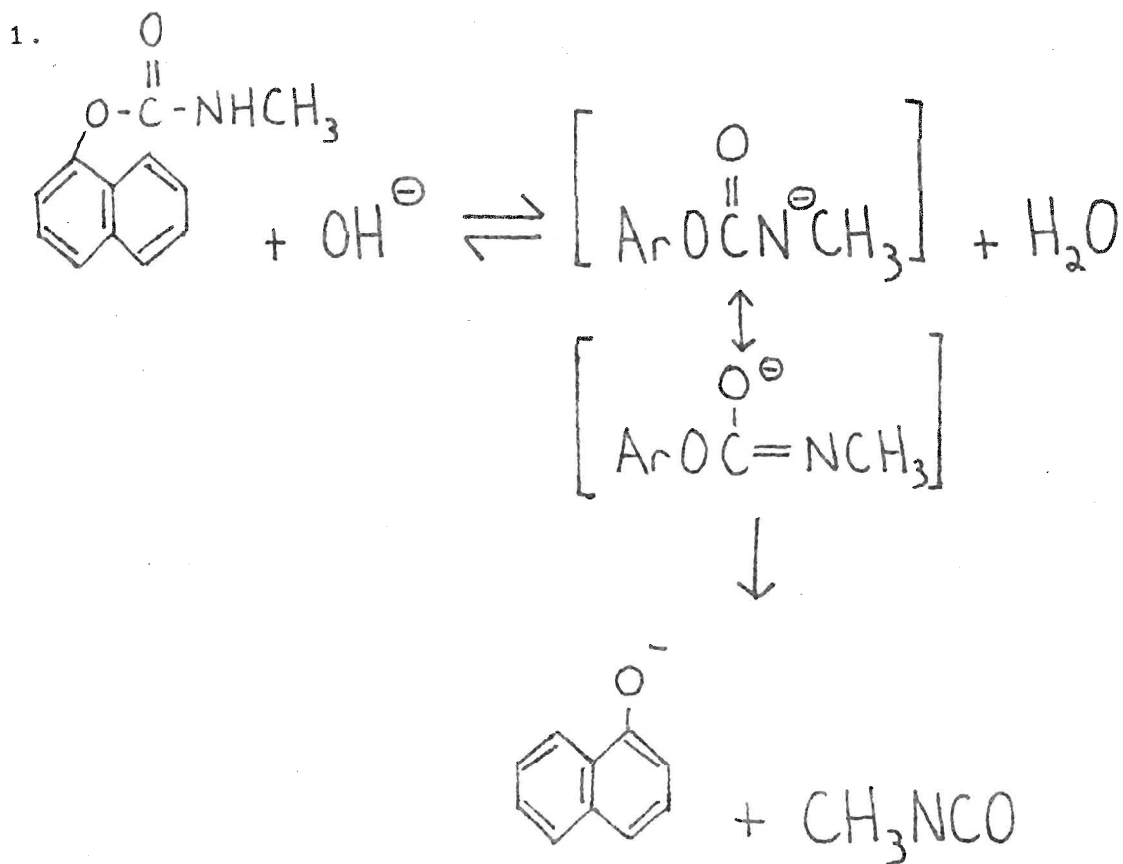
Figure 3: Synthesis Routes for the Production of 1-Naphthyl
N-Methyl Carbarmate (7)
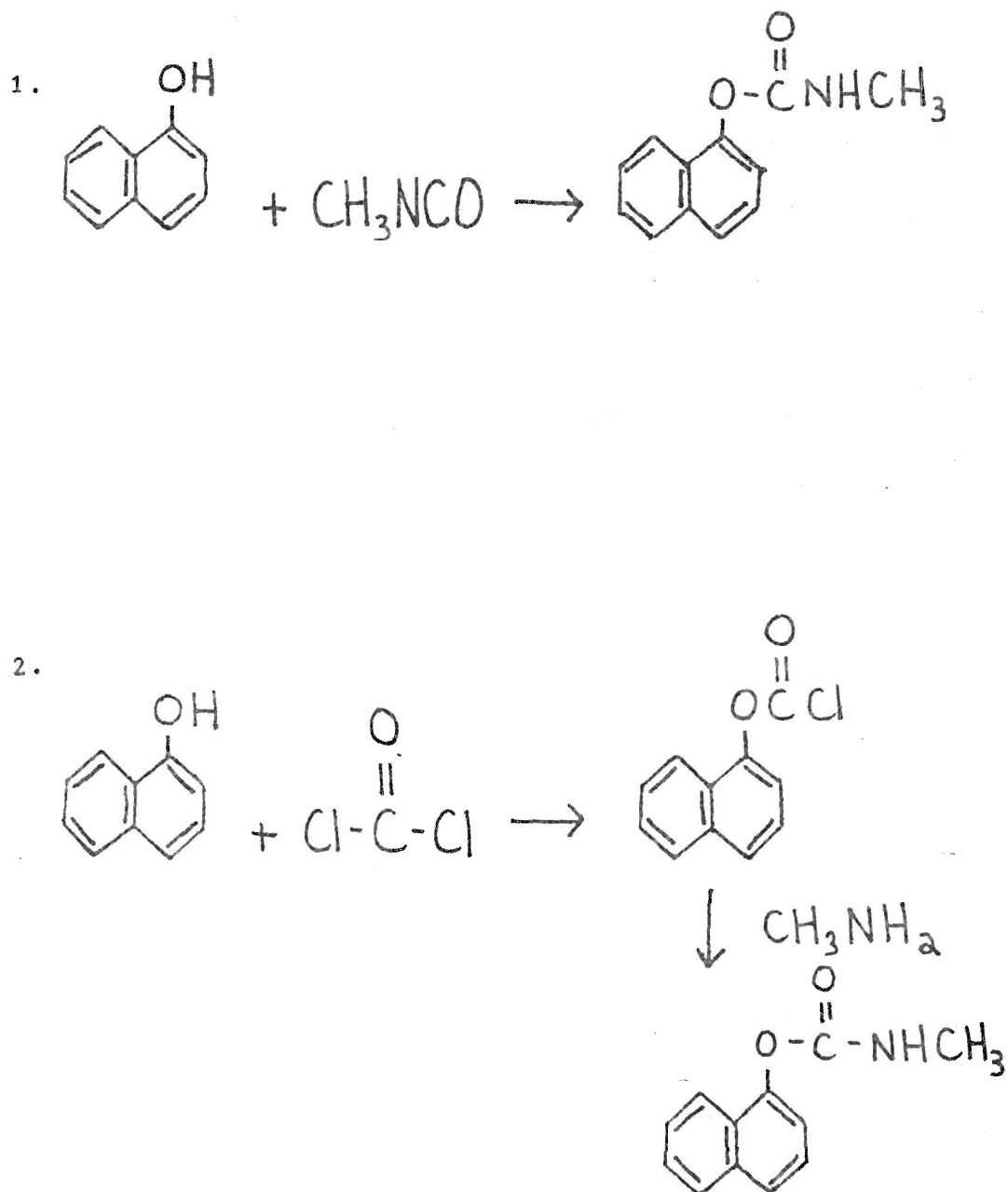
active/acre or from to 0.5 to 1.05 lb active/100 gal. of water.

B. Classical Methods of Analysis

Almost as many classical techniques for the analysis of carbaryl
exist as there are applications for the insecticide. These include
high performance liquid chromatography (HPLC) with a variety of
detection techniques (10-13), spectrophotometry (14,15), fluorimetry
(16), gas chromatography with derivatization of the analyte (17) and
thin-layer chromatography (TLC) (18). The best way to illustrate the
more important techniques is through an example of each method.

  1) High Performance Liquid Chromatography

Bottomley and Baker (19) used HPLC in the quantitative analysis of
carbaryl in wheat. The carbaryl was extracted from powdered wheat
with a 1:1 acetone:methanol mixture. Solids were removed by
centrifugation and coextractives were removed with dichloromethane.
The resulting solution was then evaporated to dryness and redissolved
in methanol. The chromatographic column was constructed of stainless
steel packed with 5 μm Spherisorb ODS and utilized a 20 μL sample
injection loop. The detector was a variable wavelength UV device set
at 224 nm and the mobile phase consisted of 4:1 methanol:water flowing
at 1 mL/min.

The method exhibited good sensitivity, the limit of determination
for carbaryl being 0.05 mg/kg of wheat. Selectivity is favourable
with no interferences being produced by a variety of organophosphorus,

organochlorine and synthetic pyrethroids known to have been present. Reproducibility was found to be excellent.

The HPLC analysis also presented the disadvantage of requiring a rather extensive and time consuming sample clean up.

2) Spectrophotometry

Chiba developed a colorimetric method for the determination of carbaryl on fruit tree foliage (14). A 5 cm^2 disk of leaf was removed and the carbaryl extracted and hydrolyzed by being immersed 2 minutes in a 0.03% w/v methanolic NaOH solution. The 1-naphthol hydrolysis product was then coupled with p-nitrobenzenediazonium tetrafluoroborate to produce the colored species desired (Figure 4). The absorbance obeyed Beer's law when measured at 580 nm within a concentration range of 0.5 -10 $\mu g/cm^2$ of leaf surface or 0.25-5 $\mu g/mL$ of alkaline solution in a test tube.

The method provides good sensitivity and selectivity with no interferences being observed when 2 $\mu g/mL$ of such common pesticides as dicofol, DDT, tetradifon, azinphosmethyl, phosmet, captan and folpet were added individually. Spectrophotometry also provides for a fairly rapid, and simple analysis of carbaryl (3 min./sample when 50 or more samples are processed).

There are two principal drawbacks to the method. At the time of publication, it was only suitable for measuring carbaryl deposits on leaves and not other materials. Second, it involves a derivatization which can reduce the efficiency of the analysis.

Figure 4:   The Colorimetric Reaction Between 1-Naphthol and
p-Nitrobenzenediazonium Tetrafluoroborate
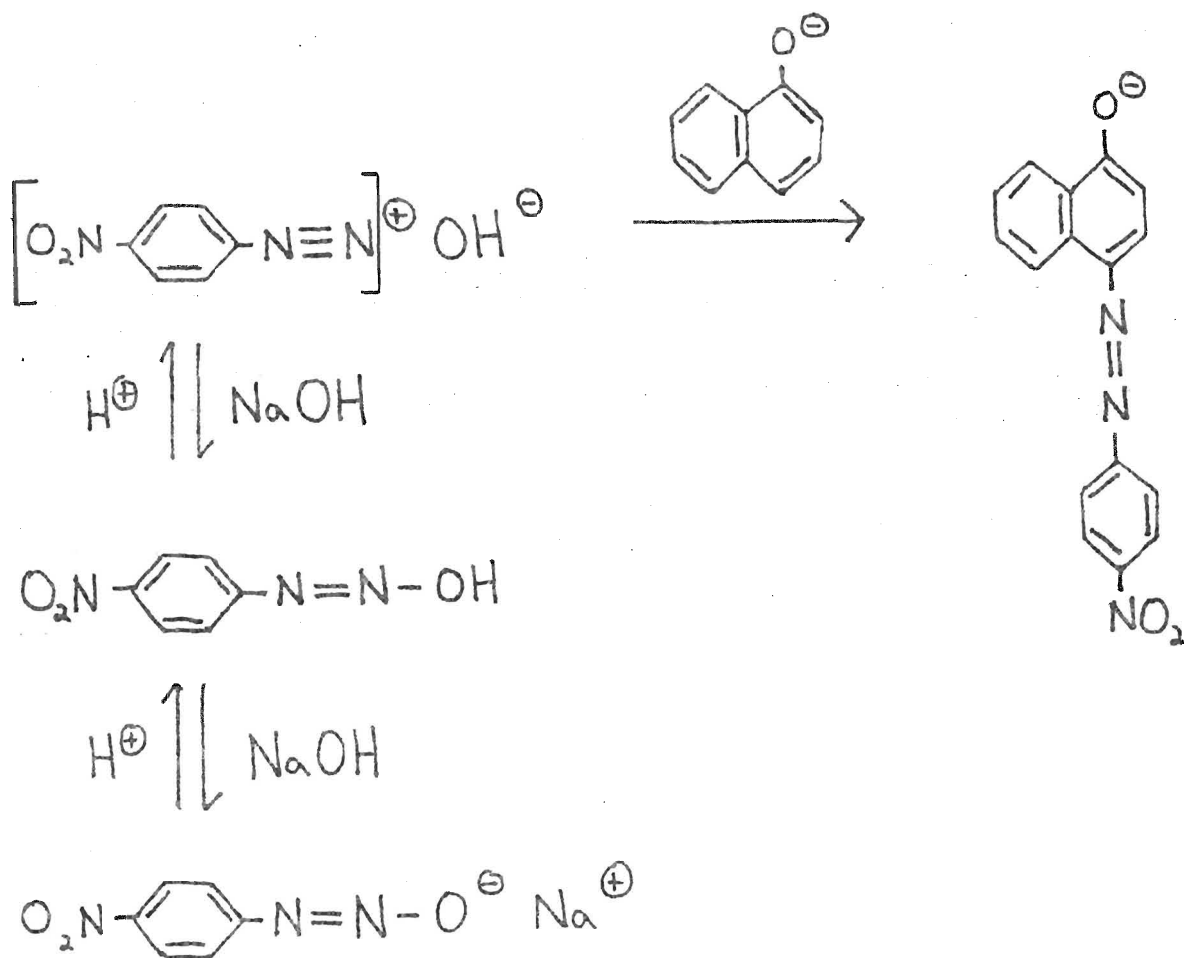
3) Thin-Layer Chromatography

Wood and Kanagasabapathy utilized inexpensive thin-layer chromatographic procedures in the estimation of carbaryl residues in fruit and vegetables (20). Carbaryl was extracted from crop samples by macerating 25g of the sample in two 50mL aliquots of dichloromethane and vacuum filtering the resultant solutions. Then, 40 mL of this resulting solution was evaporated to dryness using a rotary evaporator with a water bath at 35^0C. The residue was redissolved twice with approximately 2.0 mL of acetone and evaporated to dryness with a stream of clean, dry air. The resulting residue was redissolved in 0.2 mL of acetone. Volumes of from 5 -10 μL of this solution were then spotted on the TLC plates using disposable micropipettes. The plates consisted of Merck silica gel 60 for normal-phase chromatography and Whatman $KC_{18}F$ for reversed-phase chromatography. The mobile phase consisted of chloroform for normal-phase separation, and ethanol-water mixture (80/20 by volume) for reverse-phase separations. After developement, the solvent was allowed to evaporate from the plate which was then sprayed with ethanolic potassium hydroxide (1M) followed by a cold 4-nitrobenzenediazonium tetrafluoroborate (NBDF) solution (25 mg NBDF in 100 mL of solution containing 90 mL of ethanol and 10 mL of 2,2'-oxydiethanol).

The method provides for good sensitivity with lower limits of detection being 100 and 200 ng for normal-phase and reverse-phase analysis respectively. The method is also inexpensive, requires no complex instrumentation, and is thus a preferred method in remote

areas. However, the method chosen to quantify the analysis involves visual comparison with a range of standard spots chromatographed alongside the sample on the same plate. Precision was found to be plus or minus 50% and thus the method is semi-quantitative at best.

C. Mass Spectrometry

1) Mass Spectrometry as an Analytical Technique

A mass spectrometer is an instrument which produces ions indicative of the original sample molecules and then separates these ions according to their mass-to-charge (m/z) ratio. A mass spectrometer typically consists of an inlet system, an ion source, a mass analyzer, a detector and a recorder. Ions may be produced in a variety of manners including electron impact (EI), chemical ionization (CI), field desorption (FD), plasma desorption (PD), secondary ion mass spectrometry (SIMS), and fast atom bombardment (FAB). The ions produced can be separated in many ways, by magnetic, quadrupole and time-of-flight analyzers. The majority of mass spectrometers are designed for the efficient analysis of positive ions, though both positive and negative ions are produced in the ion source.

Mass spectrometry has proven useful when applied to a variety of analytical problems. The principal advantages offered by mass spectrometry are those of superior sensitivity and selectivity. Instrument systems combining a gas chromatograph and a mass spectrometer (GC-MS) are of high value for analysis of

complex mixtures such as biological fluids, environmental samples and industrial process streams, as illustrated by Avery and Junk (21). Systems combining high performance liquid chromatographs (LC-MS) with a mass spectrometer have been extremely helpful in the analysis of systems not amenable to GC-MS, for example, those involving components which are either thermally labile or have low vapour pressures. This usefulness was illustrated by Voyksner and Bursey, who used LC-MS to analyze for selected carbamate pesticides (22).

Quantitative analysis using chromatographic systems and mass spectrometry normally employs a process in which only a few m/z values, commonly one to eight, are monitored continuously as a function of time. This process is commonly known as selected ion monitoring. In a conventional scan, each mass in the spectrum is focused on the collector for only a few milliseconds, the exact time depending on the scan rate and the resolution. If only one m/z value is monitored continuously it is focused at the collector for the whole period of elution of a chromatographic peak. Since a chromatographic peak is several seconds wide, the number of ions detected will be several thousand times greater than it would if a conventional scan was utilized. Thus, single ion monitoring can be thousands of times more sensitive for a particular compound than the ion from a normally scanned spectrum (23).

Although, when quantitative mass spectrometry is mentioned one's thoughts turn to a GC- or LC-MS system, a study of the literature shows that much useful work is carried out by means of direct sample introduction (24,25). Without a doubt, this is a much neglected area, and one which would benefit considerably from further applications (23).

2) Present Mass Spectrometric Methods for Determining Carbaryl

A variety of chromatographic systems have been used in conjunction with mass spectrometric systems to quantify carbaryl. Cairns et al. developed a method to quantify carbaryl in pineapples and marionberries using gas chromatography/mass spectrometry with ammonia chemical ionization (10,26). Liquid chromatography/mass spectrometry has been used to analyze carbaryl quantitatively with several approaches to overcome the problems associated with coupling the effluent of the LC to the source of a mass spectrometer, including moving belt (27), direct liquid introduction (22) and thermospray (28). Perhaps the best way to illustrate the value of mass spectrometry as an analytical technique for the quantification of carbaryl is through the description of specific examples.

Cairns et al. developed a gas chromatography mass spectrometry technique using ammonia chemical ionization and selected ion monitoring to quantify carbaryl in pineapples (10). The apparatus consisted of a Finnigan 3300 quadrupole mass spectrometer equipped with a chemical ionization source and INCOS data system. The gas chromatograph utilized a 45 cm X 2 mm internal diameter glass column packed with 2% DEGS on 80/100 mesh Chromosorb W. The carrier gas was methane flowing at 25 mL/min., the column inlet temperature was 250^0C, the column temperature was 180^0C and isothermal. The electron energy was 150 eV at a source pressure of 0.8 torr. Quantitation was achieved by selected ion monitoring of the ion at m/z 145 which was the most abundant peak in the spectrum. The technique provides for excellent sensitivity with quantities of carbaryl in the range of 20

ng being detected. The correlation coefficient (r^2) for the calibration curve used for quantification was found to be 0.95. However, the response between the three replicates performed at each concentration of carbaryl was found to vary by as much as 30%. This was likely the result of the fact that carbaryl, which is thermally labile, was passed through a GC column at 180^0C.

Voyksner and Bursey, modified a Finnigan 4500 mass spectrometer to perform direct liquid introduction liquid chromatography/mass spectrometry , DLI-LC/MS (22). The mass spectrometer used was a Finnigan 4500 equipped with an INCOS data system and modified Vespel desolvation chamber. The source pressure was regulated by the positioning of the DLI probe with respect to the desolvation chamber. The LC/MS interface consisted of a Hewlett-Packard direct liquid introduction probe (DLI) of the variable split type. The split ratio was normally 1:100, resulting in approxiamtely 10-30 µL/min of mobile phase entering the mass spectrometer. The LC system consisted of a Waters 6000A pump with UK-6 injector and a model 440 fixed-wavelength UV detector at 254 nm. The column with an internal diameter of 4.6 mm was packed with 5 µm Nucleosil C_{18}. The mobile phase was acetonitrile/water (60:40) at a flow rate of 1.5 mL/min. The mass spectrometer was operated in the chemical ionization mode with an electron energy of 100 eV, an emission current of 0.3 mA and a source temperature of 180^0C. The instrument was scanned from 150 to 500 daltons at 2 seconds per scan. The LC mobile phase served as the CI reagent gas.

Preliminary results indicated that both positive and negative modes of ion detection offered similar sensitivity. The actual

DLI-HPLC/MS analysis was performed at a previously determined optimal source temperature and pressure, 180^0C and 0.63 torr respectively. These factors have a dramatic effect on sensitivity, as frequently found for samples ionized by electron capture CI processes (29). The detection limit for carbaryl was found to be 40 ng, a number which could be further reduced if not for the 1:100 split of the HPLC effluent. The principal advantage of this particular use of the mass spectrometer is the added specificity gained in the analysis. The ability to observe characteristic ions for the target compound decreases the likelihood of interferences from coeluting compounds.

Thus, it is obvious that mass spectrometric methods offer excellent sensitivity for the determination of carbaryl, better than either TLC or spectrophometry and as good or better as the HPLC methods. Furthermore, the specificity offered by mass spectrometry is superior to all the aforementioned techniques.

3) Fast Atom Bombardment (FAB)

Barber et al. introduced Fast Atom Bombardment in 1981 (30). The apparatus consisted of a cold cathode discharge ion source and a collision chamber. The ion source produced a beam of Ar^+ ions with a controlled energy of 2-10 KeV which was directed into the collision chamber filled with Ar at 10^{-3}-10^{-4} torr. Resonant charge exchange occurred with little loss of forward momentum producing a beam of Ar and Ar^+, both with the kinetic energy of the original beam. The ionic component was removed using a set of electrostatic deflector plates.

Materials for analysis were introduced into the system by deposition from solution onto a metal plate affixed to a solid insertion probe. The sample could then be introduced to the ion source, through a vacuum lock, in order to intercept the fast atom beam. The resulting collision removed sample from the probe tip into the gas phase due to a momentum transfer from the impinging particles to the target. Some of the sputtered material was in the form of positively or negatively charged ions allowing either positive or negative mass spectrometric analysis.

Barber et al. discovered that the initial means of sample preparation resulted in mass spectra of a transient nature with the exception that low vapour pressure liquids and oils gave spectra that lasted for hours (31). This led to the technique of introducing samples on the probe tip by dissolving then in a viscous solvent which came to be known as the matrix liquid.

De Pauw summarized the general requirements concerning the solvent properties of the matrix (33). The sample must be soluble in the matrix. Solvents of low vapour pressure are best since they provide a stable surface over the time scale of a recorded spectrum in the high vacuum of the mass spectrometer. The viscosity of the matrix must be low enough to ensure diffusion of solutes to the surface on the time scale of a spectrum. Ions produced by the matrix itself must be as unobstrusive as possible in the FAB mass spectrum. The matrix must be chemically inert barring reactions used to promote ion yield. Generally, hydroxylated matrices work well in combination with polar molecules and organic salts. This is the case since their high dielectric constants favor the dissociation of ion pairs, lowering the

coulombic interaction. Aprotic solvents can be used in the mass spectrometry of inorganic and organometallic complexes where acid-base reaction and solvolysis must be avoided. In the case of less polar samples for which proton or cation attachment are not possible, redox matrices can be employed. Oxidizing matrices are those with high electron affinities and reducing matrices are those with low ionization energies. Solubility problems can also be overcome using selective matrices. Aromatic matrices such as diamylphenol or 3-nitrobenzyl alcohol can be employed when solubility in aliphatic matrices is low. Table 1 contains a list of useful matrices together with their major spectral peaks and some of the suggested fields of application.

Martin et al., having undertaken a systematic investigation of the experimental variables in FAB, produced a number of recommendations for FAB experiments (32). A probe tip of 303 stainless steel was found to be superior to one of copper in that it was not etched by the 50% nitric acid used in cleaning, and produced no cluster ions with the matrix. Futhermore, it had adequate wettability and no sample memory. To determine the optimum incident angle for FAB-MS, several probe tips were machined with incident angles ranging from $\Theta = 30^0$ to $\Theta = 90^0$ in 10^0 increments. (For the definition of incident angle, see Figure 5 on page 18). Experiments carried out several times on several different samples in all cases indicated $+60^0$ as the optimal incident angle. It was found that the gas used to sputter the sample played a major role in determining the total ion current of that sample. For monatomic gases, the ionization efficiency of a specific sample was directly proportional to the mass

Table 1: Information Concerning Selected Matrices (33)

Matrix compound	MW	Base peak	Major peaks above MW	Applications	BP
Glycerol (3)	92	93, $(M + H)^+$ 91, $(M - H)^-$	$[93 + (92)_n]^+$ $[91 + (92)_n]^-$	Standard Matrix Various additives and cosolvents	182°C/20 mm
Thioglycerol (110)	108	91, $(M - OH)^+$ 107, $(M - H)^-$	$[109 + (108)_n]^+$ $[107 + (108)_n]^-$	Peptides, antibiotics organometallics	118°C/5 mm
Diethanolamine (111)	105	106, $(M + H)^+$	$[106 + (105)_n]^+$	Oligosaccharides	217°C/150 mm
Triethanolamine (111)	149	150, $(M + H)^+$ 148, $(M - H)^-$	$[150 + (149)_n]^+$	Negative ions: sulfonates; fatty acids	190°C/5 mm
Dithioerythritol (112) Dithiothreitol 1:5 1:5 (Magic Bullet)	154	119, $(M - H_2 - H_2S)^+$ 153, $(M - H)^-$	$[155 + (154)_n]^+$ $[153 + (154)_n]^-$ (weak)	Organometallics	——
Polyethyleneglycols (113)	$62 + (44)_n$	89, $(CH_2CH_2O)_2H^+$ 43, $(CHCH_2O)^-$ 61, $(HOCH_2CH_2O)^-$	$(M + H)^+$ $(M - H)^-$	Saccharides, boronates Mass marker, no clusters with solute	——
2-Nitrophenyl-octylether (114)	251	140, (M-octyl + H_2)$^+$	Many decomposition peaks: 235, 252, 265, 280, 294, 334, 348, 364, 391, 470, 485, 501	Oxidising matrix, nonpolar molecules, organometallics	——
Tetramethylenesulfone	120	121, $(M + H)^+$	241, $(2M + H)^+$	volatile, nonpolar	285°C/760 mm
3-Nitrobenzylalcohol (105)	153	154, $(M + H)^+$	$[154 + (153)_n]^+$	less polar compounds, aromatics oxidizing matrix	175°C/3 mm

17

Figure 5:   Dimensions of Sample Probe Tips Used for FAB-MS
and Definition of the Angle of Incidence (32)
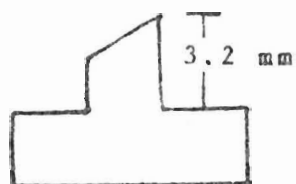
Tip Dia. = 2.5 mm

Surface Area = 5.7 mm^2
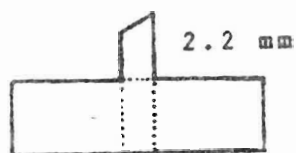
Tip Dia. = 1.0 mm

Surface Area = 1.2 mm^2

3.2 mm

2.2 mm

2.5 mm

8.3 mm
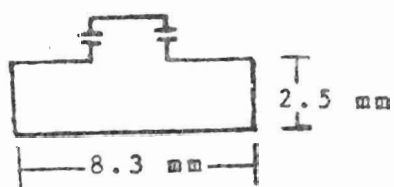
Angle of Incidence

Fab Gun

Atom Beam

60°

Normal to the Surface

Θ

Analyzer
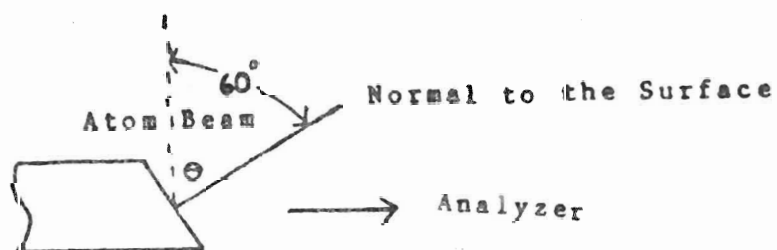
of the incident neutral particles. Of the gases normally used for ionization in FAB-MS, xenon was by far the most effective followed by argon.

Fast atom bombardment exhibits a number of advantages which have insured its wide-spread use. Ionization occurs at room temperature: since sample volatilisation is not required, thermal effects which have proven troublesome for polar and thermally unstable compounds are eliminated. Sample preparation for FAB is simple when compared to the derivatisation required for electron impact or field desorption techniques. The method can be used to produce either positive or negative ion spectra, and gives good pseudo-molecular ion sensitivity and in some cases structurally significant fragmentation unlike many of the other softer ionisation techniques. Furthermore, mass spectra may be obtained for molecules of relatively high molecular weight, above 23,000 amu for biological systems using PD-MS and above 30,000 amu using SIMS on inorganic clusters.

D. Area of Interest

Relatively little work has been done on quantitative analysis utilizing fast atom bombardment mass spectrometry. The work that has been done predominantly involves projects such as the measurement of acidity constants (34) and stability constants (35). Thus, any research conducted involving quantitative analysis of a single analyte using FAB-MS would serve to further illuminate the worth of the technique. The benefits include the sensitivity and selectivity of mass spectrometry combined with an ionization technique providing

simple sample preparation, a lack of themal effects and excellent fragmentation. Valuable information could be obtained concerning detection limits, matrices or matrix effects, and application techniques. The work would even further demonstrate the usefulness in analysis of non-chromatographic mass spectrometric techniques.

Carbaryl is an excellent choice of compound for quantitative study using FAB-MS for a number of reasons. First, carbaryl is a pesticide and with the increased public awareness, (and unfortunately, fear of such compounds) no method for its analysis can be without benefit. Furthermore, it is a pesticide which sees extremely widespread use and will likely continue to do so into the forseeable future. The thermal lability of the compound also provides the opportunity to demonstrate fast atom bombardment's benefits as a soft ionization technique. High sensitivity might make possible the analysis of carbaryl _in situ_ on environmental substrates which are easily applied to the FAB probe using double faced tape.

II. EXPERIMENTAL

A. Instrumentation

The mass spectra were obtained using an AEI MS-30 double beam, double focusing mass spectrometer. The instrument was altered after production to allow fast atom bombardment mass spectra to be obtained. This was achieved by fitting beam 1 with a Kratos FAB source and a CI fast pumping system. The mass spectrometer was run at room temperature with a resolution of 1000, a gain setting of 9.8, an accelerating voltage of 4 kV and at a source pressure of 10^{-5} torr. A scan rate of 10 sec/decade was utilized.

Samples on which fast atom bombardment ionization was performed were introduced into the mass spectrometer's source using a direct insertion probe, D.I.P. The probe consisted of a solid metal shaft, insulated from the high voltage of the source. The actual samples were placed on a removeable probe tip constructed of stainless steel and affixed to the probe with two pins. The angle of incidence of the beam with the probe tip was 60^{0}. The probe was aligned visually with respect to the FAB gun using screws implanted in both the vacuum lock and probe.

The fast atom beam was produced using a FAB gun attached to a B-50 power supply manufactured by Ion Tech of Teddington, England. The gases used to produce the fast atom beam consisted of either argon or xenon depending which proved to be available. The FAB gun was operated at a voltage of 7.2 KeV and with a current of 1-2mA. All

data collection and resulting computations were carried out on a Nova
IV computer using a Kratos DS-55 data system modified with Brock's own
software. Time to mass conversion was done offline after data
collection as time centroids. The DS-55 programs PLOT, PKAVG, QUAN,
and XSCAN were used to obtain both qualitative and quantitative
spectral data.

B. The Standard

Carbaryl standard in the form of dry white crystals were
provided by the Vineland Agricultural Station and were manufactured at
>99% purity by the City Chemical Corporation. The identity of the
crystals was confirmed by their melting point (obtained with an
electrothermal melting point apparatus) and by their EI mass spectrum,
obtained using beam 2 of the AEI MS-30.

Standard solutions were prepared by quantitatively dissolving
accurate masses of carbaryl in ACS grade acetone from Fischer
Scientific.

C. The Matrices

A large number of available matrices of varied types were tested
to determine their suitability for obtaining fast atom bombardment
mass spectra of carbaryl. The suitability of a matrix was based on a
number of factors, as follows:

i) The ion currents produced by the individual carbaryl
    fragments should be as large as was possible to give
    the greatest possible signal-to-noise, S/N , ratio.
ii) When FAB-MS is performed on a mixture of carbaryl

and the matrix, the carbaryl should produce an easily
recognizeable fragmentation pattern.

iii) The matrix molecules should not fragment or cluster under
the influence of FAB to produce ions with the same
mass-to-charge ratio as those of the analyte.
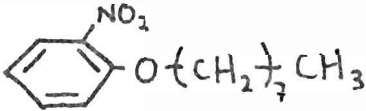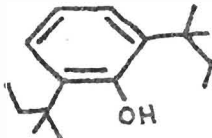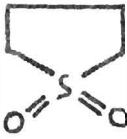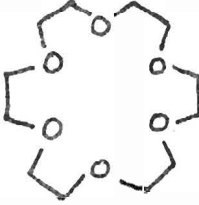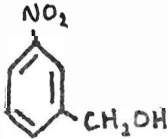
Criteria i) and ii) were tested simultaneously. A volume of 0.50 mL
of matrix liquid was placed in a spot plate and to this solution was
stirred in an excess of carbaryl crystals. After mixing, the mixture was
allowed to sit 10 minutes to allow the remaining solid to settle. The
probe tip was coated with approximately 2 µL of the resulting solution and
inserted into the source. The mass spectrometer was then tuned to give the
highest possible total ion current, TIC. The gas used for the FAB gun in
all cases was Xe. For a listing of all the matrix liquids investigated, see
Table 2 on page 24.

FAB-MS was also attempted on carbaryl without the use of a matrix
liquid. This was accomplished by placing double faced tape on the probe
tip and affixing solid carbaryl to it. The sample was then treated in the
same manner as one with a matrix liquid. Criterion iii) was tested by
visually comparing the mass spectrum of the analyte in the matrix to the
mass spectrum of the matrix alone. It should be noted that the FAB mass
spectra of the matrices were obtained from previously run samples.

D. Methods of Application

Three different modes of sample application were investigated
utilizing both NPOE and NBA (Table 2) as matrix liquids. The first method
is by far the most widely used and simplistic. It will be referred to as
simple mixing and involves mixing the solute and matrix liquid; in

Table 2: Matrices Investigated for the FAB-MS of Carbaryl and
their Structures

Matrix	Structure

Glycerol

$$CH_2-CH-CH_2$$
$$\ \ OH\ \ \ OH\ \ \ OH$$

2-Nitrophenyloctylether
(NPOE)

Monothioglycerol

$$CH_2-CH-CH_2$$
$$\ \ SH\ \ \ OH\ \ \ OH$$

Polyethylene Glycol
(PEG)

$$(CH-CH)_n$$
$$\ OH\ \ OH$$

Diamylphenol
(DAP)

Sulfolane

18-Crown-6

3-Nitrobenzylalcohol
(NBA)

this case, on the probe. The second method, which also sees wide

usage, involves mixing the solute, matrix liquid and a volatile

solvent. The purpose of the volatile solvent is to aid in the

dissolution of the solute. The third method investigated was that of

Zhang et. al . It involves precipitating the sample in situ on the

surface of the matrix liquid and is referred to as surface

precipitation (36). It should be noted that all quantitative data

were obtained using the ion current for the protonated molecular ion,

m/z 202.

1)   Simple Mixing

The first investigations were carried out using NPOE as the

matrix liquid. The initial parameter investigated was the volume of

matrix liquid to be placed on the probe tip and this was done

utilizing the following procedure. A volume of matrix liquid was

placed on the probe tip quantitatively using a 1.00 µL syringe. Then,

a volume of carbaryl standard was placed on the surface of the matrix

liquid using a 5.00 µL syringe, and the solvent was allowed to

evaporate. The resulting liquid was then mixed using a syringe tip

and a mass spectrum was obtained. The above procedure was repeated

three times for each volume of matrix liquid. The mass of carbaryl

was chosen to be well above the suspected detection limit of the

method. Volumes of matrix in excess of 2.00 µL are not easily

accommodated on the probe tips used and therefore, were not used. The

optimal volume was chosen on the basis of two factors, one being the

maximization of ion current for the peak at m/z 202 and the second

being the minimization of the standard deviation amongst the replicates for a given volume of matrix liquid.

The next parameter investigated was the detection limit. The detection limit was assumed to be indicated by a S/N ratio of two with 95% confidence. A volume of 0.50 µL of matrix liquid was placed quantitatively on the probe tip. Then, a volume of carbaryl standard was placed quantitatively on the matrix liquid and the solvent allowed to evaporate. A mass spectrum was then obtained. The above procedure was repeated three times for each volume of carbaryl standard.

The final parameter investigated was the relationship between the mass of carbaryl on the probe tip and the ion current produced. The relationship was determined by obtaining mass spectra for different masses of carbaryl and analyzing the data both statistically and graphically. In all cases, three replicates were obtained and 0.50 µL of matrix liquid were placed on the probe tip. Volumes of carbaryl standard solutions were then placed onto the individual probe tips to deliver specific masses of carbaryl. After the solvent evaporated, the resulting solution was mixed using a syringe tip.

A second set of experiments was then carried out using NBA as the matrix liquid.

2) Solvent Mixing

The initial parameters investigated for solvent mixing as the method of sample application utilized NPOE as the matrix liquid.

The first factor to be studied was the solvent to be added to the analyte and matrix liquid to enhance dissolution. It was possible to

investigate a variety of solvents due to the excellent solubility of carbaryl in most common solvents. The solvents investigated were nitrobenzene (distilled), acetonitrile (HPLC grade), acetone (ACS grade) and THF (distilled). The selection of solvents covered a range of polarities and boiling points, and contained both alkyl and aryl compounds. The actual samples were prepared in the following manner. A volume of 0.50 μL of matrix liquid was deposited on a probe tip using a 1.00 μL syringe. Then, a volume of carbaryl stock solution was deposited on the probe tip and the solvent allowed to evaporate. A large mass was utilized due to the belief that it would be well above the detection limit of the technique. An addition of 1.00 μL of solvent was then made and immediately mixed using a syringe tip and a mass spectrum obtained. This procedure was repeated three times for each of the four solvents. The optimal solvent chosen was the one that produced the best S/N ratio rather than the one that produced the highest ion current for m/z 202. The reason for using this selection criterion was that there was some fear that the solvents might introduce further chemical contaminants and/or enhance solubility of contaminants already present creating more noise in either case.

The second parameter investigated was the volume of both NPOE and nitrobenzene which would produce the highest ion current for a set mass of carbaryl. In order to find the optimal volumes simultaneously, the simplex method was utilized. The one basic assumption made was that volumes of solution were transferred most accurately in volumes of 0.50 μL. All solutions were transferred using 1.00 μL syringes and solvent, matrix and analyte combinations were mixed using syringe tips.

The third parameter studied was the detection limit for this mode of application. Again, the detection limit was assumed to be indicated by a S/N ratio of 2. A volume of matrix liquid was deposited on the probe tip and onto this was deposited quantitatively a volume of carbaryl standard. The solvent was allowed to evaporate. Next, a volume of nitrobenzene was deposited on the probe tip and the resulting bead of liquid was mixed immediately with a syringe tip and a mass spectrum obtained. This procedure was repeated three times for each volume of carbaryl standard.

The final relationship investigated was that between the mass of carbaryl on the probe tip and the ion current produced. The study was carried out by obtaining mass spectra for different masses of carbaryl on the probe tip keeping all other conditions as constant as possible. In every case, three replicates were obtained. Volumes of carbaryl standard solutions were delivered onto the individual probe tips spotted with matrix liquid and the solvent was allowed to evaporate. To each probe tip, was added a certain volume of nirobenzene and the resulting solution was mixed with a syringe tip.

A second set of experiments was carried out utilizing NBA as the matrix liquid.

3) Surface Precipitation

NPOE was utilized as a matrix liquid for the initial set of experiments carried out using surface precipitation as the method of sample preparation.

The initial experiment was carried out in order to determine the

volume of matrix liquid which would maximize ion current for the peak at m/z 202. A volume of matrix liquid was placed on a clean probe tip quantitatively. A volume of carbaryl standard solution was deposited on the surface of the matrix and the solvent was allowed to evaporate. The volume chosen was believed to deliver a mass of carbaryl well above the methods detection limit. A mass spectrum was then obtained. Three replicates being obtained for each volume of matrix liquid. Due to the problems involved in attempting to place more than 2.0 µL of solution on the probe tip at one time, the standard solution was allowed to partially evaporate on the syringe tip after ejection but prior to being placed on the probe tip.

A second experiment was carried out to determine the detection limit of the method. A volume of matrix liquid was placed on a clean probe tip and a volume of carbaryl standard solution was deposited on the surface of the matrix liquid. The process was repeated three times for each volume of standard solution.

The third experiment carried out using NPOE was designed to study the relationship between the ion current and the mass of carbaryl deposited onto the matrix's surface. A volume of matrix liquid was placed on a probe tip and volumes of carbaryl standard solutions were deposited on the matrix liquid's surface. A mass spectrum was then obtained. Three replicates were performed for each mass of analyte. The resulting data were analyzed both graphically and statistically.

A corresponding set of three experiments was carried out using NBA as the matrix liquid.

E. Interferences

Two experiments were carried out in order to determine if the
FAB-MS of some common pesticides would produce an interference with
the peak at m/z 202 in carbaryl's spectrum. Table 3 on page 31
contains a list of the pesticides investigated.

A volume of 0.50 μL of matrix liquid was placed on the probe tip
with a 1.00 μL syringe. An excess of pesticide, approximately 0.01
mg, was deposited on the probe tip and mixed with the matrix liquid.
The tip was then allowed to sit five minutes before a mass spectrum
was obtained. The process was repeated for each pesticide using both
NBA and NPOE as matrix liquids.

F. Statistical Analysis

Nth order regression analysis was performed in a number of
instances using an Apple II+ microcomputer and software provided by C.J.
Frick (37). A copy of this software can be found in Appendix A.
Due to an error in the software mentioned just previously, a second
regression analysis was performed on the data (54). The results of this
analysis accompany those obtained initially.

Table 3 :   Common Pesticides Investigated for Potential Interference
with the FAB-MS Spectrum of Carbaryl.

Pesticide	Type	Molecular Wt.	Function
Aldrin	chlorinated hydrocarbon	362	insecticide
DDT	chlorinated hydrocarbon	352	insecticide
Dieldrin	chlorinated hydrocarbon	378	insecticide
Lindane	chlorinated hydrocarbon	288	insecticide
Malathion	organo phosphorus	330	insecticide
Parathion	organo phosphorus	291	insecticide
Captan	thioimide	299	fungicide
Folpet	thioimide	295	fungicide
Ferbam	thiocarbamate	416	fungicide
Zineb	thiocarbamate	274	fungicide

NB/ Molecular weights were determined using the isotopes of highest abundance.

III. RESULTS

A. The Standard

Table 4: Physical Characteristics of the Standard

Physical Characteristic	Observation
Appearance	The standard consisted of dry white crytstals
Melting Point	142^0C

Figure 6: The EI Spectrum of Carbaryl
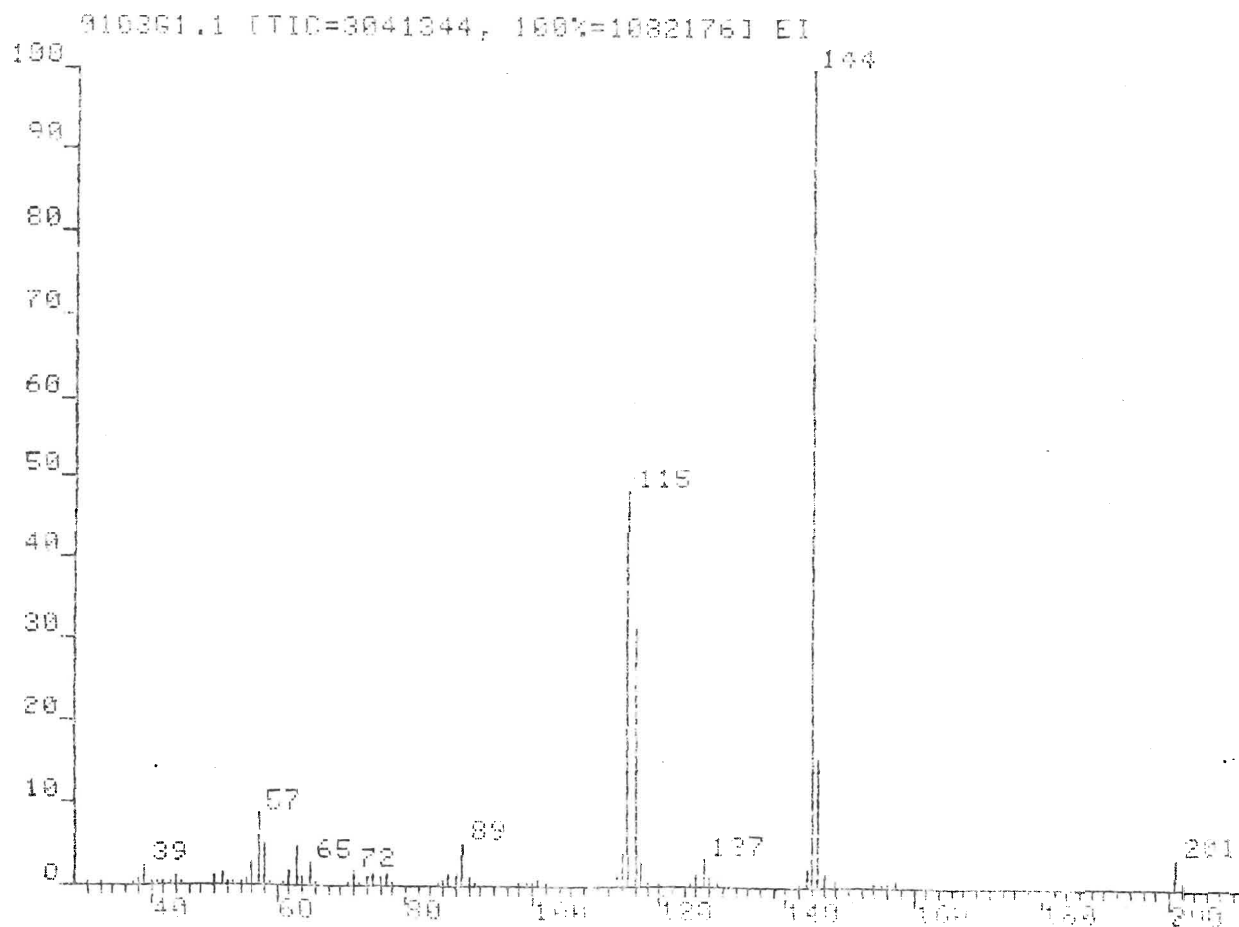
B. The Matrices

Table 5 : Mass Spectral Behaviour of Carbaryl in a Variety of Matrices

Matrix	Total Ion Current	Duration of Ion Current	Major Fragment Ions (m/z/Ion Current)
glycerol	9.3×10^4	>10 scans	$144/5 \times 10^3; 145/1.3 \times 10^4;$ $146/2 \times 10^3; 202/1.2 \times 10^4;$ $203/2 \times 10^3$
2-nitrophenyloctyl ether	4.225×10^6	>10 scans	$144/1.31 \times 10^5; 145/1.09 \times 10^5;$ $201/3.4 \times 10^4; 202/7.4 \times 10^4$
monothioglycerol	1.062×10^6	3 scans	$144/1.95 \times 10^5; 145/1.05 \times 10^5;$ $146/1.2 \times 10^4; 202/1.58 \times 10^5;$ $203/2.5 \times 10^4$
polyethylene glycol	2.14×10^5	>10 scans	$144/7.9 \times 10^4; 145/4.9 \times 10^4$
diamylphenol	2.72×10^5	>10 scans	$144/3.5 \times 10^4; 145/8.6 \times 10^4;$ $146/1.4 \times 10^4; 202/4.2 \times 10^4;$
sulfolane	3.343×10^6	5 scans	$144/4.29 \times 10^5; 145/5.43 \times 10^5;$ $146/8.2 \times 10^4; 201/7.5 \times 10^4;$ $202/3.16 \times 10^5$
18-crown-6	0	N.A.	N.A.
3-nitrobenzyl alcohol	6.22×10^5	>10 scans	$144/1.33 \times 10^5; 145/1.07 \times 10^5;$ $146/1.2 \times 10^4; 201/1.7 \times 10^4;$ $202/5.5 \times 10^4$
none	0	N.A.	N.A.

C. The Methods of Application

   1) Simple Mixing

      i) NPOE

Table 6 : Ion Currents Produced by FAB-MS of 22.8 μg of Carbaryl
           in Various Volumes of NPOE Applied by Simple Mixing

Volumes of Matrix Liquid ($\pm0.05\mu$L)	Replicate	Ion Current (m/z 202)
0.50	1	1.20×10^5
	2	1.41×10^5
	3	1.56×10^5
	$\bar{x}$	1.39×10^5
	s	0.18×10^5
1.00	1	7.2×10^4
	2	7.7×10^4
	3	1.03×10^5
	$\bar{x}$	8.4×10^4
	s	1.7×10^4
1.50	1	5.7×10^4
	2	6.0×10^4
	3	6.3×10^4
	$\bar{x}$	6.0×10^4
	s	0.3×10^4
2.00	1	4.3×10^4
	2	3.6×10^4
	3	5.1×10^4
	$\bar{x}$	4.3×10^4
	s	0.8×10^4

Graph 1a: Ion Current (m/z 202) Versus Volume of Matrix Liquid,
NPOE Applied by Simple Mixing

Ion Current for m/z 202 (counts)

Volume of Matrix Liquid NPOE (µL)
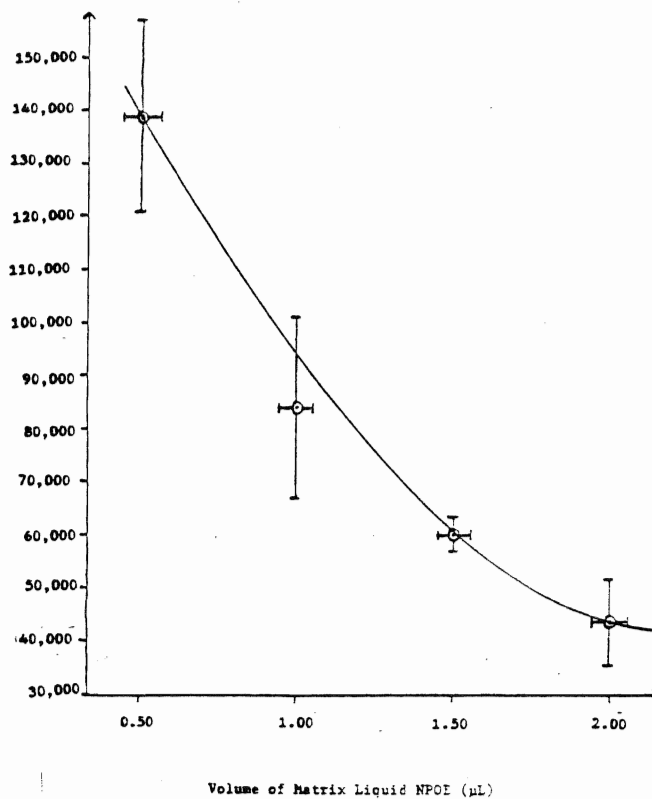
Graph 1 b: Ion Current (m/z 202) Versus (Volume of Matrix
Liquid, NPOE)$^{-3/2}$ Applied by Simple Mixing.

Ion Current (counts)

Correlation Coefficient = 0.985

(Volume of Matrix (µL))$^{-3/2}$
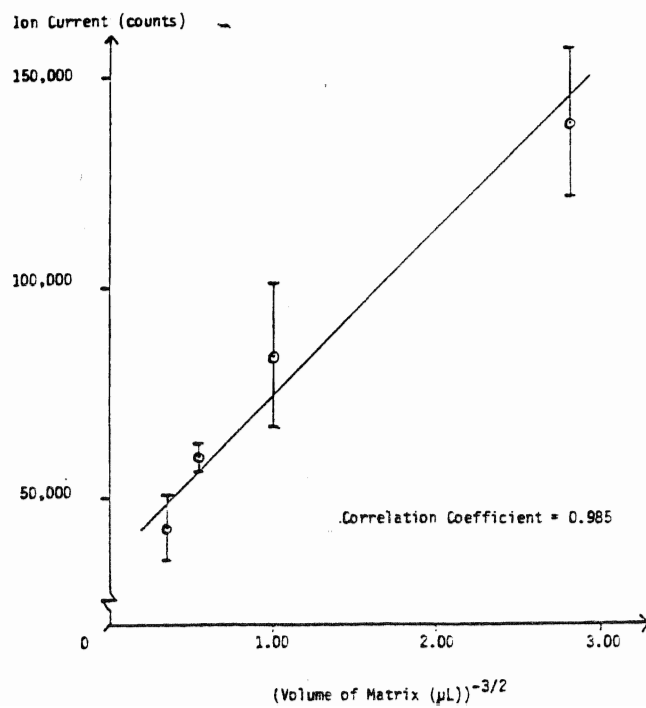
Table 7 : Data Concerning the FAB-MS Detection Limit for Carbaryl in 0.50 µL NPOE Applied by Simple Mixing

Mass of Carbaryl ($\pm 0.05 \mu g$)	Replicate	Ion Current (m/z 202)	Noise Level	S/N Ratio
0.50	1	5×10^3	1×10^3	5
	2	3×10^3	1×10^3	3
	3	4×10^3	1×10^3	4
	$\bar{x}$	4×10^3	1×10^3	4
	s	1×10^3	0	1
0.25	1	2×10^3	1×10^3	2
	2	3×10^3	1×10^3	3
	3	1×10^3	0	N.A.
	$\bar{x}$	2×10^3	1×10^3	2
	s	1×10^3	1×10^3	1

Table 8 : The Relationship Between the Mass of Carbaryl in 0.50 μL
NPOE Applied by Simple Mixing and Ion Current (m/z 202)
Produced Via FAB-MS.

Mass of Carbaryl (μg)	Replicate	Ion Current (m/z 202)	Mass of Carbaryl (μg)	Replicate	Ion Current (m/z 202)
0.50 ± 0.05	1	1.1×10^4	17.1 ± 0.06	1	4.22×10^5
	2	0.9×10^4		2	4.18×10^5
	3	1.1×10^4		3	3.92×10^5
	$\bar{x}$	1.0×10^4		$\bar{x}$	4.11×10^5
	s	0.1×10^4		s	0.16×10^5
2.00 ± 0.05	1	4.0×10^4	22.8 ± 0.6	1	4.38×10^5
	2	4.2×10^4		2	3.84×10^5
	3	4.2×10^4		3	4.62×10^5
	$\bar{x}$	4.1×10^4		$\bar{x}$	4.28×10^5
	s	0.1×10^4		s	0.40×10^5
5.7 ± 0.6	1	1.10×10^5	28.5 ± 0.6	1	3.68×10^5
	2	1.16×10^5		2	4.82×10^5
	3	1.12×10^5		3	2.43×10^5
	$\bar{x}$	1.13×10^5		$\bar{x}$	3.64×10^5
	s	0.3×10^4		s	1.19×10^5
11.4 ± 0.6	1	2.70×10^5	42.3 ± 2.1	1	3.32×10^5
	2	2.68×10^5		2	3.64×10^5
	3	2.76×10^5		3	3.24×10^5
	$\bar{x}$	2.71×10^5		$\bar{x}$	3.40×10^5
	s	0.4×10^3		s	0.21×10^5

Graph 2: Ion Current (m/z 202) Versus Mass of Carbaryl on Probe Tip For NPOE Applied By Simple Mixing.
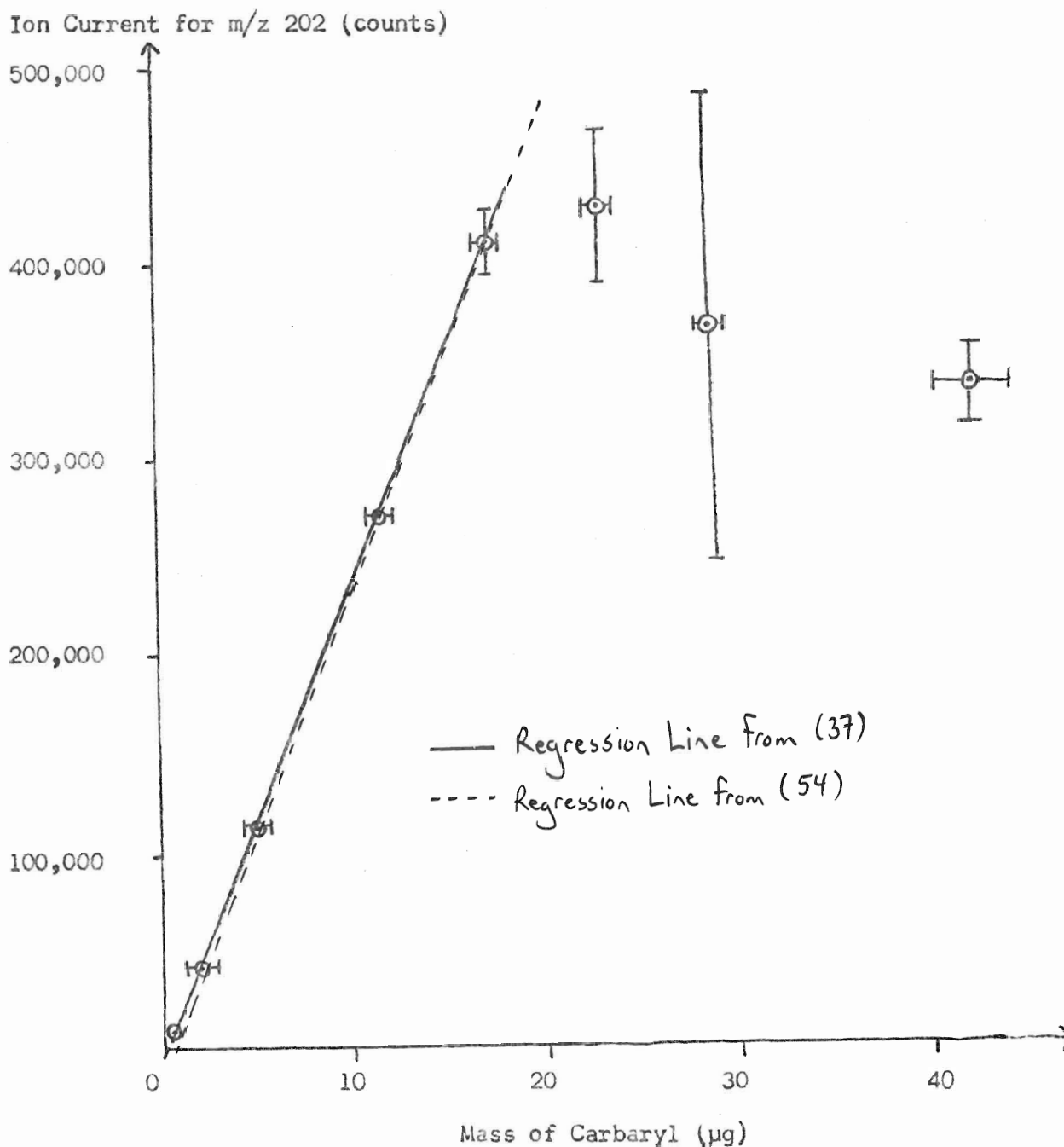
Table 9 : Nth Order Regression Analysis of the Relationship Between
The Mass of Carbaryl in NPOE Applied By Simple Mixing and
Ion Current (m/z 202) Produced by FAB-MS

a) Number of Points = 5

Degree of Fit = 1

Coefficients: $B(0) = -1.03 \times 10^4$
               $B(1) = 2.44 \times 10^4$

Coefficient of Determination (r^2) = 0.997

Coefficient of Correlation (r) = 0.999

Standard Error of Estimate = 1.07×10^4 (37)

b)

Simple Regression X_1 : mass Y_1 : intensity

DF:	R:	R-squared:	Adj. R-squared:	Std. Error:
5	.998	.997	.996	10295.509

Analysis of Variance Table

Source	DF:	Sum Squares:	Mean Square:	F-test:
REGRESSION	1	1.371E11	1.371E11	1293.061
RESIDUAL	4	423990058.745	105997514.686	p = 1.0000E-4
TOTAL	5	1.375E11		

Beta Coefficient Table

Parameter:	Value:	Std. Err.:	Std. Value:	t-Value:	Probability:
INTERCEPT	-6753.237				
SLOPE	24169.467	672.137	.998	35.959	1.0000E-4

Confidence Intervals Table

Parameter:	95% Lower:	95% Upper:	90% Lower:	90% Upper:
MEAN (X,Y)	129411.756	152754.911	132121.761	150044.906
SLOPE	22303.023	26035.911	22736.389	25602.544

(54)

ii) NBA

Table 10 : Ion Currents Produced by FAB-MS of 11.4 µg of Carbaryl
in Various Volumes of NBA Applied by Simple Mixing

Volumes of Matrix Liquid (±0.05 µL)	Replicate	Ion Current (m/z 202)
0.50	1	2.04×10^5 (omit)
	2	5.42×10^5
	3	3.96×10^5
	$\bar{x}$	4.69×10^5
	s	1.03×10^5
1.00	1	2.13×10^5
	2	3.67×10^5
	3	3.50×10^5
	$\bar{x}$	3.10×10^5
	s	0.84×10^5
1.50	1	2.76×10^5
	2	2.26×10^5
	3	3.45×10^5
	$\bar{x}$	2.82×10^5
	s	0.60×10^5
2.00	1	2.22×10^5
	2	2.82×10^5
	3	2.48×10^5
	$\bar{x}$	2.50×10^5
	s	0.30×10^5

Graph 3A: Ion Current (m/z 202) Versus Volume of Matrix Liquid, NBA, Applied By Simple Mixing.

Ion Current for m/z 202 (counts)

Volume of Matrix Liquid (μL)
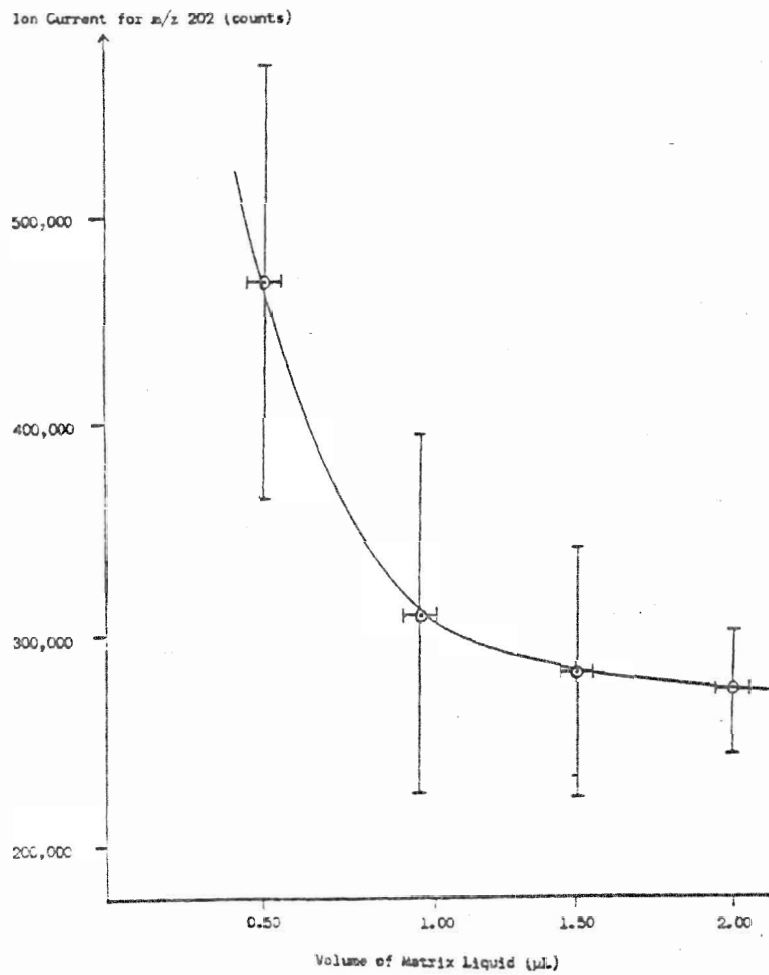
Graph 3 b: Ion Current (m/z 202) versus (Volume of Matrix Liquid, NBA)$^{-3/2}$ Applied by Surface Precipitation.

Ion Current (counts)

Correlation Coefficient = 0.966

(Volume of Matrix (μL))$^{-3/2}$
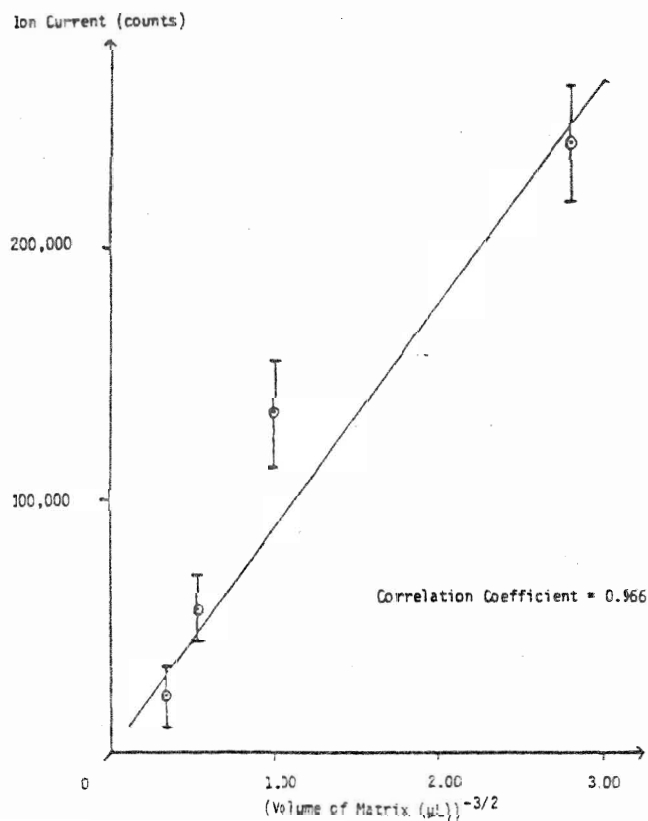
Table 11 : Data Concerning the FAB-MS Detection Limit for Carbaryl
in 0.50 µL NBA Applied by Simple Mixing

Mass of Carbaryl (µg)	Replicate	Ion Current (m/z 202)	Noise Level	S/N Ratio
6.0 ± 0.6	1	2.5×10^4	1×10^3	2.5×10^1
	2	2.1×10^4	1×10^3	2.1×10^1
	3	1.3×10^4	1×10^3	1.3×10^1
	$\bar{x}$	2.0×10^4	1×10^3	2×10^1
	s	0.6×10^4	0	1×10^1
2.00 ± 0.05	1	2.1×10^4	1×10^3	2.1×10^1
	2	1.9×10^4	1×10^3	1.9×10^1
	3	4.4×10^4	2×10^3	2.2×10^1
	$\bar{x}$	2.8×10^4	1×10^3	2×10^1
	s	1.4×10^4	1×10^3	0
0.99 ± 0.05	1	6×10^3	0	N.A.
	2	8×10^3	0	N.A.
	3	6×10^3	0	N.A.
	$\bar{x}$	7×10^3	N.A.	N.A
	s	1×10^3	N.A.	N.A.
0.50 ± 0.05	1	4×10^3	1×10^3	4
	2	4×10^3	1×10^3	4
	3	6×10^3	2×10^3	3
	$\bar{x}$	5×10^3	1×10^3	4
	s	1×10^3	1×10^3	1

Table 12 : The Relationship Between the Mass of Carbaryl in 0.50 µL NBA Applied by Simple Mixing and Ion Current (m/z 202) Produced Via FAB-MS.

Mass of Carbaryl (µg)	Replicate	Ion Current (m/z 202)	Mass of Carbaryl (µg)	Replicate	Ion Current (m/z 202)
2.0±0.0	1	6.2×10^4	24.2±0.6	1	4.76×10^5
	2	6.0×10^4		2	5.28×10^5
	3	5.3×10^4		3	5.49×10^5
	$\bar{x}$	5.8×10^4		$\bar{x}$	5.18×10^5
	s	0.5×10^4		x	0.37×10^4
6.0±0.6	1	1.43×10^5	30.2±0.6	1	5.86×10^5
	2	1.52×10^5		2	6.86×10^5
	3	1.00×10^5		3	5.77×10^5
	$\bar{x}$	1.31×10^5		$\bar{x}$	6.16×10^5
	s	0.28×10^5		s	0.61×10^5
12.1±0.6	1	2.82×10^5	42.4±0.6	1	6.73×10^5
	2	2.95×10^5		2	6.69×10^5
	3	3.85×10^5		3	6.88×10^5
	$\bar{x}$	3.20×10^5		$\bar{x}$	6.76×10^5
	s	0.56×10^5		s	0.10×10^5
18.1±0.6	1	3.64×10^5			
	2	4.01×10^5			
	3	4.60×10^5			
	$\bar{x}$	4.09×10^5			
	s	0.49×10^5			

Graph 4: Ion Current (m/z 202) Versus Mass of Carbaryl on Probe Tip for NBA Applied By Simple Mixing.
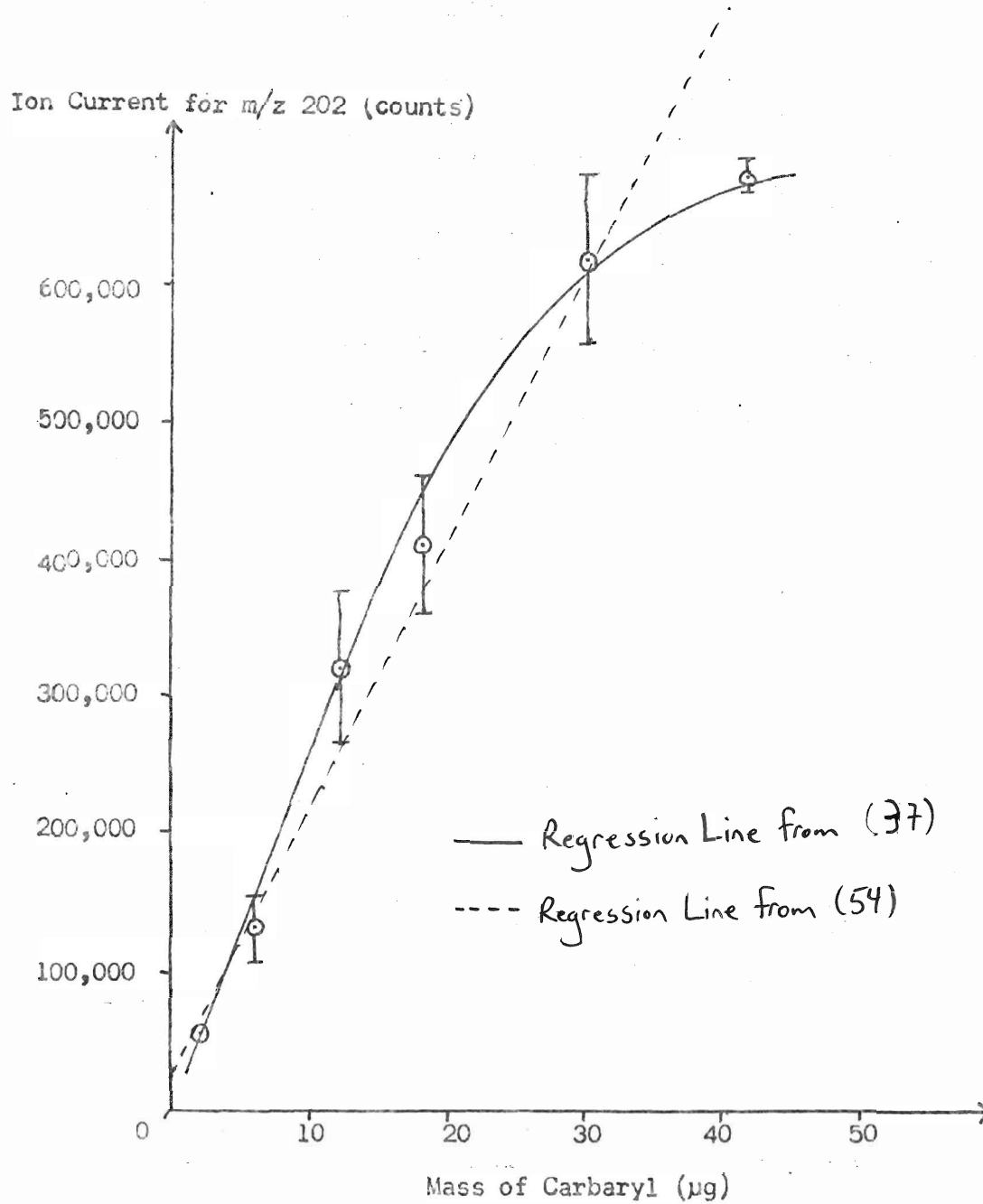
Table 13 :   Nth Order Regression Analysis of the Relationship Between
              The Mass of Carbaryl in NBA Applied By Simple Mixing and Ion
              Current (m/z 202) Produced by FAB-MS

a) Number of Points = 7

Degree of Fit = 2

Coefficients: $B(0) = -1.41 \times 10^4$
                 $B(1) = 3.00 \times 10^4$
                 $B(3) = -3.20 \times 10^4$

Coefficient of Determination $(r^2) = 0.985$

Coefficient of Correlation $(r) = 0.998$

Standard Error of Estimate $= 2.01 \times 10^4$ (37)

b)

Simple Regression X₁ : mass   Y₁ : intensity

DF:	R:	R-squared:	Adj. R-squared:	Std. Error:
6	.994	988	.986	28499.199

Analysis of Variance Table

Source	DF	Sum Squares:	Mean Square:	F-test:
REGRESSION	1	3.321E11	3.321E11	408.891
RESIDUAL	5	4.061E9	812204315.489	p = 1.0000E-4
TOTAL	6	3.362E11		

Parameter :	Value :	Std. Err.:	Std. Value :	t-Value :	Probability :
INTERCEPT	21423.176				
SLOPE	20545.764	1016.058	.994	20.221	1.0000E-4

Confidence Intervals Table

Parameter :	95% Lower :	95% Upper :	90% Lower :	90% Upper :
MEAN (X,Y)	265520.827	320907.744	271506.212	314922.359
SLOPE	17933.53	23157.999	18498.112	22593.417

(54)

2) Solvent Mixing

   i) NPOE

Table 14 : Ion Currents Produced by FAB-MS of 11.4 µg of Carbaryl
in 0.50 µL NPOE Mixed with 1.0 µL of Various Solvents

Solvent	Replicate	Ion Current (m/z 202)	Noise Level	S/N Ratio
none	1	2.99×10^5	2×10^3	1.5×10^2
	2	3.35×10^5	2×10^3	1.7×10^2
	3	3.62×10^5	2×10^3	1.8×10^2
	$\bar{x}$	3.32×10^5	2×10^3	2×10^2
	s	0.32×10^5	1×10^3	1×10^2
nitrobenzene	1	4.07×10^5	1×10^3	4.1×10^2
	2	4.63×10^5	2×10^3	2.3×10^2
	3	3.51×10^5	1×10^3	3.5×10^2
	$\bar{x}$	4.07×10^5	1×10^3	3×10^2
	s	0.56×10^5	1×10^3	1×10^2
THF	1	5.72×10^5	7×10^3	0.8×10^2
	2	7.37×10^5	7×10^3	1.0×10^2
	3	4.89×10^5	5×10^3	1.0×10^2
	$\bar{x}$	6.05×10^5	6×10^3	9×10^1
	s	1.26×10^5	1×10^3	1×10^1
acetone	1	2.85×10^5	8×10^3	3.6×10^1
	2	3.62×10^5	9×10^3	4.0×10^1
	3	5.25×10^5	4×10^3	1.3×10^2
	$\bar{x}$	3.91×10^5	7×10^3	7×10^1
	s	1.23×10^5	3×10^3	5.0×10^1
acetonitrile	1	3.52×10^5	7×10^3	5.0×10^1
	2	4.54×10^5	6×10^3	7.6×10^1
	3	4.16×10^5	6×10^3	6.9×10^1
	$\bar{x}$	4.06×10^5	6×10^3	6×10^1
	s	0.52×10^5	1×10^3	1×10^1

Table 15 :   Ion Currents Produced by FAB-MS of 11.4 μg of Carbaryl
in Varied Volumes of Nitrobenzene and NPOE

Volumes of Nitrobenzene (± 0.05 μL)	Volume of NPOE (± 0.05 μL)	Ion Current (m/z 202)
1.00	1.00	1.30×10^5
1.50	1.00	1.10×10^5
1.00	1.50	0.85×10^5
1.50	0.50	1.10×10^5
1.00	0.50	2.79×10^5
0.50	1.00	0.92×10^5
0.50	0.00	0

Graph . 5: Volume of Nitrobenzene Versus Volume of NPOE Applying
The Simplex Method to The Ion Currents Produced by
FAB-MS on 11.4 µg of Carbaryl.

Volume of Nitrobenzene (µL)

3.00

2.50

2.00

1.50   1.10 x 10^5 1.10 x 10^5
                  ⊙   ⊙

                                              0.85 x 10^5
1.00   ⊙   ⊙   ⊙
         2.79 x 10^5 1.30 x 10^5

0.50   ⊕ 0.0   ⊙
                       0.92 x 10^5

  0   0.50   1.00   1.50   2.00   2.50

                  Volume of NPOE (µL)

Table 16 : Data Concerning the FAB-MS Detection Limit for Carbaryl in 1.00 µL of Nitrobenzene and 0.50 µL of NPOE

Mass of Carbaryl (µg)	Replicate	Ion Current (m/z 202)	Noise Level	S/N Ratio
0.99±0.05	1	1.4×10^4	N.A.	N.A.
	2	1.7×10^4	1×10^3	1.7×10^1
	3	1.9×10^4	1×10^3	1.9×10^1
	$\bar{x}$	1.7×10^4	1×10^3	2×10^1
	s	0.3×10^4	0	0
0.50±0.05	1	1.2×10^4	1×10^3	1.2×10^1
	2	0.6×10^4 (omit)	N.A.	N.A
	3	1.6×10^4	2×10^3	0.8×10^1
	$\bar{x}$	1.4×10^4	2×10^3	1×10^1
	s	0.3×10^4	1×10^3	0
0.25±0.01	1	7×10^3	2×10^3	3.5
	2	5×10^3	2×10^3	2.5
	3	7×10^3	2×10^3	3.5
	$\bar{x}$	6×10^3	2×10^3	3
	s	1×10^3	0	1

Table 17 : The Relationship Between the Mass of Carbaryl in 0.50 μL
NPOE and 1.00 μL Nitrobenzene and Ion Current (m/z 202)
Produced Via FAB-MS.

Mass of Carbaryl ($\pm 0.05 \mu g$)	Replicate	Ion Current (m/z 202)	Mass of Carbaryl ($\pm 0.05 \mu g$)	Replicate	Ion Current (m/z 202)
5.1	1	3.3×10^4	15.3	1	7.2×10^4
	2	2.5×10^4		2	6.5×10^4
	3	1.8×10^4		3	6.2×10^4
	$\bar{x}$	2.5×10^4		$\bar{x}$	6.6×10^4
	s	0.8×10^4		s	0.5×10^4
10.2	1	5.3×10^4	20.4	1	8.5×10^4
	2	4.2×10^4		2	9.1×10^4
	3	4.6×10^4		3	8.0×10^4
	$\bar{x}$	4.7×10^4		$\bar{x}$	8.5×10^4
	s	0.6×10^4		s	0.5×10^4
12.8	1	6.4×10^4	25.5	1	1.05×10^5
	2	6.0×10^4		2	8.9×10^4
	3	5.9×10^4		3	2.60×10^5 (omit)
	$\bar{x}$	6.1×10^4		$\bar{x}$	9.7×10^4
	s	0.3×10^4		s	1.2×10^4

Graph 6: Ion Current (m/z 202) Versus Mass of Carbaryl
in NPOE on Probe Tip Applied by Solvent Mixing.

Table 18 : Nth Order Regression Analysis of the Relationship Between
The Mass of Carbaryl in NPOE and Nitrobenzene and Ion
Current (m/z 202) Produced by FAB-MS

a) Number of Points = 5

Degree of Fit = 1

Coefficients: $B(0) = 6.99 \times 10^4$
$B(1) = 3.90 \times 10^4$

Coefficient of Determination $(r^2) = 0.988$

Coefficient of Correlation $(r) = 0.994$

Standard Error of Estimate $= 2.78 \times 10^3$ (37)

b)

Simple Regression X_1: mass Y_1: intensity

DF:	R:	R-squared:	Adj. R-squared:	Std. Error:
6	.991	.983	.979	4819.96

Analysis of Variance Table

Source	DF:	Sum Squares:	Mean Square:	F-test:
REGRESSION	1	6.637E9	6.637E9	285.698
RESIDUAL	5	116160076.611	23232015.322	p = 1.0000E-4
TOTAL	6	6753500000		

Beta Coefficient Table

Parameter:	Value:	Std. Err.:	Std. Value:	t-Value:	Probability:
INTERCEPT	5785.278				
SLOPE	3818.623	225.919	.991	16.903	1.0000E-4

Confidence Intervals Table

Parameter:	95% Lower:	95% Upper:	90% Lower:	90% Upper:
MEAN (X,Y)	49816.312	59183.688	50828.597	58171.403
SLOPE	3237.796	4399.45	3363.33	4273.916

(54)

ii) NBA

Table 19 : Ion Currents Produced by FAB-MS of 7.8 µg of Carbaryl
in 0.50 µL NBA Mixed with 1.0 µL of Various Solvents

Solvent	Replicate	Ion Current (m/z 202)	Noise Level	S/N Ratio
none	1	3.9×10^4	1×10^3	3.9×10^1
	2	4.0×10^4	1×10^3	4.0×10^1
	3	4.3×10^4	1×10^3	4.3×10^1
	$\bar{x}$	4.0×10^4	1×10^3	4.1×10^1
	s	0.2×10^4	0	0.2×10^1
acetone	1	2.9×10^4	1×10^3	2.9×10^1
	2	3.1×10^4	1×10^3	3.1×10^1
	3	3.2×10^4	1×10^3	3.2×10^1
	$\bar{x}$	3.1×10^4	1×10^3	3.1×10^1
	s	0.2×10^4	0	0.2×10^1
THF	1	10.0×10^4	1×10^3	10.0×10^1
	2	6.1×10^4	1×10^3	6.1×10^1
	3	3.5×10^4	1×10^3	3.5×10^1
	$\bar{x}$	6.5×10^4	1×10^3	6.5×10^1
	s	3.3×10^4	0	3.3×10^1
nitrobenzene	1	5.4×10^4	1×10^3	5.4×10^1
	2	5.1×10^4	1×10^3	5.1×10^1
	3	15.5×10^4	4×10^3 (omit)	N.A.
	$\bar{x}$	8.7×10^4	1×10^3	5.1×10^1
	s	0.2×10^4	0	0.2×10^1

Table 20 : Ion Currents Produced by FAB-MS of 7.8 μg of Carbaryl
in Varied Volumes of Nitrobenzene and NBA

Volumes of Nitrobenzene ($\pm$0.05 uL)	Volume of NBA ($\pm$0.05 uL)	Ion Current (m/z 202)
1.00	1.50	1.45×10^5
1.00	1.00	1.88×10^5
1.50	1.00	0.76×10^5
0.50	1.50	1.12×10^5
1.00	0.50	1.36×10^5
1.00	0.75	1.40×10^5

Graph 7: Volume of Nitrobenzene Versus Volume of NBA Applying
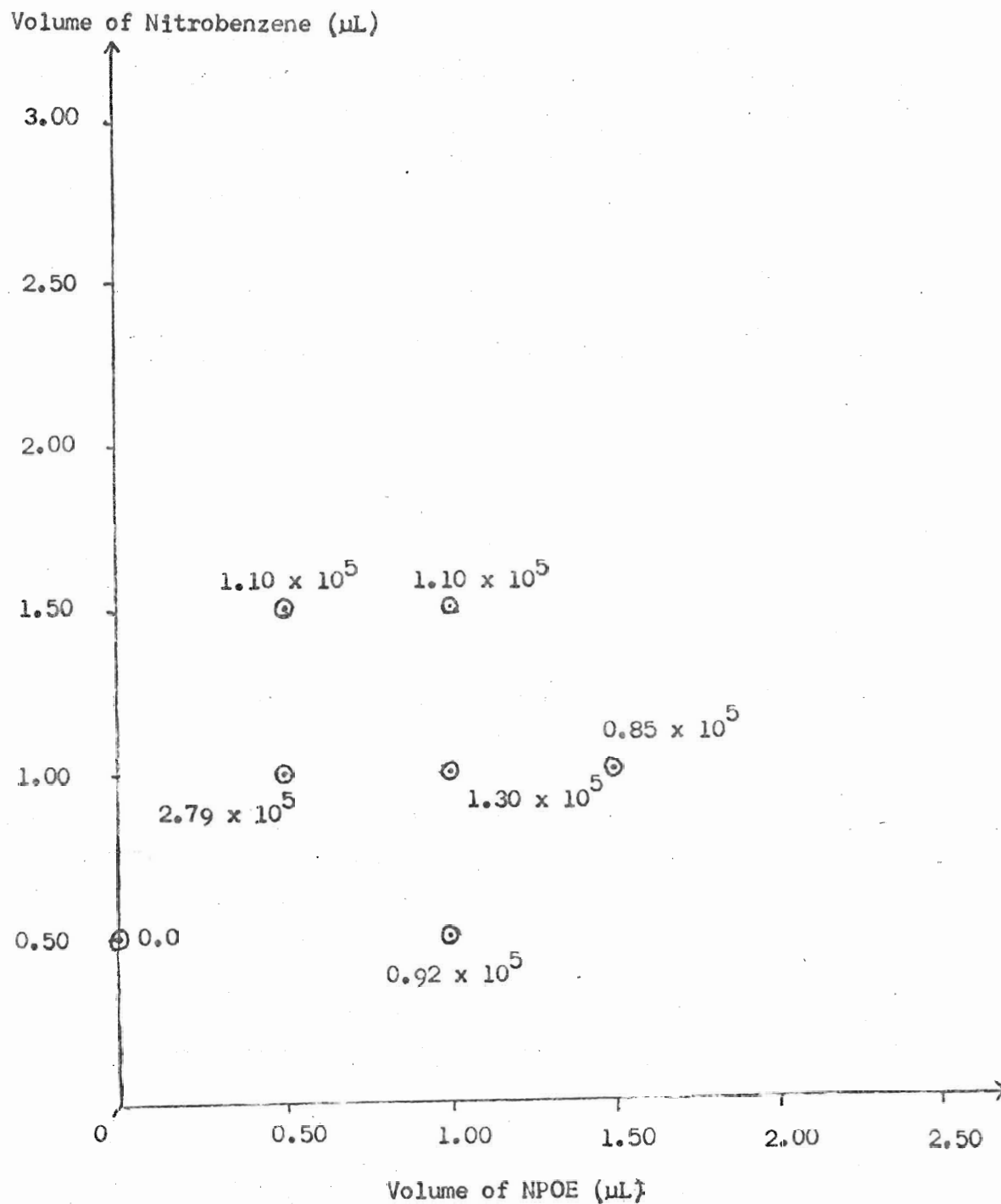The Simplex Method to The Ion Currents Produced by
FAB-MS of 7.8 µg of Carbaryl.

Volume of Nitrobenzene (µL)

Volume of NBA (µL)
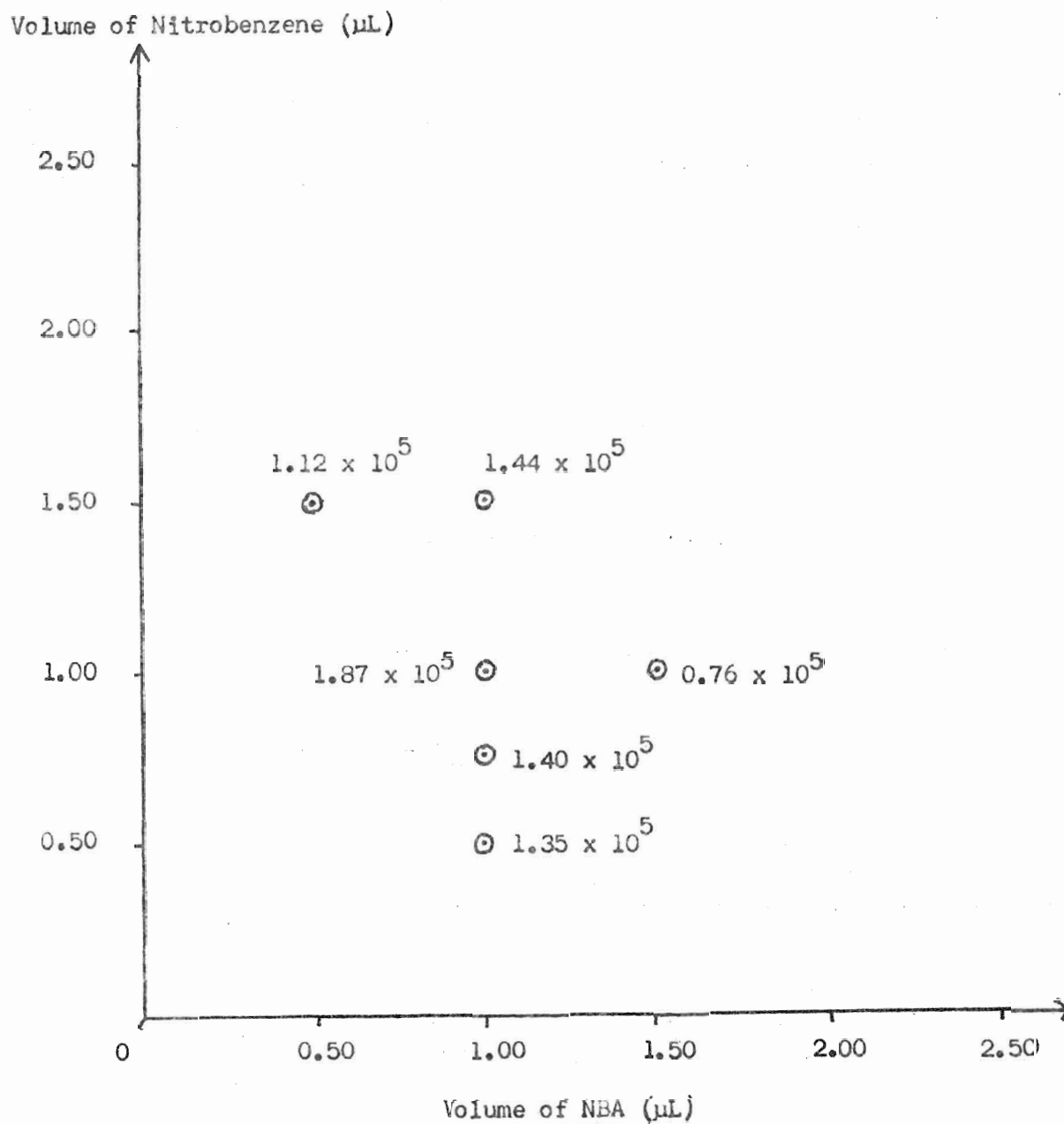
Table 21 : Data Concerning the FAB-MS Detection Limit for Carbaryl in 1.00 μL of Nitrobenzene and 1.00 μL of NBA

Mass of Carbaryl (± 0.05 ug)	Replicate	Ion Current (m/z 202)	Noise Level	S/N Ratio
2.00	1	3.2×10^4	4×10^3	8.0
	2	1.9×10^4	2×10^3	9.5
	3	1.3×10^4	2×10^3	6.5
	$\bar{x}$	2.1×10^4	3×10^3	8
	s	1.0×10^4	1×10^3	2
0.74	1	6×10^3	1×10^3	6.0
	2	8×10^3	2×10^3	4.0
	3	6×10^3	2×10^3	3.0
	$\bar{x}$	7×10^3	2×10^3	4
	s	1×10^3	1×10^3	2
0.30	1	2×10^3	1×10^3	2.0
	2	0×10^3	2×10^3	0.0
	3	1×10^3	2×10^3	0.5
	$\bar{x}$	1×10^3	2×10^3	1
	s	1×10^3	1×10^3	1

Table 22 : The Relationship Between the Mass of Carbaryl in 1.00 µL
NBA and 1.00 µL Nitrobenzene and Ion Current (m/z 202)
Produced Via FAB-MS.

Mass of Carbaryl ($\pm 0.6\mu g$)	Replicate	Ion Current (m/z 202)
6.4	1	0.3×10^4
	2	1.2×10^4
	3	4.4×10^4 (omit)
	$\bar{x}$	7×10^3
	s	6×10^3
12.7	1	2.0×10^4
	2	1.8×10^4
	3	0.8×10^4
	$\bar{x}$	1.5×10^4
	s	0.8×10^4
19.1	1	2.7×10^4
	2	2.1×10^4
	3	accidentally destroyed
	$\bar{x}$	2.4×10^4
	s	0.4×10^4
25.4	1	2.6×10^4
	2	2.8×10^4
	3	accidentally destroyed
	$\bar{x}$	2.7×10^4
	s	0.1×10^4
31.8	1	3.4×10^4
	2	2.9×10^4
	3	3.1×10^4
	$\bar{x}$	3.1×10^4
	s	0.2×10^4

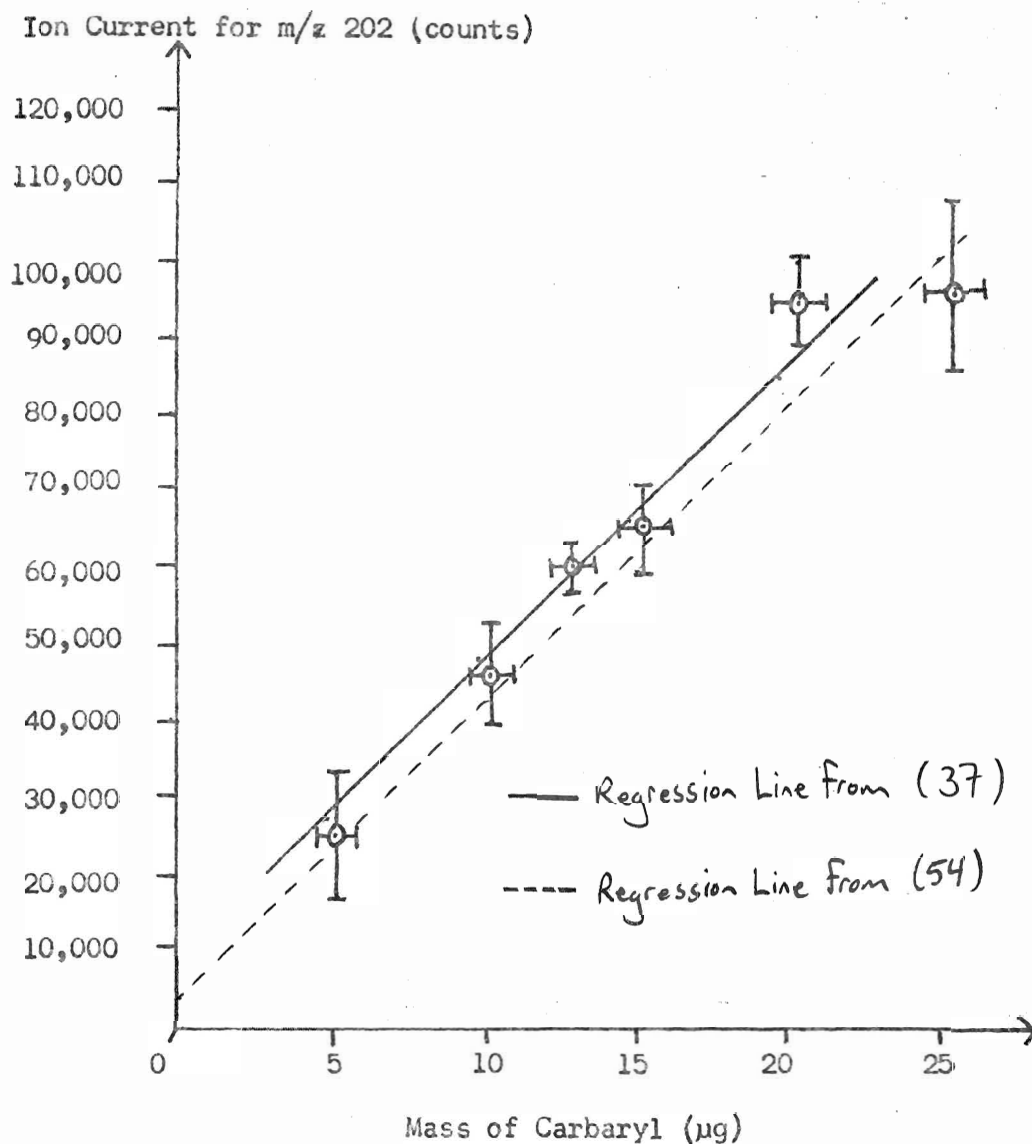Graph 8: Ion Current (m/z 202) Versus Mass of Carbaryl in 1.00μl of NBA and 1.00μl Nitrobenzene Produced by FAB-MS.
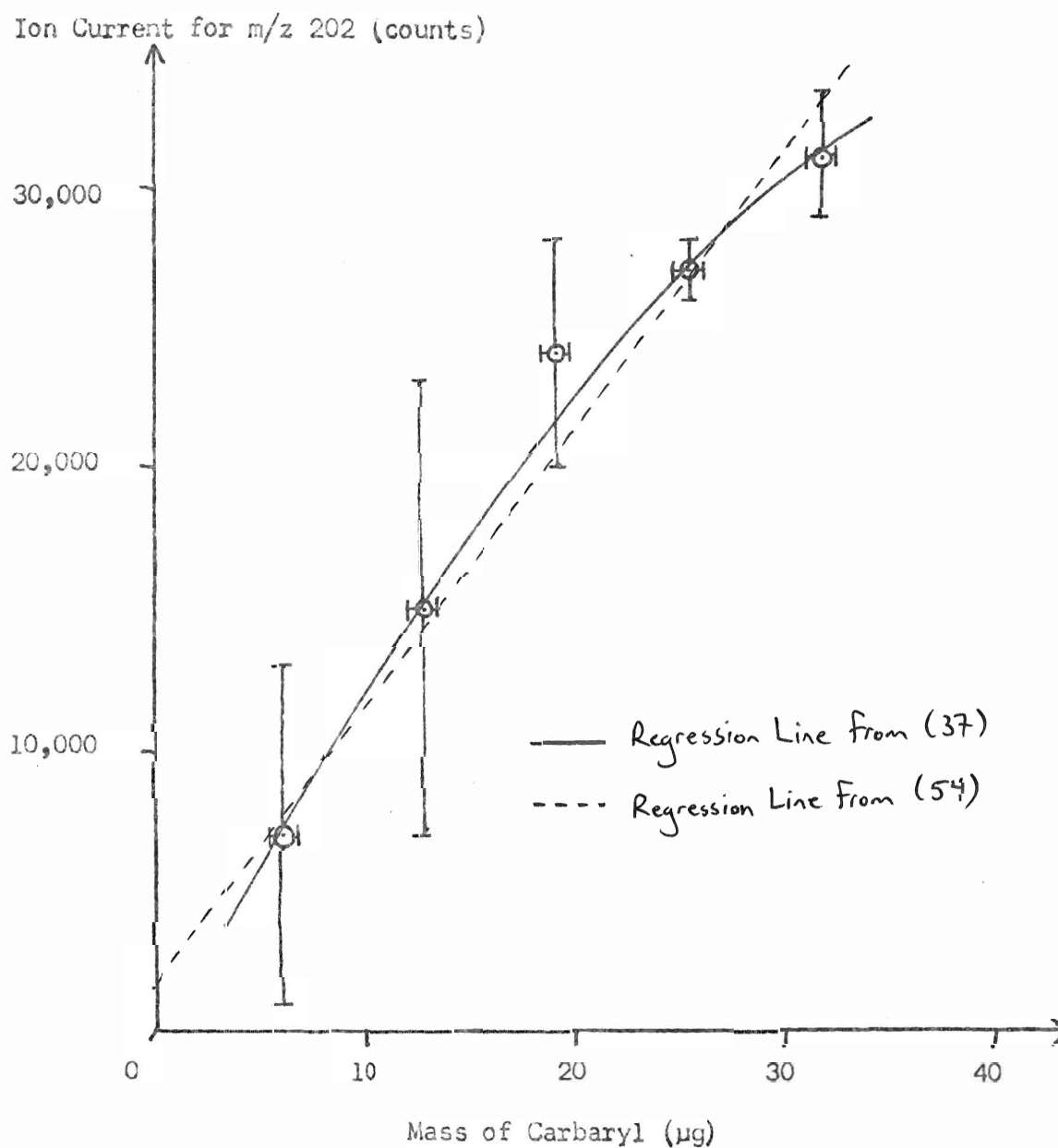
Table 23 : Nth Order Regression Analysis of the Relationship Between
The Mass of Carbaryl in NBA and Nitrobenzene and Ion
Current (m/z 202) Produced by FAB-MS

a) Number of Points = 5

Degree of Fit = 2

Coefficients: $B(0) = -4.32 \times 10^3$
$B(1) = 1.90 \times 10^3$
$B(3) = -2.50 \times 10^1$

Coefficient of Determination $(r^2) = 0.993$

Coefficient of Correlation $(r) = 0.996$

Standard Error of Estimate $= 1.15 \times 10^3$ (37)

b)

Simple Regression X₁ : mass Y₁ : intensity

DF :	R :	R-squared :	Adj. R-squared :	Std. Error :
5	.987	.973	.967	2196.408

Analysis of Variance Table

Source	DF :	Sum Squares :	Mean Square :	F-test :
REGRESSION	1	700911495.188	700911495.188	145.29
RESIDUAL	4	19296838.145	4824209.536	p = 3.0000E-4
TOTAL	5	720208333.333		

Beta Coefficient Table

Parameter :	Value :	Std. Err. :	Std. Value :	t-Value :	Probability :
INTERCEPT	1580.798				
SLOPE	995.967	82.628	.987	12.054	3.0000E-4

Confidence Intervals Table

Parameter :	95% Lower :	95% Upper :	90% Lower :	90% Upper :
MEAN (X,Y)	14926.693	19906.641	15504.836	19328.497
SLOPE	766.519	1225.414	819.794	1172.139

(54)

3) Surface Precipitation

    i) NPOE

Table 24 : Ion Currents Produced by FAB-MS of 18.6 µg of Carbaryl
               Applied by Surface Precipitation

Volumes of NPOE (± 0.05 µL)	Replicate	Ion Current (m/z 202)
0.50	1	7.29×10^5
	2	6.48×10^5
	3	6.18×10^5
	$\bar{x}$	6.65×10^5
	s	0.57×10^5
1.00	1	3.46×10^5
	2	5.74×10^5
	3	2.64×10^5
	$\bar{x}$	3.94×10^5
	s	1.61×10^5
2.00	1	7.8×10^4
	2	7.7×10^4
	3	1.00×10^5
	$\bar{x}$	8.5×10^4
	s	1.3×10^4

Graph 9a: Ion Current (m/z 202) Versus Volume of Matrix Liquid, NPOE, For 18.6 µg of Carbaryl Deposited by Surface Precipitation.

Ion Current for m/z 202 (counts)
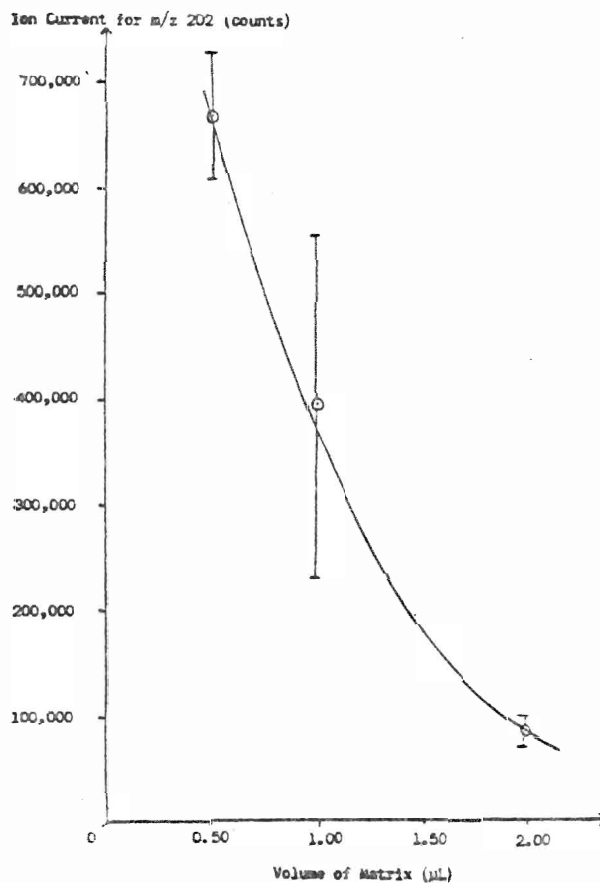
Volume of Matrix (µL)

Graph 9 b: Ion Current (m/z 202) Versus (Volume of Matrix Liquid, NPOE)$^{-3/2}$ for 18.6 µg of Carbaryl Deposited by Surface Precipitation.

Ion Current (counts)

Correlation Coefficient = 0.954

(Volume of Matrix (µL))$^{-3/2}$
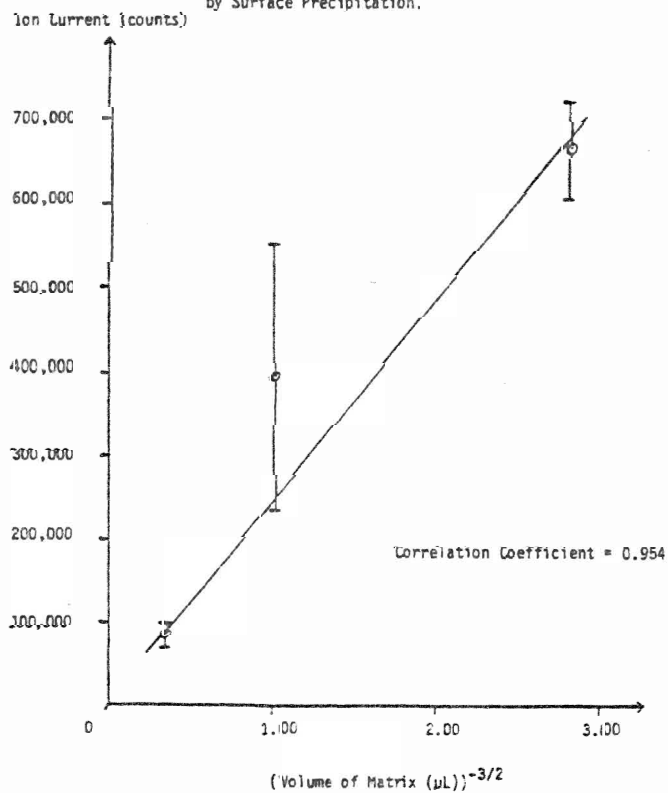
Table 25 : Data Concerning the FAB-MS Detection Limit for Carbaryl in 0.50 µL of NPOE Applied by Surface Precipitation

Mass of Carbaryl ($\pm 0.05\mu g$)	Replicate	Ion Current (m/z 202)	Noise Level	S/N Ratio
0.50	1	8×10^3	1×10^3	8
	2	7×10^3	0	N.A.
	3	1.1×10^4	2×10^3	5.5
	$\bar{x}$	9×10^3	2×10^3	7
	s	2×10^3	1×10^3	2
1.00	1	1.8×10^4	1×10^3	1.8×10^1
	2	2.1×10^4	1×10^3	2.1×10^1
	3	1.7×10^4	1×10^3	1.7×10^1
	$\bar{x}$	1.8×10^4	1×10^3	2×10^1
	s	0.2×10^4	0	1×10^1
2.00	1	6.9×10^4	2×10^3	3.4×10^1
	2	7.6×10^4	2×10^3	3.8×10^1
	3	6.9×10^4	2×10^3	3.4×10^1
	$\bar{x}$	7.1×10^4	2×10^3	4×10^1
	s	0.4×10^4	0	0

Table 26 : The Relationship Between the Mass of Carbaryl in 0.50 μL
            NPOE Applied by Surface Precipitation and Ion Current (m/z 202)
            Produced Via FAB-MS.

Mass of Carbaryl ($\pm$0.6μg)	Replicate	Ion Current (m/z 202)
5.7	1	1.4×10^4
	2	1.5×10^4
	3	1.3×10^4
	$\bar{x}$	1.4×10^4
	s	0.1×10^4
11.4	1	1.7×10^4
	2	1.2×10^4
	3	1.3×10^4
	$\bar{x}$	1.4×10^4
	s	0.2×10^4
17.1	1	2.9×10^4
	2	3.2×10^4
	3	3.1×10^4
	$\bar{x}$	3.1×10^4
	s	0.2×10^4
22.8	1	2.5×10^4
	2	4.9×10^4
	3	4.3×10^4
	$\bar{x}$	3.9×10^4
	s	0.5×10^4
28.5	1	8.0×10^4
	2	6.1×10^4
	3	5.7×10^4
	$\bar{x}$	6.6×10^4
	s	1.2×10^4
34.2	1	8.6×10^4
	2	8.4×10^4
	3	7.9×10^4
	$\bar{x}$	8.3×10^4
	s	0.3×10^4
42.3	1	1.0×10^4
	2	3.4×10^4
	3	3.6×10^4
	$\bar{x}$	2.7×10^4
	s	1.4×10^4

Graph 10: Ion Current (m/z 202) Versus Mass of Carbaryl in 0.50 μL NPOE Applied by Surface Precipitation Produced by FAB-MS.
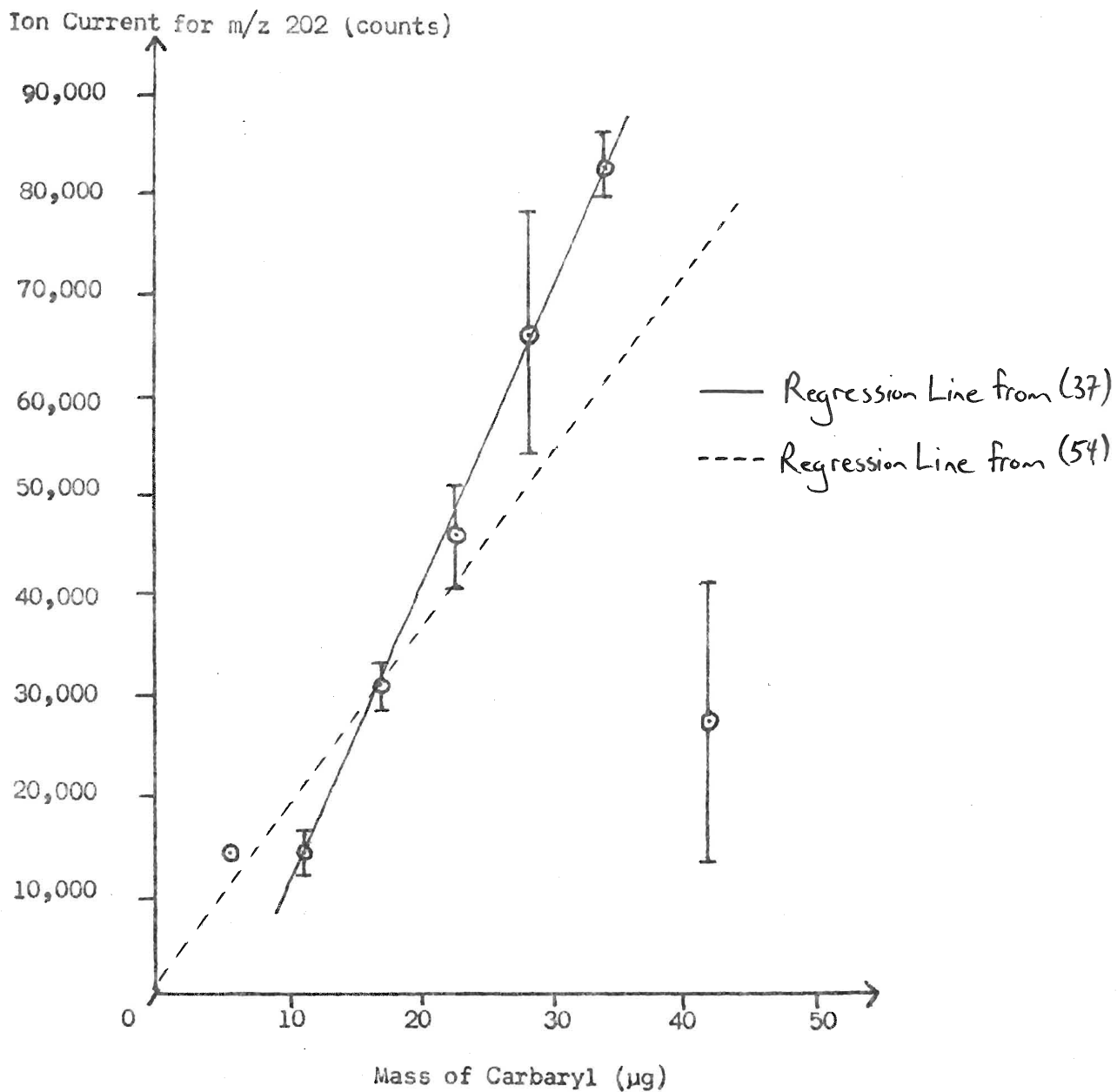
Table 27 : Nth Order Regression Analysis of the Relationship Between The Mass of Carbaryl in 0.05 uL NPOE Applied by Surface Precipitation and Ion Current (m/z 202) Produced by FAB-MS

a) Number of Points = 5

Degree of Fit = 1

Coefficients: $B(0) = -2.12 \times 10^4$
$B(1) = 3.04 \times 10^3$

Coefficient of Determination $(r^2) = 0.998$

Coefficient of Correlation $(r) = 0.999$

Standard Error of Estimate = 1.30×10^3 (37)

b)

Simple Regression X₁ : mass   Y₁ : Intensity

DF:	R.:	R-squared:	Adj. R-squared:	Std. Error:
6	.981	.962	.954	6461.839

Analysis of Variance Table

Source	DF:	Sum Squares:	Mean Square:	F-test:
REGRESSION	1	5.253E9	5.253E9	125.794
RESIDUAL	5	208776785.714	41755357.143	p = 1.0000E-4
TOTAL	6	5.461E9		

Parameter:	Value:	Std. Err.:	Std. Value:	t-Value:	Probability:
INTERCEPT	-4732.143				
SLOPE	2402.882	214.241	.981	11.216	1.0000E-4

Confidence Intervals Table

Parameter:	95% Lower:	95% Upper:	90% Lower:	90% Upper:
MEAN (X,Y)	30077.996	42636.29	31435.107	41279.178
SLOPE	1852.08	2953.685	1971.125	2834.64

(57)

ii) NBA

Table 28 : Ion Currents Produced by FAB-MS of 11.4 µg of Carbaryl Applied by Surface Precipitation to NBA

Volumes of NBA (µL)	Replicate	Ion Current (m/z 202)
0.50	1	2.15×10^5
	2	2.60×10^5
	3	2.49×10^5
	$\bar{x}$	2.42×10^5
	s	0.23×10^5
1.00	1	1.17×10^5
	2	1.58×10^5
	3	1.32×10^5
	$\bar{x}$	1.35×10^5
	s	0.21×10^5
1.50	1	7.2×10^4
	2	5.2×10^4
	3	4.6×10^4
	$\bar{x}$	5.7×10^4
	s	1.3×10^4
2.00	1	1.6×10^4
	2	3.6×10^4
	3	1.3×10^5
	$\bar{x}$	2.2×10^4
	s	1.2×10^4

Graph 11a: Ion Current (m/z 202) Versus Volume of Matrix Liquid, NBA, For 11.4 µg of Carbaryl Applied by Surface Precipitation.
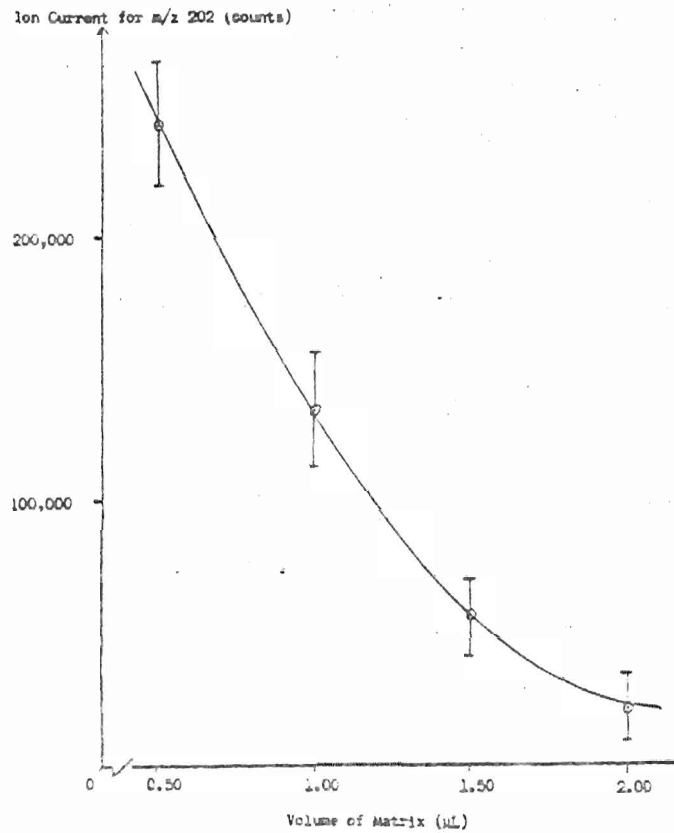
Graph 11 b: Ion Current (m/z 202) Versus (Volume of Matrix Liquid, NBA)$^{-3/2}$ For 11.4 µg of Carbaryl Applied by Surface Precipitation.

Correlation Coefficient = 0.985
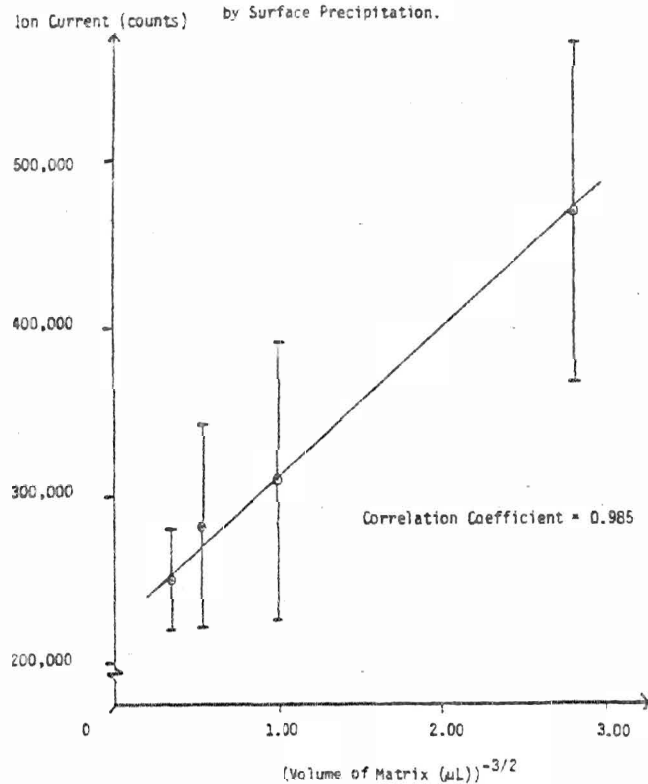
Table 29 : Data Concerning the FAB-MS Detection Limit for Carbaryl in 0.50 µL of NBA Applied by Surface Precipitation

Mass of Carbaryl ($\pm 0.05 \mu g$)	Replicate	Ion Current (m/z 202)	Noise Level	S/N Ratio
2.0	1	4.3×10^4	1×10^3	4.3×10^1
	2	3.6×10^4	1×10^1	3.6×10^1
	3	2.8×10^4	1×10^3	2.8×10^1
	$\bar{x}$	3.5×10^3	1×10^3	4×10^1
	s	0.8×10^3	0	1×10^1
0.75	1	5×10^3	1×10^3	5
	2	1.2×10^4	1×10^3	1.2×10^1
	3	1.1×10^4	1×10^3	1.1×10^1
	$\bar{x}$	8×10^3	1×10^3	1×10^1
	s	7×10^3	0	4
0.30	1	5×10^3	2×10^3	2.5
	2	5×10^3	2×10^3	2.5
	3	5×10^3	2×10^3	2.5
	$\bar{x}$	5×10^3	2×10^3	2.5
	s	0	0	0

Table 30 : The Relationship Between the Mass of Carbaryl in 0.50 µL
NBA Applied by Surface Precipitation and Ion Current (m/z 202)
Produced Via FAB-MS.

Mass of Carbaryl (µg)	Replicate	Ion Current (m/z 202)
2.00±0.20	1	6.3×10^4
	2	4.6×10^4
	3	2.8×10^4
	$\bar{x}$	4.6×10^4
	s	1.7×10^4
6.0±0.60	1	1.09×10^5
	2	8.4×10^4
	3	8.0×10^4
	$\bar{x}$	9.1×10^4
	s	1.6×10^4
12.1±0.60	1	1.57×10^5
	2	1.87×10^5
	3	1.20×10^5
	$\bar{x}$	1.55×10^5
	s	0.34×10^5
15.1±0.60	1	2.16×10^5
	2	2.41×10^5
	3	2.32×10^5
	$\bar{x}$	2.30×10^5
	s	0.12×10^5
18.1±0.60	1	2.88×10^5
	2	2.81×10^5
	3	2.86×10^5
	$\bar{x}$	2.85×10^5
	s	0.04×10^5
24.2±0.60	1	2.96×10^5
	2	3.11×10^5
	3	3.14×10^5
	$\bar{x}$	3.07×10^5
	s	0.10×10^5

Graph 12: Ion Current (m/z 202) Versus Mass of Carbaryl in
0.50 μl of NBA Applied by Surface Precipitation
Produced by FAB-MS.
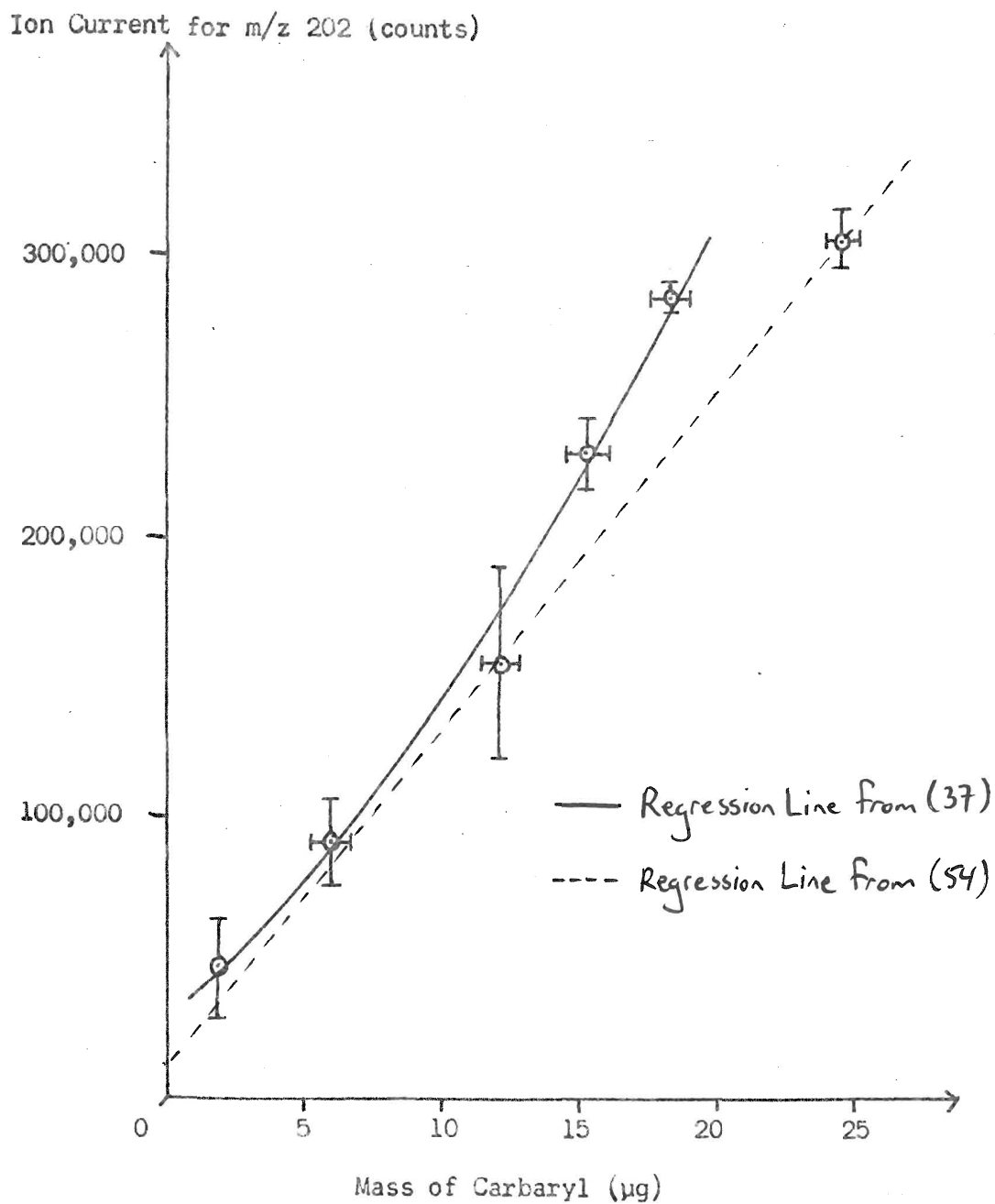

Ion Current for m/z 202 (counts)

Table 31 : Nth Order Regression Analysis of the Relationship Between
The Mass of Carbaryl in NBA Applied By Surface Precipitation
Produced by FAB-MS

a) Number of Points = 5

Degree of Fit = 2

Coefficients: $B(0) = 3.84 \times 10^4$
$B(1) = 4.35 \times 10^3$
$B(3) = 5.16 \times 10^2$

Coefficient of Determination $(r^2) = 0.993$

Coefficient of Correlation $(r) = 0.996$

Standard Error of Estimate $= 1.18 \times 10^4$ (37)

b)

Simple Regression X_1 : mass Y_1 : ion current

DF :	R :	R-squared :	Adj. R-squared :	Std. Error :
6	.985	.97	.964	22656.112

Analysis of Variance Table

Source	DF :	Sum Squares :	Mean Square :	F-test :
REGRESSION	1	8.279E10	8.279E10	161.281
RESIDUAL	5	2.566E9	513299403.943	p = 1.0000E-4
TOTAL	6	8.535E10		

Beta Coefficient Table

Parameter :	Value :	Std. Err. :	Std. Value :	t-Value :	Probability :
INTERCEPT	12219.908				
SLOPE	13276.912	1045.455	.985	12.7	1.0000E-4

Confidence Intervals Table

Parameter :	95% Lower :	95% Upper :	90% Lower :	90% Upper :
MEAN (X,Y)	137198.716	181229.856	141956.939	176471.632
SLOPE	10589.099	15964.725	11170.015	15383.808

(54)

D. Interferences

1) NPOE

Table 32 : Data Concerning Potential Interferences in the
FAB-MS Spectrum of Carbaryl in NPOE

Pesticide	Type	Total Ion Current	Interference (m/z 202)
Aldrin	chlorinated hydrocarbon	5.8×10^4	1×10^3
DDT	chlorinated hydrocarbon	3.99×10^5	1×10^3
Dieldrin	chlorinated hydrocarbon	2.76×10^5	0
Lindane	chlorinated hydrocarbon	6.0×10^4	0
Malathion	organo-phosphorus	1.696×10^6	0
Parathion	organo-phosphorus	3.474×10^6	1.4×10^4
Captan	thioimide	2.81×10^5	0
Folpet	thioimide	2.26×10^5	0
Ferbam	thiocarbamate	1.036×10^6	0
Zineb	thiocarbamate	3.00×10^5	0

2) NBA

Table 33 : Data Concerning Potential Interferences in the
FAB-MS Spectrum of Carbaryl in NBA

Pesticide	Type	Total Ion Current	Interference (m/z 202)
Aldrin	chlorinated hydrocarbon	1.74×10^5	0
DDT	chlorinated hydrocarbon	2.16×10^5	0
Dieldrin	chlorinated hydrocarbon	3.6×10^4	0
Lindane	chlorinated hydrocarbon	5.6×10^4	0
Malathion	organo-phosphorus	9.7×10^4	0
Parathion	organo-phosphorus	8.76×10^5	2×10^3
Captan	thioimide	1.77×10^5	0
Folpet	thioimide	9.0×10^4	0
Ferbam	thiocarbamate	6.3×10^4	0
Zineb	thiocarbamate	6.0×10^4	0

IV. DISCUSSION

A. The Standard

An initial concern was that the standard carbaryl powder obtained was indeed as described. Its appearance, homogeneous dry white crystals (see Table 4 on page 32), was consistent with that found in the literature. This was also the case with the melting point, 142^0C. The electron impact spectrum obtained for the standard (Figure 6 on page 32) exhibited significant peaks at m/z 201 (the molecular ion), m/z 144, m/z 145, m/z 115 and m/z 116. The relative intensities of these peaks were 4.5:100:16:50:32 respectively. This fragmentation pattern is consistent with that found in the literature, as shown in Figure 7 on page 75. Furthermore, no peaks appear in the mass spectrum which could indicate the presence of contamination. This leads one to conclude that the carbaryl standard provided was indeed pure.

B. The Matrices and the Spectra Produced

A number of readily available matrices were tested to determine their suitability for use in obtaining FAB mass spectra of carbaryl. The results can be seen in Table 5 on page 33. Attempts to obtain a mass spectrum from carbaryl affixed to the probe tip with double faced tape with matrix liquid totally absent proved fruitless. In each instance, little or no ion current was detected.
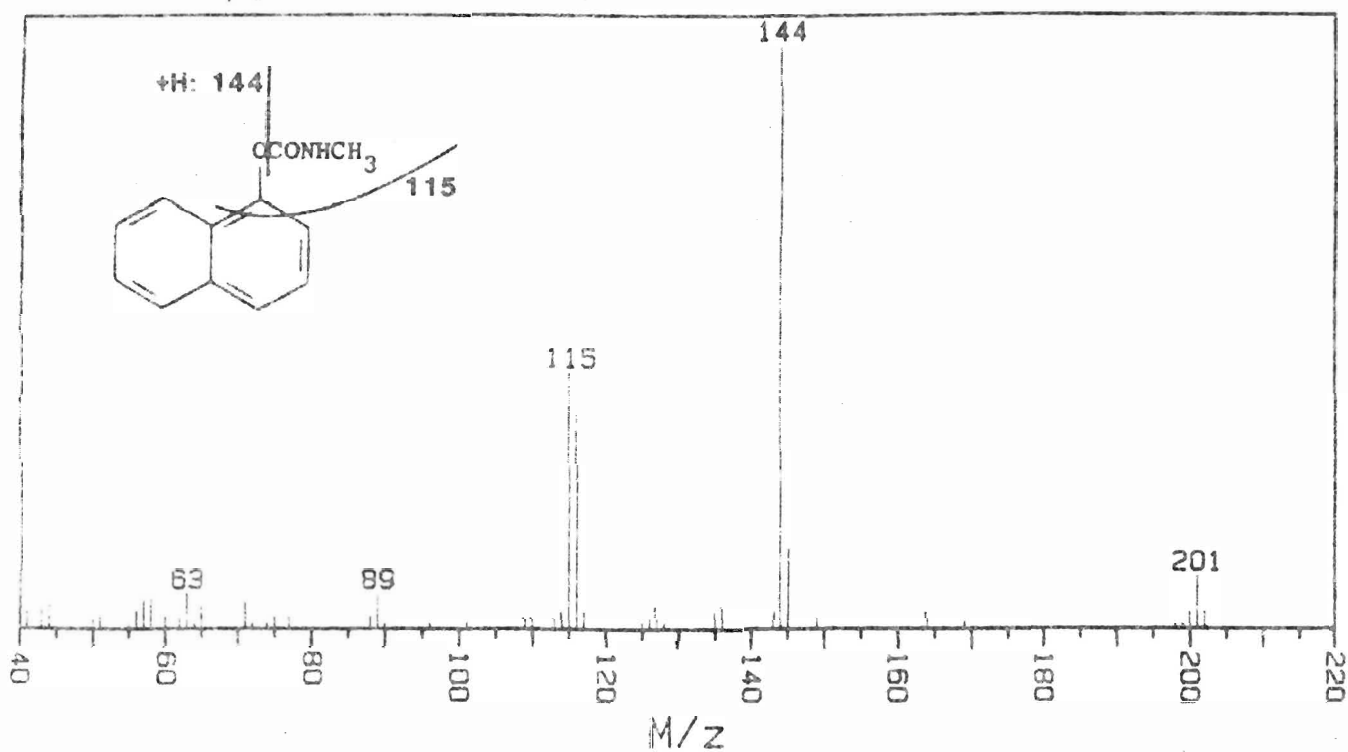
A crown ether, 18-crown-6, which has been used quite sucessfully for organometallic sytems was found, not surprisingly, to produce no FAB

Figure 7: The EI Mass Spectrum of Carbaryl (53)

Carbaryl, Merck No: 1766
CAS No: 63-25-2, Formula: $C_{12}H_{11}NO_2$, MW: 201
Intense peaks: 144 (100), 115 (44), 116 (37), 145 (14)

1-Naphthalenol, methylcarbamate

mass spectrum for carbaryl (38). The most popular matrix liquid, glycerol, was found to be unsuitable because the FAB mass spectra contained analyte peaks with intensities lower than other liquids utilized. Similarly, diamylphenol was also found unsuitable. Polyethylene glycol proved to be a poor choice of matrix liquid for two reasons: first, the peaks obtained were relatively low in intensity and second, only two peaks appeared in the spectrum of carbaryl; m/z 144 and m/z 145. This is significant because no molecular ion was present and it is notable that this was the only matrix liquid, producing some ion current, which did not exhibit a peak at m/z 202 due to the protonated molecular ion.

Two matrices, monothioglycerol and sulfolane, produce FAB mass spectra for carbaryl which exhibit both excellent intensity and fragmentation. However, the duration over which mass spectra may be obtained, three and five scans respectively, would make quantitative analysis of the carbaryl difficult. This rapid dissipation of the sample would make it difficult to optimize ion current before the sample disappeared and would ultimately yield imprecise results. Spectra of short duration seem to result from the nature of the matrices themselves rather than the analyte, as was indicated by Miller (39).

The two matrices found to be the most suitable for performing FAB-MS on carbaryl were 2-nitrophenyloctyl ether and 3-nitrobenzyl alcohol. Both produce spectra exhibiting molecular ions, protonated molecular ions and substantial fragment ions, all of good intensity. Furthermore, sample lifetime was in excess of ten scans. The only potential problem these matrices might have produced was that interfering peaks might have been created by their substantial clustering and/or fragmentation. Fortunately, this problem did not manifest itself.

Interestingly, the initial and primary usage of 2-nitrophenyloctyl ether (NPOE) was as an oxidizing matrix for non-polar and organometallic molecules (40). Given the success of the present usage, it would seem that NPOE can be employed equally well with at least one polar compound, carbaryl. It should be noted that attempts to obtain negative ion FAB mass spectra for carbaryl in these two matrices proved fruitless. A typical spectrum for carbaryl in each of NBA and NPOE can be found in Appendix B.

Observation of the X-SCAN reports (ie. specific masses versus scan number or time) obtained when FAB-MS was performed on carbaryl, in each of NPOE and NBA, can help elucidate the behaviour of carbaryl in the matrix liquid (see Figure 8 on page 78). In both cases, one observes a gradually sloping line. This indicates that ion current, both total ion current and that of the molecular ion, decreases steadily with increasing scan number. The lack of any observable ion current in the first scan of the NBA carbaryl spectrum was caused by a badly adjusted base-line. The observed behaviour is easily explained since the matrix liquid can be considered immobile only in the time frame of a single impact and not in the time frame of spectra recording (41). The area sputtered by the atom beam is replenished by a number of processes including diffusion, mechanical mixing and solvent evaporation (33). Should the replenishment process be slow on the time scale of the data collection then one would observe a diminishing of ion current with each successive scan. This was most likely the explanation for the observed cross scan behaviour when FAB-MS was performed on carbaryl with either NBA or NPOE as the matrix liquid.

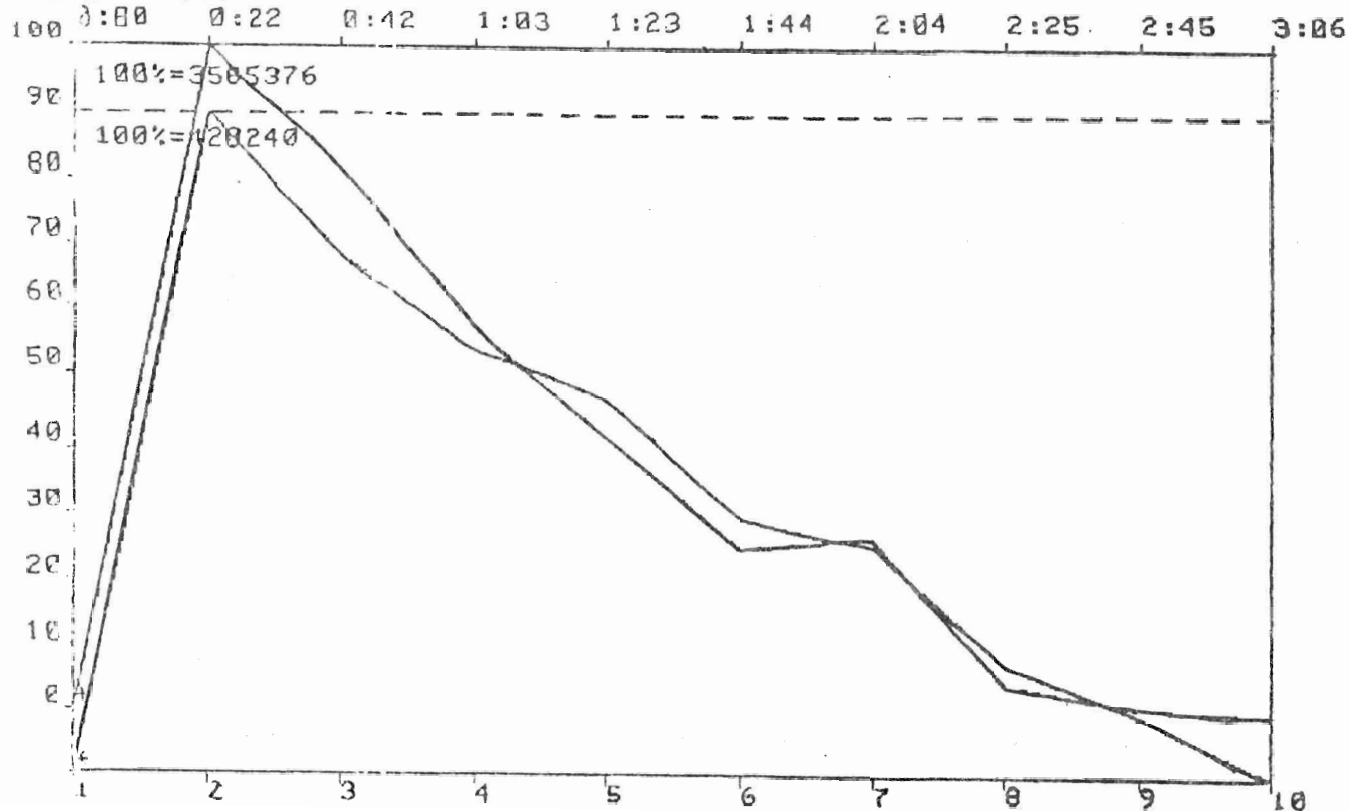Figure 8:   Cross Scan Reports.

i) 18.6 µg of Carbaryl Mixed in 0.50 µL NPOE.
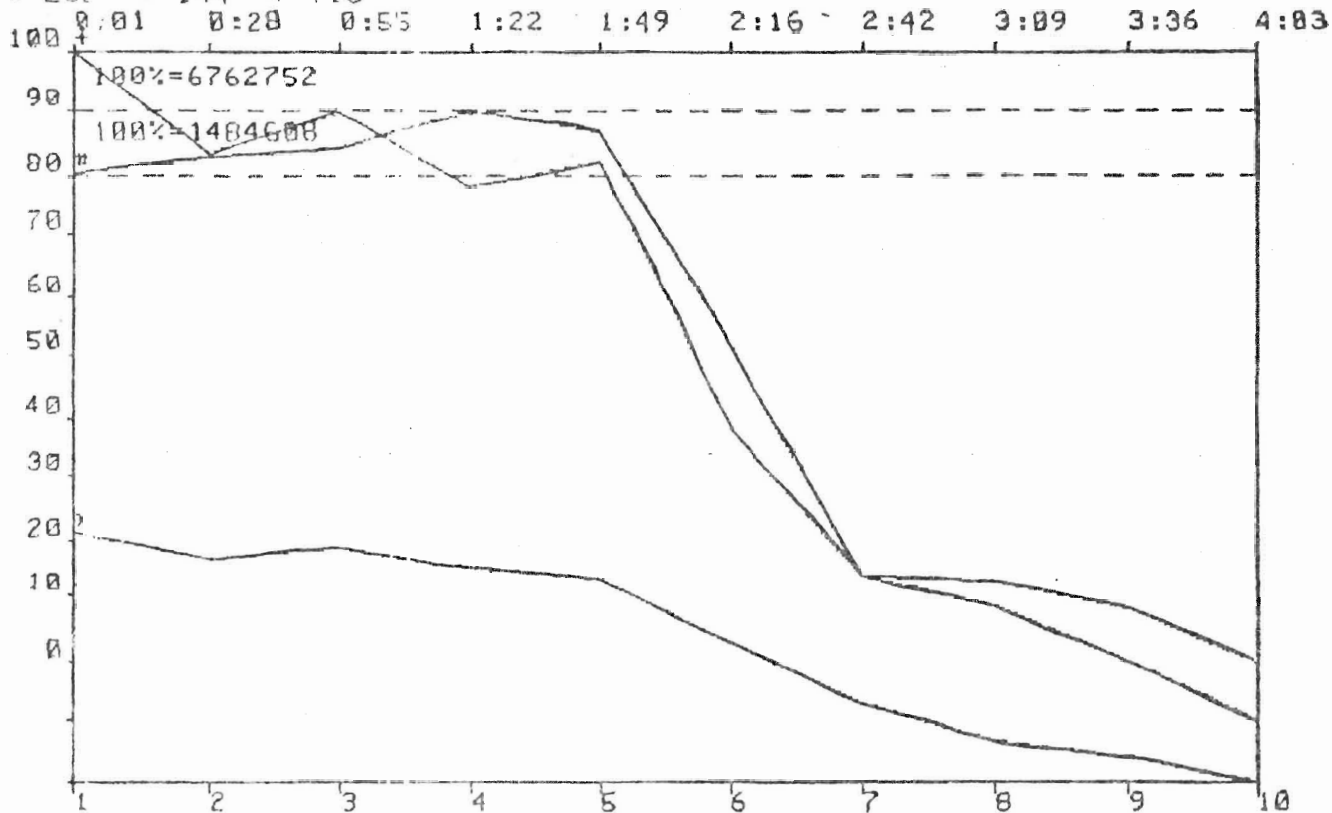
ii) 11.4 µg of Carbaryl Mixed in 0.50 µL NBA.

C.   Methods of Application of the Analyte to the FAB Probe

   1)   Simple Mixing

   The initial parameter investigated when FAB-MS was performed on
carbaryl was that of the optimal volume of matrix liquid, NPOE, to
apply to the probe tip. Observation of Table 6 on page 34 and Graph 1a
on page 35 illustrates quite clearly that the ion current produced
decreases as the volume of matrix liquid was increased. This
relationship is not surprising in that, as the amount of matrix liquid
was increased, the amount of carbaryl per unit surface area decreased.
The fact that the relationship was not linear is also as expected if
one assumes that the shape of the bead of matrix on the probe tip
approximates a half-sphere. If the bead were indeed a half-sphere
then Equations 1-5 would apply.

1) $V = 4/3 \pi r^3$ where V = volume of a sphere   (42)

A = area of a sphere

2) $A = 4 \pi r^2$ r = radius of a sphere

[c] = concentration of the analyte

3) $V \propto A^{3/2}$

4) $[c] \propto 1/A$

5) $[c] \propto \bar{v}^{-3/2}$

The approximation leaves us with the relationship that concentration
and thus, ion current was proportional to the volume of matrix to the
negative 3/2 power. Graph 1b illustrates this relationship previously
mentioned for the data in Table 6. One observes that the relationship
between ion current and volume to the -3/2 power is linear with a
correlation coefficient of 0.985. Similar plots of this relationship
when different application techniques were used appear in Graph 3b on
page 41, Graph 9b on page 61 and graph 11b on page 67. In the case of
Graph 3b and 9b the relationship appears to be non-linear. This

non-linearity is not surprising since the relationship developed depends on the matrix liquid approximating a half-sphere. In many cases observation of the actual samples showed the matrix to be present in a shape other than a half-sphere. Graph 1a also illustrates that there was no correlation between ion current and precision. Standard deviations were 13%, 20%, 5% and 21% when volumes of 0.50, 1.00, 1.50, and 2.00 μL of NPOE respectively were utilized. It would seem clear that the optimal volume of NPOE was 0.50 μL. It maximized ion current produced by carbaryl with no appreciable loss of precision incurred by delivering or utilizing such a small volume. It should be noted that the use of less than 0.50 μL of matrix liquid would be likely to produce problems since the volume could be to small to completely cover the probe tip.

Table 7 on page 36 contains the data concerning the detection limit for the FAB-MS of carbaryl using simple mixing and NPOE as the matrix liquid. It should be noted that a quantitative definition of the detection limit is the concentration of the analyte which produced a signal-to-noise ratio of 2. Further, detection limits are usually defined at a 95% confidence level ($\bar{x}+2\delta$) (43), where δ is the standard error. A mass of 0.25 μg of carbaryl produces a S/N ratio of 2. However, not all values of the S/N within 2δ of the mean would be greater than or equal to two. A mass of 0.50 μg of carbaryl did produce a S/N ratio of at least 2 with 95% confidence.

Table 8 on page 37, Graph 2 on page 38 and Table 9 on page 39 contain information pertaining to the relationship between ion current and the mass of carbaryl applied to NPOE by simple mixing. The five points of lower mass on Graph 2 illustrate quite clearly a linear relationship, with a correlation coefficient of 0.99 between the mass of carbaryl and ion current. The graph also fails to show a definite

correlation between precision and the mass of carbaryl. This indicated that it was correct to use non-weighted regression on the data (44). This relationship is typical of a system where the analyte does not act as a surfactant and does not preferentially diffuse to the matrix surface. The surface was the region from which secondary particles were ejected (33). Graph 2 also illustrates an interesting phenomenon which was observed to occur with all three modes of sample application. The intensity of the peak used to quantify the carbaryl was found to increase with the mass of carbaryl applied up to a maximum and then it fell off again. Zhang and Liang using surface precipitaion with chlorophyll a on PEG, also noted this to occur with a sample dosage of circa 75 µg (36). They postulated the existence of an optimal surface concentration of the sample particles. Above this concentration the surface mobility of these particles becomes restricted and replenishment of the beam's target area becomes retarded. It would seem a simple and logical step to postulate a similar occurrence in a three dimensional situation such as with simple mixing, instead of the essentially two dimensional environment created by surface precipitation. In this instance, the maximum appeared at a mass of carbaryl of approximately 20 µg. This was substantially lower than in the previously reported system. However, many conditions differed between the systems which were likely to affect this phenomenon. Indeed, this would be an ideal topic for further study. One could study the effect on the maximum of differing matrices, volumes of matrix, viscosity of matrix, etc.

The optimal volume of matrix liquid to be used when applying samples by simple mixing was also investigated using NBA as the matrix liquid. The data from this investigation is contained in Table 10 on page 40 and Graph 3a on page 41. It illustrates quite clearly that

ion current from the analyte decreases in a non-linear manner as the amount of matrix liquid is increased. It is also clear that relative precision neither increased or decreased consistently with increased volume of matrix liquid. The standard deviations are 22%, 27%, 21% and 12% of the mean for volumes of matrix of 0.50, 1.00, 1.50, and 2.00 μL.

Table 11 on page 42 presents data concerning the FAB-MS detection limit for carbaryl applied to the probe tip in NBA by simple mixing. Given the previously mentioned definition of a detection limit, a mass of carbaryl of 0.50 μg meets the criteria. The noise produced when 0.99 μg of carbaryl is used appears to be zero. This resulted because of a poorly adjusted instrument rather than some significant physical occurrence.

Graph 4 on page 44 illustrates the relationship between ion current and the mass of carbaryl mixed into the NBA matrix. The numerical data can be found in Table 12 on page 43. The appearance of the graph is substantially different from that illustrating the use of NPOE. In this case, the ion current increased exponentially as the mass of carbaryl on the probe tip increased. It is also notable that the rate of increase decreases with increasing mass of the analyte. This behaviour is indicative of system where preferential diffusion of the analyte to the surface of the matrix droplet is occurring. There was no obvious correlation between precision and mass of analyte, standard deviations were between a high of 21% and a low of 2% in a seemingly random manner. The application of an Nth order regression analysis identified the relationship as being of the 2nd order (Table 13 on page 45).

2) Solvent Mixing

The initial concern when attempting FAB-MS on a sample of
carbaryl in NPOE was which solvent to mix the analyte with. The four
solvents compared were varied in that they covered a wide range of
polarities, vapour pressures and chemical natures. The only solvent
of the four which produced a signal-to-noise ratio greater than
carbaryl in NPOE alone was nitrobenzene (Table 14 on page 46) . This
increase occurred because the solvent was either enhancing the
carbaryl's signal or suppressing the degradation of the matrix (the
principle noise source in FAB-MS (45)), or a combination of both
effects. The exact manner in which the nitrobenzene accomplished this
was not immediately evident. Most likely the nitrobenzene being, a
fairly polar solvent(E_T being 42.0), enhanced the solubility of the
carbaryl in the matrix liquid (46). The other two solvents of high
polarity used were acetone and acetonitrile, E_T being 42.2 and 46.0
respectively. They did not produce the same effect as nitrobenzene.
The reason for this was that their vapour pressures are substantially
higher than that of nitrobenzene, as shown by Riddick and Bunger
(47). This meant that both acetone and acetonitrile were quickly
removed from the probe tip in the mass spectrometer's high vacuum.
The increased S/N ratio observed when utilizing nitrobenzene
identified it as an excellent solvent to use for the rest of the
study.

Table 15 on page 47 and graph 5 on page 48 illustrate the data
obtained in the determination of the optimal volumes of NPOE and
nitrobenzene to combine with carbaryl to obtain the highest ion
currents from FAB-MS. It was easily seen that the optimal combination
occurred with the mixing of 0.50 μL of 2-nitrophenyloctyl ether with

1.00 µL of nitrobenzene. Two things are notable in this determination. One, the optimal combination of the two compounds produced ion currents significantly higher than other combinations investigated. In fact, the ion current was higher by not less than a factor of two. Second, the use of nitrobenzene in the absence of 2-nitrophenyloctyl ether produced no signal. This indicated that nitrobenzene alone was unsuitable as a matrix liquid in conjuction with carbaryl.

The data in Table 16 on page 49 shows that a mass of carbaryl of 0.25 µg produced a signal-to-noise ratio of 3 with a standard error of 0.60 for carbaryl in NPOE and nitrobenzene. This signal-to-noise ratio identified 0.25 µg of carbaryl as being below the detection limit. A mass of 0.50 µg of carbaryl produces a S/N ratio well above the detection limit with 95% confidence. This makes it evident that the detection limit for the FAB-MS anlysis of carbaryl in NPOE and nitrobenzene lies between 0.50 µg and 0.25 µg of carbaryl.

Graph 6 on page 51 illustrates the numerical data in Table 17 on page 50 concerning the relationship between ion current and the mass of carbaryl mixed with NPOE and nitrobenzene. The graph shows an apparently linear relationship between ion current and the mass of the analyte. Indeed, the Nth order regression analysis was first order with a coefficient of correlation of 0.994. The information can be found in Table 18 on page 52. This linearity held only until the mass of carbaryl on the probe tip exceeded an apparent maximum occurring between the mass of carbaryl of 20.4 and 25.5 µg. Standard deviations for the points of the graph were found to vary randomly between a maximum of 32% of the mean for 5.1 µg of carbaryl and a minimum of 5% of the mean for 12.8 µg of carbaryl. Thus, there was no apparent relationship between precision and the mass of the analyte. This

allowed the use of non-weighted regression analysis.

Table 19 on page 53 contains the data obtained when performing FAB-MS on carbaryl in NBA mixed with a number of varied solvents. The only solvent of those investigated which improved the signal-to-noise ratio, with respect to carbaryl in NBA alone, was nitrobenzene. The reasons for the increase are most likely the same as when NPOE was the matrix liquid. Nitrobenzene is quite polar, as is carbaryl. A polar molecule is a molecule which the center of positive charge is not coincident with the center of negative charge (48). This would have made it possible for the solvent to enhance solubility of the analyte and thus, its signal. The other polar solvents failed to do this because of their high vapour pressures which would eliminate them quickly from the probe tip when introduced into the source. The magnitude of the enhancement was approximately 25% of the S/N ratio for the system using a neat matrix liquid.

The data obtained in investigating the optimal volumes of nitrobenzene and nitrobenzyl alcohol to combine with carbaryl appears in Table 20 on page 54. The illustration of this data in Graph 7 on page 55 shows that combining carbaryl with 1.00 μL each of NBA and nitrobenzene produces the best ion currents. The graph also shows that the ion current produced using the optimal volumes was not significantly larger than other less suitable combinations.

A mass of 0.74 μg of carbaryl was found to produce a signal-to-noise ratio of 4. The standard error of the determination was such that not all values of the ratio would exceed 2 with 95% confidence (Table 21 on page 56). A mass of 2.00 μg of analyte produced a signal-to-noise ratio well above the defined value for a detection limit. Thus, it can be said that the detection limit for FAB-MS analysis of carbaryl in NBA and nitrobenzene occurs between

2.00 µg and 0.74 µg.

The relationship between ion current and the mass of carbaryl was non-linear when the analyte was mixed with NBA and nitrobenzene. Ion current increased with mass but the slope of the curve illustrating the relationship decreased with mass (see Graph 8 on page 58 and Table 22 on page 57). Standard deviations in this case were found to vary somewhat with concentration. It should be noted that one point was anomalous, 25.4 µg of carbaryl. Still, a good argument could be made for using either weighted or non-weighted regression in this case. Non-weighted regression identified the observed relationship as being second order with a correlation coefficient of 0.996 (Table 23 on page 59). A second anomaly appears in Graph 8 in that no concentration maximum was observed using carbaryl in NBA and nitrobenzene. It is possible that if the study had proceeded with higher masses of analyte a maximum might have become evident. This was entirely likely since the volume of material on the probe tip was greatest using this application technique. Therefore, one might expect the maximum to occur with a mass of analyte greater than with any of the other application techniques investigated.

3) Surface Precipitation

The method as suggested by Zhang and Liang assumed that the analyte was insoluble in the matrix liquid and thus was precipitated onto the matrix surface (36). This method allows concentrating the analyte in the beam's target area. Logical extrapolation would suggest that an analyte soluble in the matrix liquid could also be concentrated in the target area using this method. The success of this method would require that the rate with which the analyte diffuses into the matrix be slow on the time-scale of a mass spectrum. There would be no advantage to the method over simple mixing if the rate of diffusion was fast.

The initial concern when applying carbaryl to the probe tip was the optimal volume of NPOE, the matrix liquid, to use. The relationship observed was that ion current produced by a given mass of carbaryl decreased with increased volume (Table 24 on page 60 and Graph 9a on page 61). This follows logically since as the volume of matrix increases so does the surface area over which the carbaryl is distributed. This would result in smaller amounts of analyte being present in the beam's target area and this would produce lower ion currents. This should have been an exponential decay and may well be. However, this could not be said with any certainty because of the large standard deviations involved. The most suitable volume of NPOE to use was obviously 0.50 µL. It gave by far the highest ion current and also produced the most precise data with the standard deviation being 8.6% of the mean. Volumes of 1.00 µL and 2.00 µL produced standard deviations of 41% and 15% of their means respectively.

Table 25 on page 62 contains the data obtained in order to determine the detection limit for the analysis of carbaryl surface precititated on NPOE. The data presented does not identify the actual detection limit. Rather, it suggests that this detection limit was less than 0.50 µg of carbaryl. If a mass of 0.25 µg of carbaryl had been used then the detection limit could no doubt have been identified more specifically.

Graph 10 on page 64 illustrates the relationship between ion current and the mass of carbaryl. The numerical data appears in Table 26 on page 63. One observes an apparently linear relationship between the two with ion current increasing with increased mass of carbaryl. The point representing 42.3 µg of carbaryl had an ion current of 2.7×10^4 counts, much lower than the previous point, 34.2 µg. This occurs as a result of the concentration maximum being exceeded. In this case, the maximum occurred between 34.2 µg and 42.3 µg of carbaryl. Precision does not vary as a function of the mass of carbaryl. It varied in a seemingly random manner. The standard deviations in the linear region vary between 14% for 11.4 µg of carbaryl and 3.6% for 34.2 µg of carbaryl. The Nth order regression analysis (Table 27 on page 65) identifies the relationship between ion current and the mass of carbaryl as being linear.

The application technique of surface precipitation was also investigated using NBA as the matrix liquid. The initial concern was to identify the optimal volume of matrix liquid to use. Table 28 on page 66 and Graph 11a on page 67 exhibit the data with respect to the determination of this volume. Once again, one observes that ion current decreased exponentially as the volume of matrix liquid increased. Presumably, this occurred for the same reasons as when

NPOE was used as the matrix liquid. Precision was best when 0.50 µL of NBA was used, standard deviations steadily increasing to a high of 55% of the mean when a volume of 2.00 µL of matrix was present on the probe tip.

An interesting observation was made while investigating optimal matrix volume. It was found that the analyte suppressed the signal created by the matrix liquid in a substantial manner. This suppression decreased with increasing volume of matrix liquid. In all previous instances, the ratio of the m/z 202 peak to the m/z 154 peak in the unsubtracted spectra was substantially less than 0.5. (The peak at m/z 202 is due to the protonated molecular ion of carbaryl and m/z 154 is the base peak in the mass spectrum of NBA). The ratios of the ion currents for m/z 202 and m/z 154 are 2.21 ± 0.52, 0.921 ± 0.068, 0.497 ± 0.019 and 0.383 ± 0.023 respectively for matrix volumes of 0.50, 1.00, 1.50, and 2.00 µL. This behaviour can be explained if the analyte was acting as a surfactant in the matrix liquid and thus, the surface would be enriched with the analyte. This behaviour has been observed for a number of systems including dipeptides (49) and various organic salts (50). In fact, one would expect this suppression to be most pronounced using an application technique like surface precipitation. The reason is that the analyte would be immediately concentrated on the matrix's surface and would exhibit little tendency to leave that surface. The reason that the suppression decreased with increased volume was most likely that the available carbaryl was spread over a larger surface area.

The data in Table 29 on page 68 concerns the detection limit for the FAB-MS determination of carbaryl applied by surface precipitation

on NBA. The detection limit was 0.30 µg of carbaryl which produced a signal-to-noise ratio of 2.5 with the desired 95% confidence level.

Table 30 on page 69 and Graph 12 on page 70 contain data illustrating the relationship between ion current and the mass of carbaryl applied to NBA. The graph is of interest in that it shows that ion current increased exponentially with increased mass up to a maximum. The rate of this increase also increased with the mass of carbaryl. This was not observed in any other system studied. Again, no obvious relationship was found between precision and ion current. Nth order regression (Table 31 on page 71) showed the relationship to be second order with a respectable correlation coefficient of 0.996. This is consistent with a system where the solute was acting as a surfactant in the matrix liquid, NBA. It was most likely this tendency which caused the anomalous slope of the curve. Each addition of carbaryl to the target area would further increase the suppression of the matrix in a cumulative manner. The concentration maximum was also found to occur with NPOE as the matrix. The maximum occurred between 18.1 and 24.2 µg of carbaryl.

D. General Trends

1) The Volume of Matrix

It was observed that the optimal volume of matrix liquid to use in order to maximize the ion current created by the analyte was 0.50 µL. This was the case regardless of whether the matrix liquid was NPOE or NBA or if it was applied by simple mixing, solvent mixing or

surface precipitation, with one exception, occurring when carbaryl was applied by solvent mixing with nitrobenzene and NBA. In that case, 1.00 µL of matrix liquid appeared to be the optimal amount. The reason for this anomaly was either that the simplex determination of the optimal volume should have been carried further or was indeterminate. The general trend was not surprising in that the smaller the volume of matrix liquid, the greater the amount of carbaryl in the beam's target area. The more analyte which is available for ionization, the greater the ion current.

2) The Detection Limit

The detection limit for carbaryl in NPOE appeared relatively constant at 0.50 µg regardless of the application technique. The detection limit for carbaryl in NBA varied according to which application technique was utilized. In all three cases, the detection limits were within an order of magnitude of each other. The highest detection limit was encountered using NBA and nitrobenzene with the analyte to produce a spectrum. The reason for this was most likely that the nitrobenzene was decomposing to form species which added to the background interference, caused mainly by the matrix (45), thus lowering the observed signal-to-noise ratio. The lowest detection limit was produced when carbaryl was applied to NBA using surface precipitation. This was not surprising if one considers that carbaryl was acting as a surfactant in NBA and causing a suppression of the matrix's signal. The same factors suppressing the matrix's signal would suppress the formation of the species responsible for noise.

This would increase the signal-to-noise ratio observed. This effect would be most evident using surface precipitation. The reason was that the analyte was being introduced immediately to the surface of the matrix and there would be little or no tendency for it to diffuse into the body of the matrix liquid.

The detection limits observed using the FAB-MS techniques appeared to be generally higher than were observed using other mass spectrometric techniques. The detection limit was said to be 40 ng using DLI LC-MS (22) and 3-5 ng using thermospray LC-MS (28). The literature suggests that the sensitivity of the technique is limited by the high background resulting from the necessary use of an involatile solvent, the matrix (51). A number of techniques are available to circumvent the technique's limitation. Perhaps the most promising possibility in this case would be to use higher resolution to resolve the carbaryl from potentially interfering species at the nominal mass of 202 amu. The exact mass of carbaryl to four decimal places is 201.0790 amu. Another promising technique involves the use of a moving belt/FAB interface (52). The interface presents a fresh sample surface to the FAB beam as the belt rotates eliminating the need for a matrix liquid.

3) The Relationship Between Ion Current and the Mass of Carbaryl

In each case, the use of NPOE as the matrix liquid produced a linear relationship between ion current and the mass of analyte regardless of the application technique. This would indicate that the primary mode for replenishment of the beam's target area was simple

diffusion. The opposite was true of NBA. Regardless of application technique, the relationship between ion current and the mass of carbaryl was non-linear. This indicated that the system was quite dynamic with the carbaryl being selectively pumped to the surface of the matrix liquid. Although this behaviour would make quantitation more difficult, it would by no means be made impossible. The actual curves obtained using NBA vary slightly. Surface precipitation produced a relationship where the slope of the curve increases with increased mass of carbaryl. Simple mixing or solvent mixing had the opposite effect. The reason for the anomalous behaviour when utilizing surface precipitation was not immediately obvious. Thus, it would seem that the choice of matrix liquid used in conjunction with the analyte can have a substantial effect on the behaviour of the analyte and ultimately on the mass spectra produced.

The use of NPOE as a matrix liquid produced a concentration maximum in conjunction with all three application techniques. The mass of carbaryl at which the maximum occurred varied slightly in all three cases. The reason for this variation could be due to a number of potential factors, other than the application technique, as previously discussed. Thus, it would be incorrect to attempt to identify a trend based on the limited information obtained in this study. A similar situation existed when NBA was used as the matrix. However, a maximum was observed only when surface precipitation was the method of sample preparation. Again, the reason for not observing a maximum in conjunction with the other two application techniques may be because the appropriate mass was not exceeded, rather than because of some more complex effect. It would seem obvious that this phenomenon would make an excellent topic for further study.

E. Interferences

The selectivity of the method was demonstrated by performing
FAB-MS on a variety of common pesticides applied to the probe tip by
simple mixing in both NPOE and NBA. It was found that when NPOE was
used as the matrix liquid only three of the ten pesticides
investigated produced a total ion current greater than one million
counts (see Table 32 on page 72). More significantly, only three of
the pesticides (aldrin, DDT and parathion) produce a signal at m/z 202
which would interfere with the determination of carbaryl. Further,
only one of the three, parathion, produces an ion current large enough
to be problematic with the analysis of any but the smallest mass of
carbaryl. The presence of the interfering pesticide, parathion, would
be unlikely to escape the attention of the analyst because the mass
spectrum would contain other anomalous peaks created by parathion.
The problem could then be eliminated by using a different matrix
liquid one in which the parathion did not produce an interfering
signal. A second possibility would be to use higher resolution to
differentiate between the peaks created at nominal mass 202 by
parathion and carbaryl.

The use of 3-nitrobenzyl alcohol produced similar results (Table
33 on page 73). However, it appeared to be somewhat more selective
than NPOE. None of the pesticides investigated produced total ion
currents greater than 1×10^6 counts. In fact, only four of the ten
produced a total ion current in excess of one hundred thousand counts.
The only pesticide which produced a peak at nominal mass 202 was
parathion. The magnitude of this peak was such that it would only
interfere with masses of carbaryl near the method's detection limit

(see Table 33 on page 73). It should be noted that the magnitude of
the interference was made even less significant when one considers
that a large excess of the pesticide was used.

It seems clear that the FAB-MS analysis of carbaryl exhibits the
superior selectivity typical of mass spectrometric techniques.

V CONCLUSION

The purpose of the study was to demonstrate the benefits of quantitatively analyzing the carbamate pesticide carbaryl using FAB-MS. Principally, it was hoped there would be superior sensitivity and selectivity combined with simple sample preparation and a lack of thermal effects. At the same time, the work would provide valuable information concerning detection limits, application techniques and matrix affects. The possibility of actual analysis of carbaryl in situ on environmental samples was also to be investigated.

Of all the matrices examined, only 2-nitrophenyloctyl ether and 3-nitrobenzyl alcohol were suitable. Both exhibited large ion currents, good fragmentation of the analyte, minimal interference between matrix and analyte fragments and signals of relatively long duration. Total ion current was observed to decrease more or less continually with the duration of the collection of the spectrum.

The largest ion currents were produced using the smallest volumes of matrix liquid. This was the case for both NPOE and NBA regardless of the application technique used. The reason was a concentration effect. The analyte was most concentrated in smaller volumes of matrix liquid and thus, produced the largest number of ions.

The detection limit of the FAB-MS determination of carbaryl was found to be a relatively constant 0.50 μg regardless of the application technique. The detection limit using NBA as the matrix liquid varied depending on the application technique. The reason probably was the apparently complex system existing in the solution created by mixing carbaryl and NBA. Carbaryl was found to preferentially diffuse to the surface of the matrix liquid. The

lowest detection limit, 0.30 μg, was observed when carbaryl was applied to NBA using surface precipitation. This method also produces a rather interesting suppression of the signal created by the matrix liquid. The detection limits were comparable to those observed for the analysis techniques mentioned in the introduction, with the exception of other mass spectrometric techniques. The reason for this is the interference created by the necessary use of the matrix liquid. Several possibilities have been suggested to correct this problem. Unfortunately, the relatively poor sensitivity combined with time constraints precluded the study of carbaryl on environmental substrates.

The relationship between ion current and the mass of carbaryl was found to depend upon the interaction between the analyte and the individual matrix liquid. The relationship was first order when NPOE was used as a matrix liquid regardless of the manner in which the samples were prepared. The relationship between ion current and the mass of carbaryl was found to be exclusively second order when NBA was the matrix liquid.

The most interesting discovery warranting further study was the existance of a concentration maximum. The maximum was the mass of carbaryl on the probe tip which, when exceeded, resulted in a lowering of ion current with increased mass of analyte. A maximum was discovered using NPOE as a matrix liquid when the sample was applied using all three application techniques. A maximum observed using NBA only when the carbaryl was applied by surface precipitation. It was postulated the reason that no maximum was observed using simple and solvent mixing only because the study was not taken to a sufficiently high mass of analyte.

The selectivity of the method was demonstrated by showing that

only one of ten common pesticides produced an interference. The magnitude of the interference was minimal especially when one considered the parathion was present in large excess. Further, methods of eliminating even this single interference were suggested.

It would seem clear that the quantitative FAB-MS analysis of carbaryl has been shown viable, exhibiting good sensitivity and selectivity with simple sample preparation and no thermal effects. Further, information concerning detection limits, application techniques and matrix affects may prove of interest and value to others in the field.

REFERENCES

1. H. Gysin, Chimia, <u>8</u> , 205 (1954).

2. J. A. Lambrech (Union Carbide Corp.), U.S. Patent, 2903478 September 8, 1959.

3. H. L. Haynes, J. A. Lambrech and H. H. Moorefield, Contrib. Boyce Thompson Inst., <u>18</u> , 507 (1957).

4. R. C. Back, J. Agric. Food Chem., <u>13</u> , 198 (1965).

5. "The Merck Index: An Encyclopedia of Chemicals, Drugs and Biochemicals", 10th edition, Merck and Co. Inc., Rahway, N.J. (1983).

6. J. B. Houston, D. G. Upshall and J. W. Bridges, Xenobiotica, <u>5</u> , 637 (1974).

7. R. J. Kuhr and H. W. Dorough, "Carbamate Insecticides: Chemistry, Biochemistry and Toxicology", CRC Press, Inc., Cleveland, Ohio, 22 (1976).

8. M. R. Vandekar, R. Plestina and K. Wilhelm, Bull. Wld. Hlth. Org., <u>44</u> , 241 (1971).

9. P. Mitov, G. Pepelyankov and D. Dyakov, Gradinar. Lozar. Nauka, <u>17</u> , 9 (1980) from Chemical Abstracts, <u>95</u> , 216307 (1981).

10. T. Cairns, E. G. Siegmund, G. M. Doose, W. S. Langham and K. S. Chiu, Bull. Environ. Cont. Tox., <u>32</u> , 310 (1984).

11. E. Papadopoulou-Mourkidou, Y. Iwata and F. A. Gunther, J. Liq. Chrom., <u>4</u> , 1663 (1981).

12. K. M. Hill, R. H. Hollowell and L. A. Dal Cortivo, Anal. Chem., <u>56</u> , 2465 (1984).

13. P. Cabras, P. Diana, M. Meloni and F. M. Piris, J. Agric. Food Chem., <u>30</u> , 569 (1982).

14. M. Chiba, J. Agric. Food Chem., <u>29</u> , 118 (1981).

15. S. K. Handa and A. K. Dikshit, Analyst, <u>104</u> , 1185 (1979).

16. M. J. Larkin and M. J. Day, Anal. Chim. Acta, <u>108</u> , 425 (1979).

17. B. E. Wallbank, J. Chrom., <u>208</u> , 305 (1981).

18. A. Ambrus, E. Hargital, G. Karoly, A. Fulop and J. Lantos, J. Assoc. Off. Anal. Chem., <u>64</u> , 3, 743 (1981).

19. P. Bottomley and P. G. Baker, Analyst, <u>109</u> , 85 (1984).

20.   A. B. Wood, and L. Kanagasabapathy, Pestic. Sci., 14 , 108, (1983).

21.   M. J. Avery, G. A. Junk, Anal. Chem., 57 , 790 (1985).

22.   R. D. Voyksner, and J. T. Bursey, Anal. Chem., 56 , 1582 (1984).

23.   B. J. Millard, "Quantitative Mass Spectrometry", Heyden & Sons Ltd., Philadelphia Pa. U.S., (1978).

24.   T. T. Chang, J. O. Lay and R. J. Francel, Anal. Chem., 56 , 109 (1984).

25.   T. T. Chang, Abstr. Annu. Conf. Mass Spectrom. Allied Top., 30th Honolulu, 318 (1982).

26.   T. Cairns, E. G. Siegmund, G. M. Doose, Bull. Environ. Contam. Toxicol 30 , 93 (1982).

27.   W. H. McFadden, H. L. Schwartz, and S. Evans, J. Chromatogr., 122 , 389 (1976).

28.   R. D. Voyksner, J. T. Bursey, and E. D. Pellizzari, Anal. Chem., 56 , 1507 (1984).

29.   M. Dedieu, C. Juin, P. J. Arpino, and G. Guiochon, Anal. Chem., 54 , 2372 (1982).

30.   M. Barber, S. Bordoli, R. D. Sedgwich, and A. Tyler, J. Chem. Soc., Chem. Commun., 325 (1981).

31.   M. Barber, R. S. Bordoli, E. J. Elliot, R. P. Sedgwick, and A. N. Tyler, Anal. Chem., 54 , 645A (1982).

32.   S. A. Martin, C. E. Costello, and K. Blemann, Anal. Chem., 54 , 2362 (1982).

33.   E. De Pauw, Mass Spectrometry Reviews, 5 , 191 (1986).

34.   R. M. Caprioli, Anal. Chem., 55 , 2387 (1983).

35.   M. A. Baldwin, K. J. Welham, Results Presented at the 10th Int. Conf. Mass Spectrom., Swansea, (1985).

36.   M. Y. Zhang, X. Y. Liang, Y. Y. Chen, and X. G. Liang, Anal. Chem., 56 , 2288 (1984).

37.   C. J. Frick, "The Practical Aspects of Hydrodynamic Chromatography", Masters Thesis, University of Waterloo, (1983), originally obtained from Hewlett-Packard.

38.   R. D. Minard, and G. L. Geoffroy, Abstr. Annu. Conf. Mass Spectrom. Allied Top., 30th Honolulu, 321 (1982).

39.   J. M. Miller, Advances in Inorganic Chemistry and Radiochemistry, 28 , 1 (1984).

40. J. Meili, and J. Seibl, Organic Mass Spectrometry, <u>19</u> , 581, (1984).

41. J. Marien and E. De Pauw, Int. J. Mass Spectrom. Ion Phys., <u>43</u> , 233 (1982).

42. "Handbook of Chemistry and Physics", 43rd ed., Edited by C. Hodgman, The Chemical Rubber Publishing Co., Cleveland, Ohio, 344 (1962).

43. H. Willard, L. Merritt, J. Dean, and F. Settle, "Instrumental Methods of Analysis", 6th ed., D. Van Nostrand Co., Toronto, 848 (1981).

44. R. Caulcutt and R. Boddy, "Statistics for Analytical Chemists", Chapman and Hall, New York, 100 (1983).

45. J. Page, Pestic. Sci., <u>18</u> , 291 (1987).

46. M. R. J. Dack, "Solutions and Solubilities Part II - Techniques of Chemistry Volume VIII", John Wiley and Sons Inc., Toronto, 133 (1976).

47. J. A. Riddick, W. B. Bunger, "Organic Solvents - Techniques of Chemistry II", 3rd ed., John Wiley and Sons Inc., Toronto (1970).

48. R. T. Morisson, and R. N. Boyd, "Organic Chemistry", 3rd ed., Allyn and Bacon Inc., Toronto, 22 (1979)

49. W. V. Ligon, Anal. Chem., <u>58</u> , 487 (1986).

50. E. De Pauw, G. Pelzer, J. Marien, J. L. Piette, and M. C. Pardon, Org. Mass Spectrom., <u>20</u> , 692 (1985).

51. H. R. Morris, M. Panio, M. Judkins, A. Dell, and R. McDowell, Abstr. Annu. Conf. Mass Spectrom. Allied Top., 29th, Minneappolis, USA, 375 (1981).

52. P. Dobberstein, E. Korte, G. Meyerhoff, and R. Pesch, Int. J. of Mass Spectrom. and Ion Phys., <u>46</u> , 185 (1983).

53. R. A. Hites, "Handbook of Mass Spectra of Environmental Contaminants", CRC Press, Inc., Boca Raton, Florida, 226 (1985).

54. Statview 5/2 +, Brainpower Inc. © Abacus Concepts Inc., Calabasas, California (1986).

Appendix A: Nth Order Regression

N th Order Regression

This program finds the coefficients of an N th order equation using the method of least squares. The equation is of the following form:

$$y = c + a_1 x + a_2 x^2 + \ldots a_n x^n$$

where: y = dependent variable
c = constant
$a_1, a_2 \ldots a_n$ = coefficients of independent variables $x, x^2, \ldots x^n$, respectively

The equation coefficients, coefficient of determination, coefficient of correlation and standard error of estimate are printed.

You must provide the x - and y -coordinates for known data points. Once the equation has been computed you may predict values of y for given values of x.

The dimension statement at line 30 limits the degree of the equation. You can change this limit according to the following scheme:

30 DIM A(2·D+1), R(D+1,D+2), T(D+2)

where D = maximum degree of equation.

Example:

The table below gives the stopping distance (reaction plus braking distance) of an automobile at various speeds. Fit an exponential curve to the data. Estimate the stopping distance at 55 m.p.h.

m.p.h.	20	30	40	50	60	70
stopping distance	54	90	138	206	292	396

```
:30 DIM A(5),R(3,4),T(4)
:RUN
NTH-ORDER REGRESSION

DEGREE OF EQUATION? 2
NUMBER OF KNOWN POINTS? 6
X,Y OF POINT 1 ? 20,54
X,Y OF POINT 2 ? 30,90
X,Y OF POINT 3 ? 40,138
X,Y OF POINT 4 ? 50,206
X,Y OF POINT 5 ? 60,292
X,Y OF POINT 6 ? 70,396


        CONSTANT = 41.771428569
 1 DEGREE COEFFICIENT =-1.095714285598
 2 DEGREE COEFFICIENT = 8.78571428E-02


COEFFICIENT OF DETERMINATION (R↑2) = .9999279597663
COEFFICIENT OF CORRELATION = .99996397923
STANDARD ERROR OF ESTIMATE = 1.4209319536
```

INTERPOLATION:(ENTER 0 TO END PROGRAM)
X =? 55
Y = 247.2750000003

X =? 0

END PROGRAM

PROGRAM LISTING

```
 10   PRINT "NTH-ORDER REGRESSION"
 20   PRINT
 29   REM - SET LIMITS ON DEGREE OF EQUATION TO A(2D+1),R(D+1,D+2),T(D+
      (WHERE D=MAXIMUM DEGREE OF EQUATION)
 30   DIM A(13),R(7,8),T(8)
 40   PRINT "DEGREE OF EQUATION";
 50   INPUT D
 60   PRINT "NUMBER CF KNOWN POINTS";
 70   INPUT N
 80   A(1)=N
 89   REM - ENTER COORDINATES OF DATA POINTS
 90   FOR I=1  TO N
100   PRINT "X,Y OF POINT";I;
110   INPUT X,Y
118   REM - LINES 120-200 POPULATE MATRICES WITH
119   REM - A SYSTEM OF EQUATIONS
120   FOR J=2  TO 2*D-1
130   A(J)=A(J)+X↑(J-1)
140   NEXT J
150   FOR K=1  TO D+1
160   R(K,D+2)=T(K)+Y*X↑(K-1)
170   T(K)=T(K)+Y*X↑(K-1)
180   NEXT K
190   T(D+2)=T(D+2)+Y↑2
200   NEXT I
209   REM - LINES 210-490 SOLVE THE SYSTEM OF EQUATIONS IN THE MATRICES
210   FOR J=1  TO D+1
220   FOR K=1  TO D+1
230   R(J,K)=A(J+K-1)
240   NEXT K
250   NEXT J
260   FOR J=1  TO D+1
270   FOR K=J  TO D+1
280   IF R(K,J)<>0  THEN  320
290   NEXT K
300   PRINT "NO UNIGLE SOLUTION"
310   GOTO  790
320   FOR I=1  TO D+2
330   S=R(J,I)
340   R(J,I)=R(K,I)
350   R(K,I)=S
360   NEXT I
370   Z=1/R(J,J)
380   FOR I=1  TO D+2
390   R(J,I)=Z*R(J,I)
400   NEXT I
```
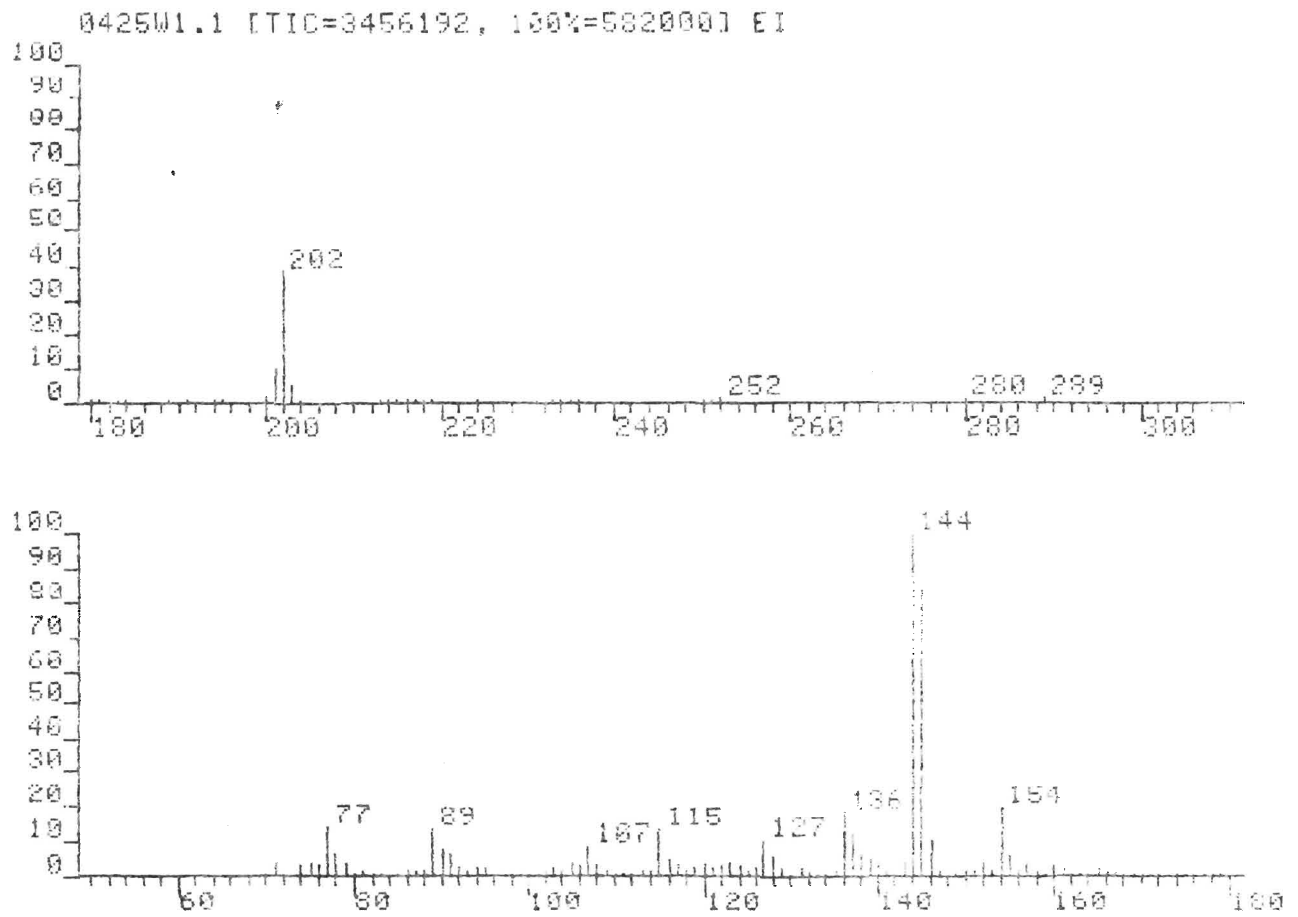
```
410  FOR K=1  TO D+1
420  IF K=J  THEN  470
430  Z=-R(K,J)
440  FOR I=1  TO D+2
450  R(K,I)=R(K,I)+Z*R(J,I)
460  NEXT I
470  NEXT K
480  NEXT J
490  PRINT
495  PRINT "                CONSTANT =";R(1,D+2)
499  REM - PRINT EQUATION COEFFICIENTS.
500  FOR J=1  TO D
510  PRINT J;"DEGREE COEFFICIENT =";R(J+1,D+2)
520  NEXT J
530  PRINT
539  REM - COMPUTE REGRESSION ANALYSIS
540  P=0
550  FOR J=2  TO D+1
560  P=P+R(J,D+2)*(T(J)-A(J)*T(1)/N)
570  NEXT J
580  Q=T(D+2)-T(1)+2/N
590  Z=Q-P
600  I=N-D-1
620  PRINT
630  J=P/Q
640  PRINT "COEFFICIENT OF DETERMINATION (R+2) =";J
650  PRINT "COEFFICIENT OF CORRELATION =";SQR(J)
660  PRINT "STANDARD ERROR OF ESTIMATE =";SQR(Z/I)
670  PRINT
679  REM - COMPUTE Y-COORDINATE FROM ENTERED X -COORDINATE
680  PRINT "INTERPOLATION:(ENTER 0 TO END PROGRAM)"
690  P=R(1,D+2)
700  PRINT "X =";
710  INPUT X
720  IF X=0  THEN  790
730  FOR J=1  TO D
740  P=P+R(J+1,D+2)*X^J
750  NEXT J
760  PRINT "Y =";P
770  PRINT
780  GOTO  690
790  END
```

Appendix B: Typical FAB Mass Spectra of Carbaryl
in NPOE and NBA

The FAB Mass Spectrum of Carbaryl in NPOE

0425W1.1 [TIC=3456192, 100%=582000] EI

The FAB Mass Spectrum of Carbaryl in NBA

0206W1.1 [TIC=7842816, 100%=1332416] EI