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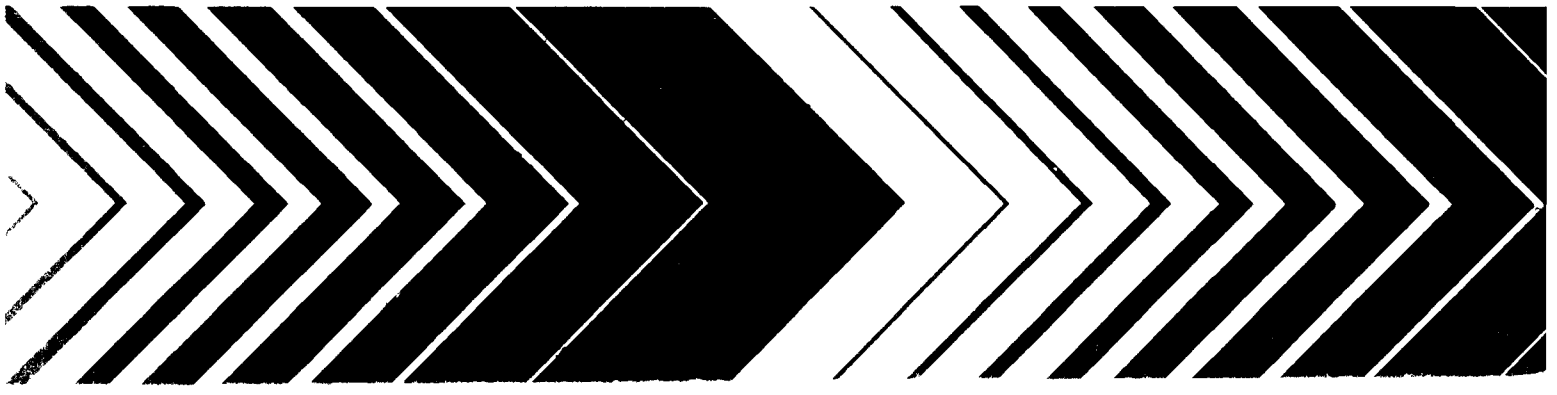
A One Step Method for the Determination of Carbamate Pesticides by Derivatization with α-Bromo-2,3,4,5, 6-Pentafluorotoluene



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A ONE STEP METHOD FOR THE DETERMINATION OF CARBAMATE PESTICIDES BY DERIVATIZATION WITH α-BROMO-2,3,4,5,6-PENTAFLUOROTOLUENE

by

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FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The Health Effects Research Laboratory, Research Triangle Park, conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, non-ionizing radiation, environmental carcinogenesis and the toxicology of pesticides as well as other chemical pollutants. The Laboratory participates in the development and revision of air quality criteria documents on pollutants for which national ambient air quality standards exist or are proposed, provides the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is primarily responsible for providing the health basis for non-ionizing radiation standards. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of health care and surveillance of persons having suffered imminent and substantial endangerment of their health.

Pursuant to the mission of the laboratory to investigate the effects of pesticide and toxic substances on human health, this project was undertaken to investigate an analytical method which would permit the analysis of many of the carbamate pesticides using the standard Environmental Protection Agency gas chromatographic parameters already set for the organochlorine pesticides. The method and analytical parameters for the carbamate pesticides tested by this method are presented.

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ABSTRACT

A procedure was developed for the determination of trace quantities of a broad range of carbamate pesticides. The carbamates were hydrolyzed and derivatized in a single step, using alkali and α-bromo-2,3,4,5,6-pentafluorotoluene (PFBB), and were subsequently analyzed using electron capture gas chromatography. This one step derivatization method created a novel derivative in which one fluorine on the PFB ring was displaced by an ethoxide ion via aromatic nucleophilic substitution.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGMENTS

The cooperation of Dr. Lynn Wright in running the CI mass spectra and Dr. Dan Zehr for helpful suggestions is gratefully acknowledged.

SECTION I

CONCLUSIONS

A method has been evaluated for the general analysis of carbamate pesticides. This method involves the hydrolysis of the intact carbamate pesticide to a substituted phenoxide ion which is then derivatized by the addition of α-bromo-2,3,4,5,6-pentafluorotoluene (PFBB). The method provided chromatographiable peaks using the standard EPA gas chromatographic parameters with 18 of the 23 carbamate pesticides tested.

Mass spectra were run on selected carbamate derivatives. It was determined from these that those carbamates which would hydrolyze to form phenolic intermediates formed derivatives with one fluorine displaced by an ethoxy group in the PFBB characterized by an abundant fragment ion of m/z 179, while those carbamates which would not form the phenolic intermediates followed no discernible pattern.

SECTION II

INTRODUCTION

Since the introduction of carbaryl in 1956, carbamate pesticides have become widely used in agricultural pest control programs. With the advent of this wide use, problems of analysis have become evident. Carbamates generally give poor electron capture response and are too thermally unstable to be analyzed by conventional gas chromatography. However, many methods have been developed to overcome these problems. A large number of these methods involve some type of chemical derivatization. Three basic types of derivatization procedures have been developed; derivatization of the intact carbamate, derivatization of the subsequent substituted phenol or phenol analog generated through hydrolysis, or derivatization of the subsequent amine generated through hydrolysis.

There have been several methods developed for the direct conversion of carbamates to chromatographiable compounds. Silylation,[1] acetylation,[4-6] alkylation,[7-9] transesterification,[10,11] and perfluorination[12,13] of various carbamates have been accomplished. Other methods involve hydrolysis of phenol generating carbamates and subsequent bromination,[14] chloroacetylation,[15-20] thiophosphorylation,[21] and silylation[2,3] of the phenolic intermediates. Other reagents used for the derivatization of phenolic intermediates include dinitrophenyl reagents,[22-25] and α-bromo-2,3,4,5,6-pentafluorotoluene (pentafluorobenzyl bromide).[26-30] Not all carbamates form phenols during hydrolysis. For those carbamates which hydrolyze to give amines, methods have been developed for derivatization of the

amines. Bromination,[31] iodination,[32] and p-bromobenzoylation[33] of the intermediate amines are several of the methods used. Also, as with the phenolic intermediates previously mentioned, dinitrophenyl,[34,35] and pentafluorobenzyl[36,37] reagents have been used.

While all of these methods are relatively sensitive by electron capture detection, no single procedure covered a wide range of carbamate pesticides.

The EPA Pesticide Analytical Manual[39] contains general procedures for the organochlorine and organophosphorus pesticides. The purpose of this study was to determine if one of the carbamate derivatization methods could be extended to a wide range of carbamate pesticides at the residue level and still use the standard gas chromatographic columns and operating conditions described in the EPA manual.[39]

SECTION III

EXPERIMENTAL

Reagents and Solvents

Alcoholic potassium hydroxide: Dissolved 1.0 g of solid potassium hydroxide in 100 ml of 95% ethanol (1% w/v).

Derivatizing reagent: Diluted 0.1 ml of α-bromo-2,3,4,5,6-pentafluorotoluene (Aldrich Chemicals, Milwaukee, WS) in 10 ml of 95% ethanol (CAUTION: This reagent is a strong lacrymator).

Carbamate Standards: Analytical grade pesticides (Pesticide Repository, U.S. Environmental Protection Agency, Research Triangle Park, NC) were dissolved in either benzene, n-hexane or toluene (1 mg/ml). Appropriate dilutions were prepared.

n-Hexane: pesticide quality

Benzene: pesticide quality

Toluene: pesticide quality

Ethanol: 95%

Equipment

Gas chromatograph: Model MT-220 equipped with a nickel^{63} electron capture detector (Tracor, Inc., Austin, TX). Glass columns (182 x 0.2 cm i.d.) containing either 1.50% OV-17/1.95% OV-210 or 4% SE-30/6% OV-210 on Gas Chrom Q, 80-100 mesh were used. All columns were preconditioned at 225°C for 24 hours prior to use. Operating parameters were: inlet, 220°C; column oven, 220°C; detector, 350°C; nitrogen carrier gas, 100 ml/min.

Mass spectrometers: Model HP-5930A equipped with an HP-5700A gas chromatograph and a 5933A data system was used in the electron impact mode (Hewlett Packard, Palo Alto, CA). Standard 70 eV conditions were used with a filament emission of 120 μa and an ion source temperature of 190°C. All samples were scanned from m/z 50 to 550 at m/z 160 per sec. The gas chromatograph was equipped with a 182 x 0.2 cm i.d. glass column packed with 1.50% OV-17/1.95% OV-210 on Gas Chrom Q, 80-100 mesh. The operating parameters were: helium flow, 40 ml/min; inlet temperature, 200°C; transfer line temperature, 210°C; and the oven and membrane separator were temperature programmed from 80°C (2 min) to 230°C at 8°C/min. Model 3200 quadrupole mass spectrometer equipped with a CI source, Model 9500 gas chromatograph and Model 6100 data system (Finnigan Corp., Sunnyvale, CA). The experimental conditions were: ionization source temperature 120°C; source pressure 130 Pa; reagent and carrier gas, (ultra pure) methane, 20 ml/min; separator oven 220°C and transfer lines 200°C; injection port temperature 225°C. The 182 x 0.2 cm i.d. glass GC column contained 1.50% OV-17/1.95% OV-210 on Gas Chrom Q, 80-100 mesh and was operated at 210°C.

Tube block heater: CRC Rubber Co., Cleveland, OH

Tube rotator: Kraft Apparatus, Inc., Mineola, NY

Culture tube: 15 ml, screw capped, teflon lined caps

Centrifuge tube, 15 ml graduated, glass stoppered

Teflon tape, 1 cm wide

Procedure

Pipet 1 ml of alcoholic potassium hydroxide, 0.1 ml of derivatizing reagent and 1 ml of carbamate standard into a 15 ml culture tube with a teflon lined screw cap. Place the culture tube in a pre-heated (95 ± 1°C) tube block heater for two hours. The length of time and temperature are critical, for overheating can cause an increase in the formation of extraneous gas chromatographic peaks.[38] Remove, allow to cool at room temperature, and add 5 ml of distilled water and 4 ml of n-hexane to the culture tube. Place the culture tube on the tube rotator (60 rpm) for two minutes and at the end of this time transfer the n-hexane layer to a 15 ml centrifuge tube. Add an additional 4 ml of n-hexane to the culture tube, and place in the tube rotator for an additional two minutes. Combine the n-hexane layer with the previous n-hexane extract. Bring the final volume of the centrifuge tube to 10 ml with n-hexane. The sample is now ready for further cleanup or gas chromatographic analysis.

Characterization

The PFB derivative was characterized by electron capture gas chromatography and the derivatization procedure evaluated utilizing the following criteria:

1. G.C. Retention Time Relative to Aldrin
2. Derivatization Linearity. Linearity was checked over a concentration range from 0.1 ng/µl to 1,000 ng/µl, if possible, or to the limits of detection. Allowances of ± 15% were tolerated in determining the range of derivatization linearity.

3. Linearity of Electron Capture Detector Response. The response linearity of the derivatives were determined on two gas chromatographic columns. A concentration of the derivative was selected so that a 5 µl injection would produce a peak height of approximately 40-45% full scale deflection (FSD). Injections of 2 to 8 µl, at 1 µl increments, were made, with an allowance of ± 10% tolerated in determining linearity.

4. Minimum Detectable Level. Minimum detectable level was defined to be 10% full scale deflection, provided that this was at least twice the background noise. (This might be a combination of gas chromatographic baseline and background from the derivatization procedure.) The theoretical concentration for this response was calculated and the proper concentration prepared.

5. Quantity of Derivative Required to Give 50% Full Scale Deflection. This quantity is not necessarily five times the minimum detectable level, since this level was determined using a "clean" baseline. A clean baseline was achieved by preparing a derivative at a sufficient concentration such that dilution by a factor of 100 was necessary to bring the derivative peak(s) on scale. In this way, blank interference peaks were negated.

6. Storage of Derivatized Samples. One sample was stored at 4°C (refrigeration) and a second sample was stored in the dark at ambient conditions. These samples were chromatographed at 0, 1, 2, 4, and 8 days to determine their stability under storage conditions.

SECTION IV

RESULTS AND DISCUSSION

Derivatization

The derivatization procedure used is similar to that of Coburn and Chau.[40] The hydrolysis and the derivatization steps have been combined into one step, to save time and minimize chances for error.

All of the pesticides which were tested with this method are given in Table 1. Of the 23 carbamate pesticides tested, only five (asulam, pebulate, propham, triallate and vernolate) did not form a gas chromatographable derivative.

The characterization data on the derivatives is located in the appendix. During the course of the characterization of the carbamate derivatives, two main difficulties were encountered. These difficulties were a decrease in the extent of reaction at low concentrations (i.e., $\geq$ 10 ng/µl) and large background interference caused by the derivatization reagent (this interference is discussed in the Mass Spectrometric Identification section). It is not clear why the extent of the reaction decreases at low concentrations, but it could be caused by competing reactions of the PFBB with ethoxide ions, or a small loss of derivative in the extraction procedure, which becomes a large percentage of the derivative at low concentrations. With some of the carbamate derivatives, the background interference was so great that dilution of the final extract by a factor of 100 to quantitate the gas chromatographic peaks was required.

Table 1. Carbamate Pesticides Evaluated

Common Name	Chemical Name
Aldicarb (Temik)	2-Methyl-2-(methylthio)propional= dehyde-O-(methylcarbamoyl)oxime
Aminocarb (Matacil)	4-Dimethylamino-m-tolyl methyl carbamate
Asulam (Asulox)	Methyl(4-amino benzenesulfonyl) carbamate
Barban (Carbyne)	4-Chlorobut-2-ynyl-3-chloro- phenyl carbamate
Benthiocarb (Bolero)	S-4-Chlorobenzyl diethyl- thiocarbamate
Carbaryl (Sevin)	1-Naphthyl N-methylcarbamate
Carbofuran (Furadan)	2,3,-Dihydro-2,2-dimethylbenzo= furan-7-yl methylcarbamate
CDEC (Sulfallate)	2-Chlorallyl diethyldithio- carbamate
Chlorpropham (CIPC)	Isopropyl N-(3-chlorophenyl) carbamate
Desmedipham (Betanex)	3-Ethoxy carbonyl amino-phenyl phenylcarbamate
Formetanate Hydrochloride (Carzol SP)	m-((Dimethylamino)methylene) amino)phenyl methylcarbamate hydrochloride
Kabutilate (Tardex)	m-(3,3-Dimethylureido)phenyl tert-butylcarbamate
Meobal	3,4-Dimethylphenyl N-methylcarbamate
Methiocarb (Mesurol)	4-(Methylthio)-3,5-xylyl N-methylcarbamate

Table 1. Carbamate Pesticides Evaluated
(Continued)

Common Name	Chemical Name
Methomyl (Lannate)	S-Methyl N-((methylcarbamoyl) oxy)thioacetimidate
Pebulate (Tillam)	S-Propyl butylethylthiocarbamate
Phenmedipham (Betanal)	3-Methyloxy-carbonylamino-phenyl N-(3'-methylphenyl)carbamate
Promecarb (Carbamult)	3-Isopropyl-5-methylphenyl methylcarbamate
Propham (IPC)	Isopropyl-N-phenylcarbamate
Propoxur (Baygon)	o-Isopropoxyphenyl N-methyl-carbamate
Thiophanate-Methyl	1,2-Di(3-methoxycarbonyl-2-thioureido)benzene
Triallate	S-(2,3,3-Trichloroallyl)di= isopropylthiocarbamate
Vernolate (Vernam)	S-Propyl-N,N-dipropylthiocarbamate

This interference was especially troublesome when retention times of the derivatives were short (less than 0.6 relative to aldrin), or when retention times were near 1.2. The level of interference can be expected to increase when samples from environmental media are used instead of analytical standards. Hence, the value of this method is limited unless a suitable cleanup procedure can be found. Another limiting factor was that unless the carbamate can form a substituted phenoxide ion in the alkaline reaction mixture, the structure of the derivative may be difficult to determine. However, this appears to be a fairly sensitive method for the determination of carbamates which can form a substituted phenoxide ion in the reaction mixture.

During the course of this project, it was found that the sensitivity of the carbamate derivatives fell into two categories. One group had minimum detectable levels of approximately 200 pg, while the other group generally had minimum dectable levels of greater than 5 ng. This suggested that there were multiple routes of derivatization.

Mass Spectrometric Identification

Carbaryl, meobal, promecarb, thiophanate-methyl, CDEC, aminocarb, and barban derivatives were analyzed by gas chromatography-mass spectrometry. The mass spectra of these derivatives along with the spectra of the reagent blank products are located in the appendix.

In many of the recorded mass spectra (exceptions--CDEC, aldicarb and two minor peaks which appear in the spectra of carbaryl and aminocarb), two ions were found; m/z 207 and m/z 179. The pentafluorobenzyl (PFB) ion at m/z 181, found by Coburn et al.[30] to be the significant fragment in the mass spectrum of the normal unsubstituted PFB derivative of mobam

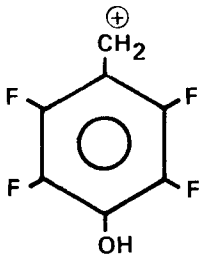
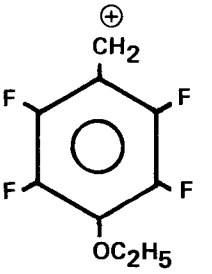
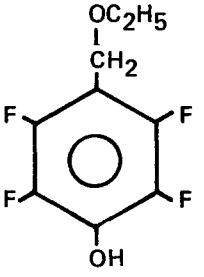
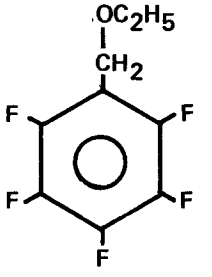
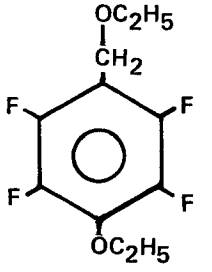
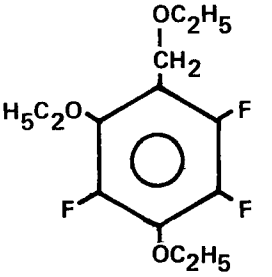
(4-Benzothienyl-N-methylcarbamate) and which would be expected in all unsubstituted derivatives, was not generally found. The exceptions were the presence of this ion in the mass spectra of the minor (ca 10% based on peak heights) gas chromatographic peaks in the chromatograms of carbaryl and aminocarb and the main peak of the aldicarb derivative.

The m/z 207 fragment, assigned as an ethoxytetrafluorobenzyl ion, was designated as originating in the mass spectral fragmentation reactions of an ethoxide displacement product of PFB, with one of the fluorines being displaced. A logical ethylene loss of 28 mass units from the m/z 207 fragment yielded the intense m/z 179 fragment, and in certain cases, a further loss of CHO yielded a m/z 150 fragment, and a further fluorine loss yielded a m/z 131 fragment. These fragments were initially recognized in the gas chromatographic-mass spectrometric analysis of a reagent blank. See Table 2 for the structures of the compounds formed in the reagent blank mixture.

Considering the alkalinity of the reaction mixture and the electronegativity of the fluorines, the likely mechanism for the ethoxide displacement of the fluorine is aromatic nucleophillic substitution. This mechanism involves attack by the nucleophile $C_2H_5O^-$, upon the PFB ring to form a carbanionic intermediate, and subsequent expulsion of the corresponding fluoride ion from the carbanion to yield the final product. The outline for this mechanism is found in Figure 1.

Of the carbamates analyzed, four (carbaryl, promecarb, aminocarb, and meobal) are capable of forming the substituted phenoxide ions in the alkaline reaction mixture. The mass spectra of the resulting products are consistent with the expected ether derivative.

Table 2. PFBB Reaction Products and Major MS Fragments

Mass	Structure	Mass	Structure
179		207	
224	 Product I	226	 Product III
252	 Product II	278	 Product IV

(The exact position of the OC_2H_5 group on the ring is not known. The ethoxy groups are placed arbitrarily.)

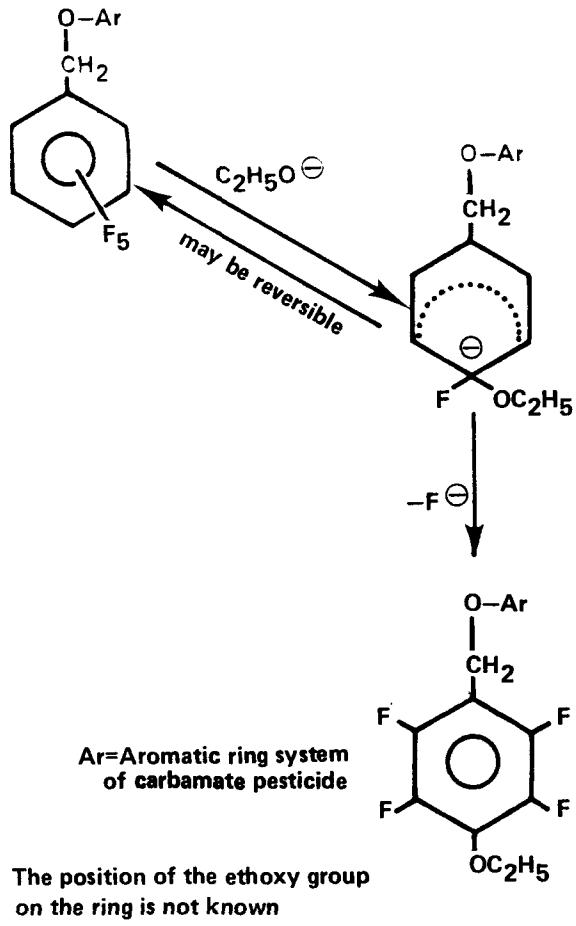


Figure 1. General mechanism of fluorine displacement by ethoxide ion.

The derivative resulting from the reaction of thiophanate-methyl, although the most sensitive of the carbamate derivatives analyzed, did not follow this route of derivatization. The derivative, of mass 414, was determined to be a di-ethoxytetrafluorobenzyl sulfide (see Figure 2). It should be noted that thiophanate-methyl cannot form a phenoxide ion, and hence does not form a derivative consistent with Figure 3. The structure of what we call the thiophanate-methyl derivative was confirmed by independent synthesis through reaction of sodium sulfide and PFBB in alcoholic KOH. The gas chromatographic retention times, and mass spectrum of the synthesized compound were identical to that of the thiophanate-methyl derivative. Thiophanate-methyl may be degraded to yield the sulfide ions for the reaction mixture, or the sulfide may have come from an impurity in our thiophanate-methyl standard..

The spectra of aminocarb and carbaryl proved to be particularly interesting. Two derivatives were found; the minor (approximately 10% by relative peak height) derivative formed contained the m/z 181 pentafluorobenzyl fragment, while the major (90%) derivative formed contained the m/z 207 fragment from the ethoxy substituted PFBB. This could mean that the replacement of a fluorine by the ethoxy group takes place after formation of the ether linkage between the substituted phenoxide ion and pentafluorobenzyl group. The general scheme of the derivatization route of substituted phenoxide ion forming carbamates is located in Figure 3.

The derivatization of aldicarb proved to be another exception of the scheme outlined in Figure 3. Although it is impossible for aldicarb

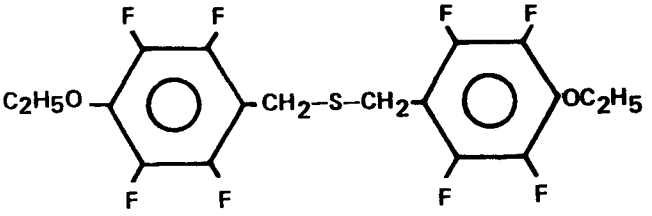


Figure 2. Thiophanate-Methyl Derivative.
Di-ethoxytetrafluorobenzyl sulfide

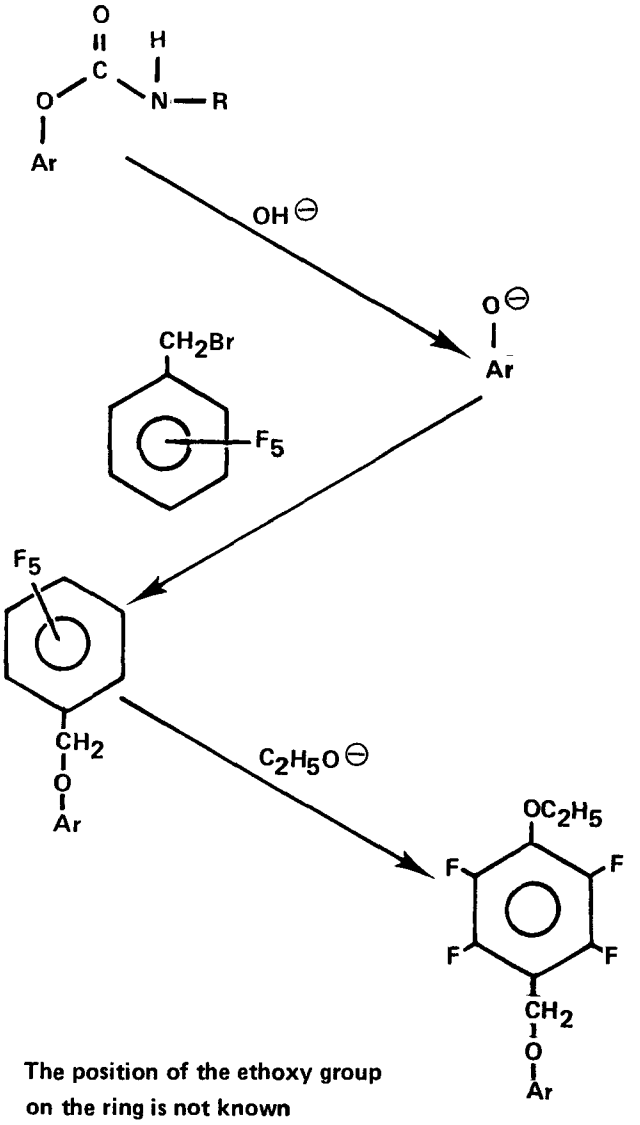


Figure 3. General derivatization route of substituted phenoxide forming carbamates.

to form a substituted phenoxide ion, aldicarb cleaved at the C-O ester linkage and formed the normal PFB type derivative (unsubstituted by an ethoxide ion). The structure of the aldicarb PFB derivative is given in Figure 4.

Certain carbamates which had the ability to form substituted phenoxide ions did not form derivatives which were very sensitive to gas chromatography (i.e. karbutilate, desmedipham). Possible reasons for this were a very slow rate of formation or rapid destruction of substituted phenoxide ions, attack of substituent groups on the phenolic ring by PFBB, resulting in derivatives with prohibitively long retention times, or competing reactions of the carbamate with ethoxide ions.

The mass spectra of barban derivative seems to support some of these hypotheses. Several compounds were created in the derivatization reaction. Of these, two were found to be ethoxy replacement products of barban and one was found to be the m/z 207 ethoxy PFB addition derivative of 3-chloroaniline (which was formed during hydrolysis).

The structure of the CDEC derivatives proved to be the most difficult to determine. Three peaks were found in the total ion chromatogram, the largest of which was determined to be underivatized CDEC. Structures (see Appendix) have been proposed which seem to fit the mass spectra of the remaining two peaks.

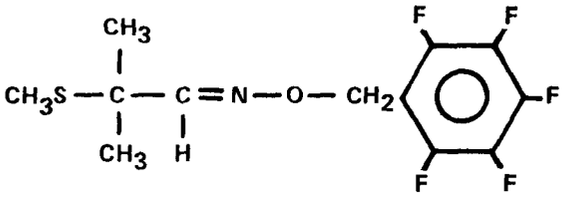


Figure 4. Aldicarb derivative.

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APPENDIX

For each carbamate pesticide, the following information is given:

1. Gas chromatographic retention time (aldrin = 1)
2. Derivatization Linearity
3. Linearity of electron capture detector response
4. Minimum Detectable Level
5. Quantity of derivative required to give 50% full scale deflection
6. Storage of derivatized samples
7. Mass spectra and comments as applicable

ALDICARB

DERIVATIZATION LINEARITY

Linear from 1 to 100 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
0.080 ng	0.040 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
0.080 ng	0.070 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

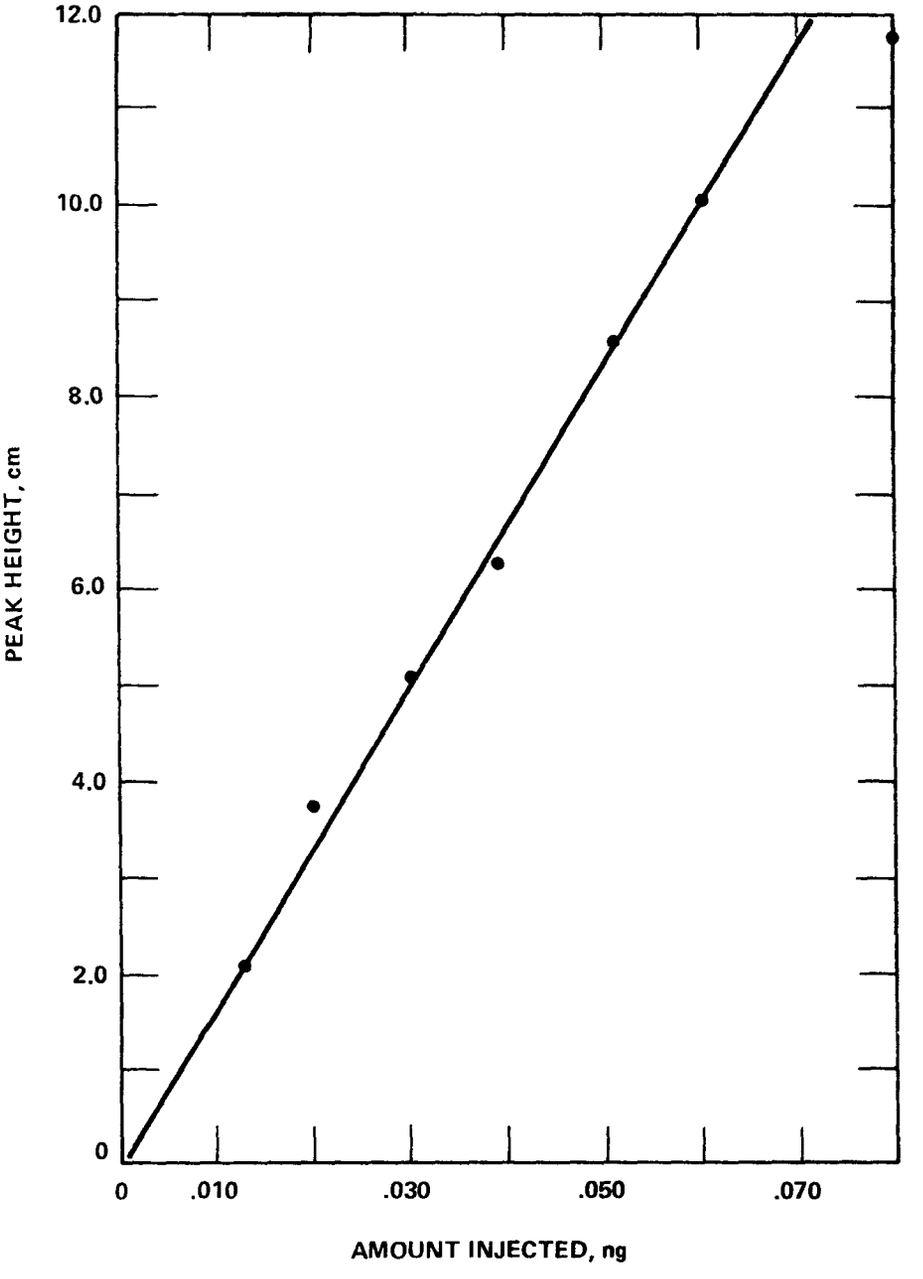
OV-17/OV-210	SE-30/OV-210
0.56	0.60

COMMENTS

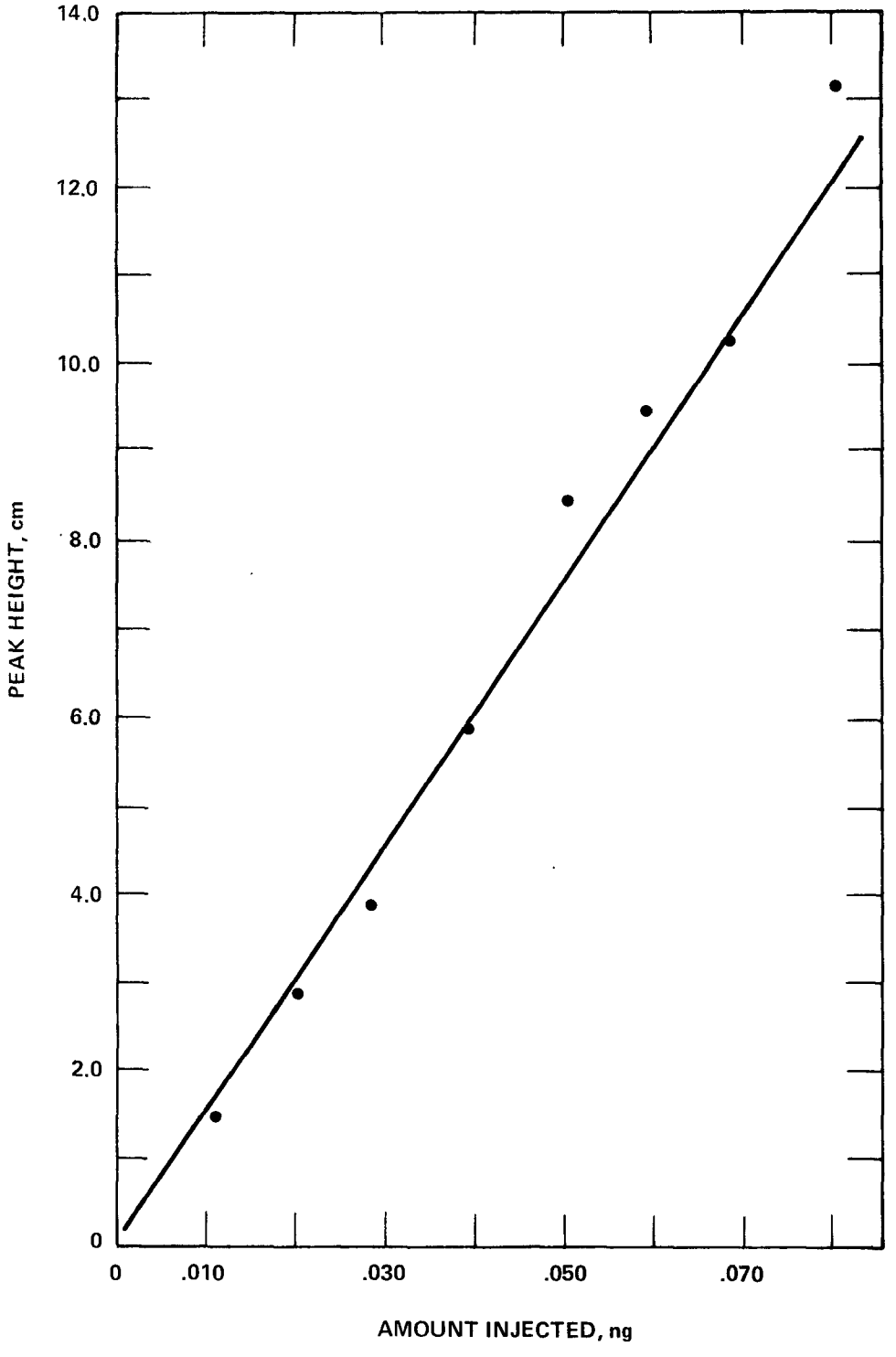
Must be diluted 100 fold due to background interference

DECAY

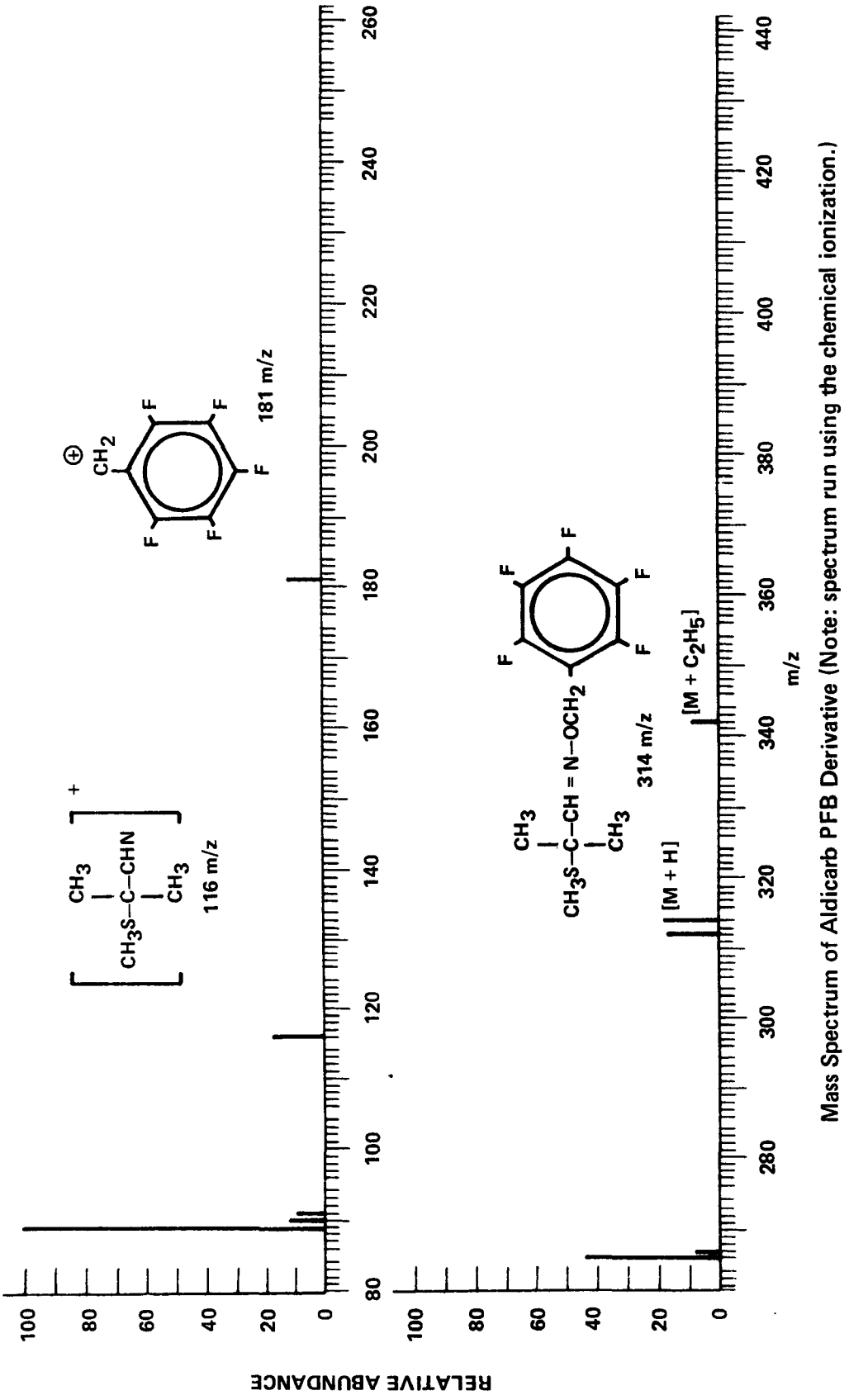
Stable under test conditions



Column Linearity Check of Aldicarb Derivative on OV–17/OV–210.



Column Linearity Check of Aldicarb Derivative on SE–30/OV–210.



Mass Spectrum of Aldicarb PFB Derivative (Note: spectrum run using the chemical ionization.)

DERIVATIZATION LINEARITY

Linear from 1 to 100 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
1.6 ng	0.49 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
2.7 ng	2.6 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

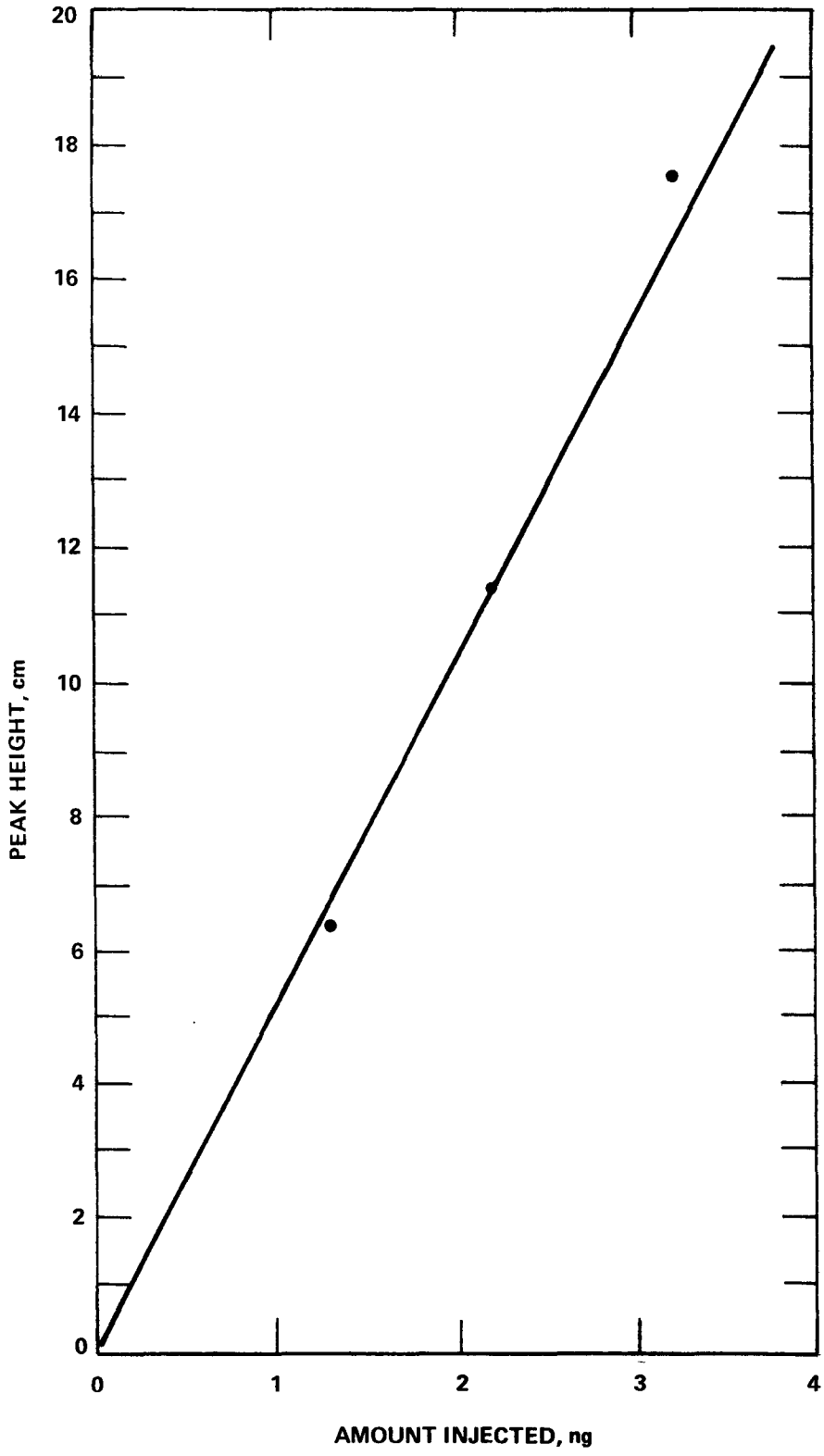
OV-17/OV-210	SE-30/OV-210
2.0	1.9

COMMENTS

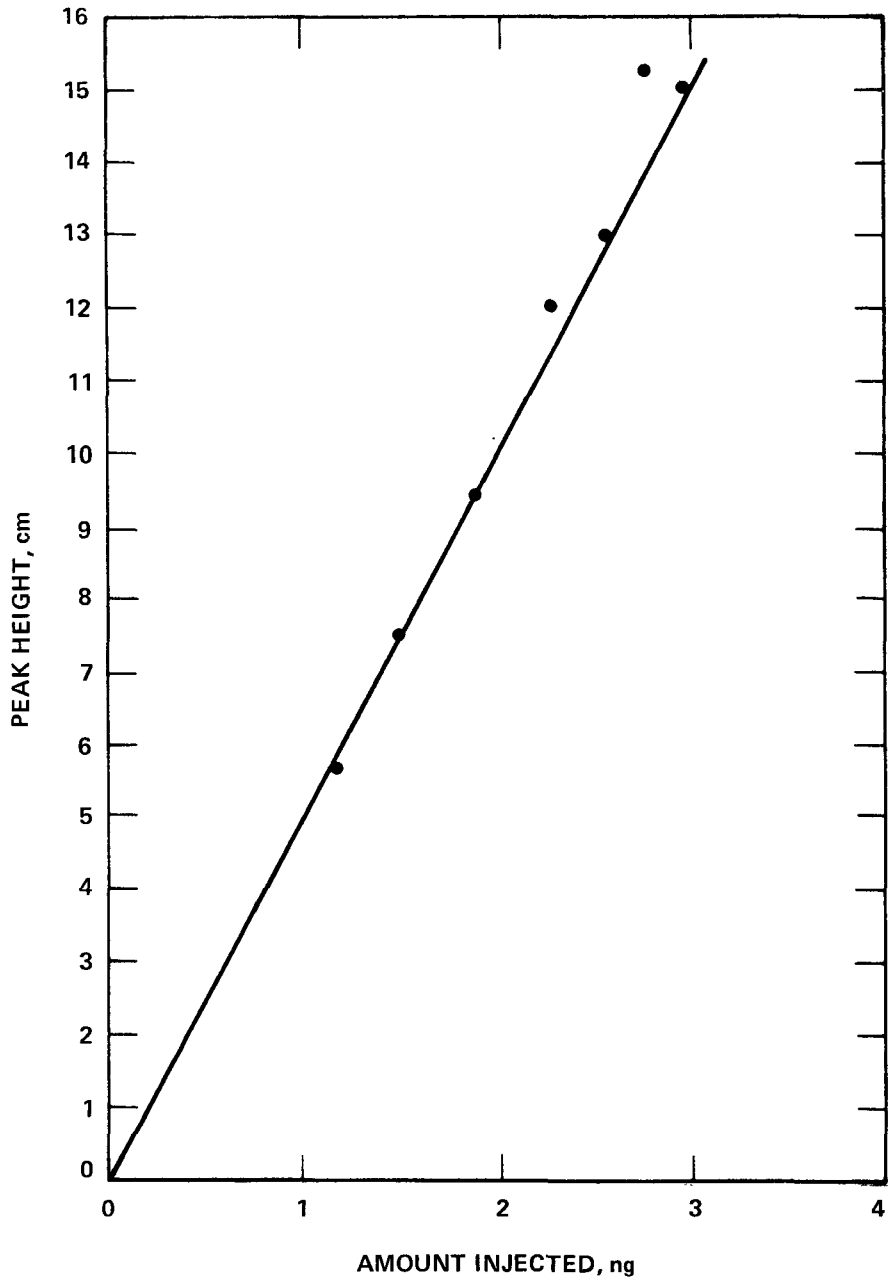
The standard is very light sensitive. Must handle with care.

DECAY

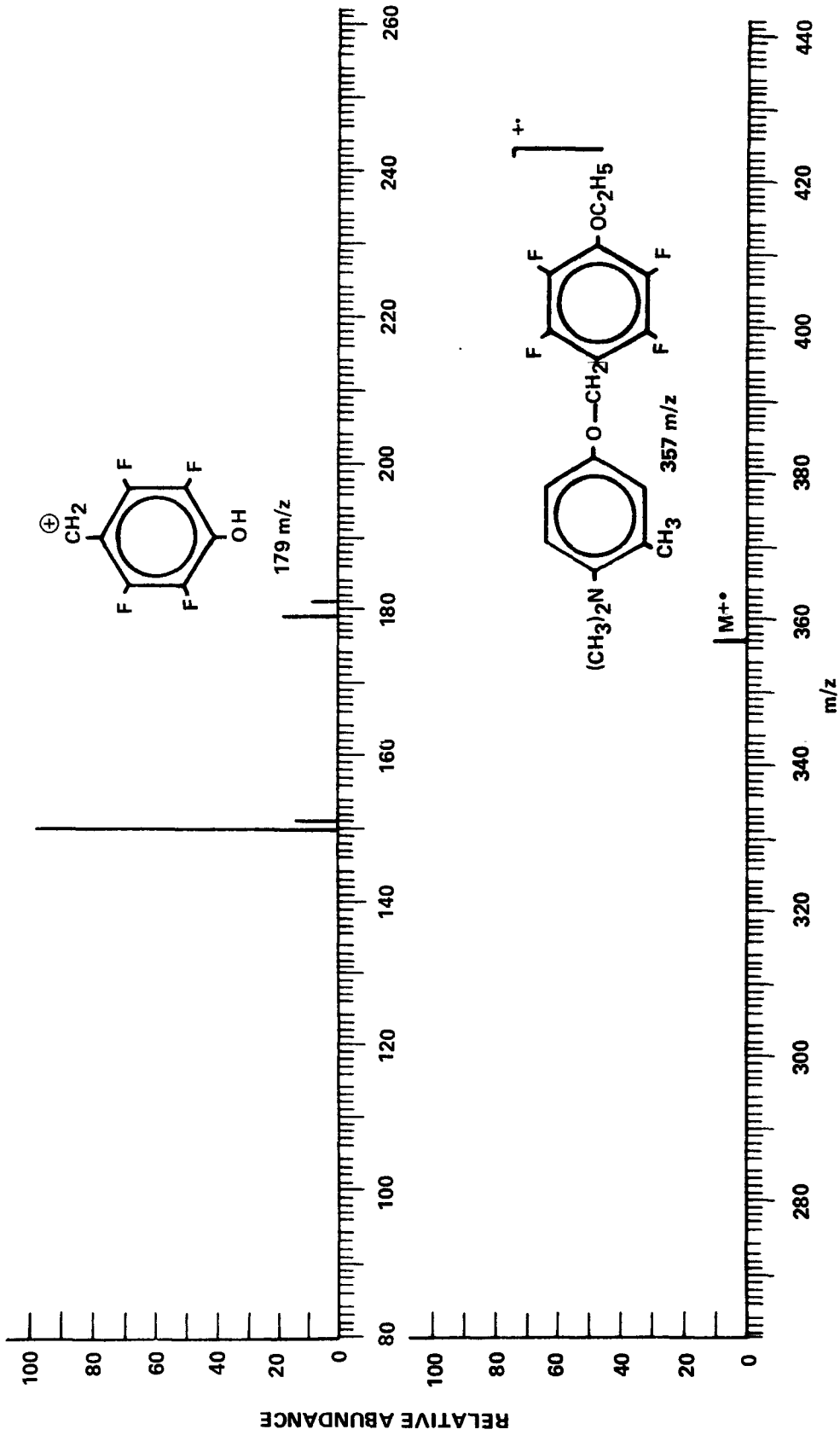
Stable under test conditions.



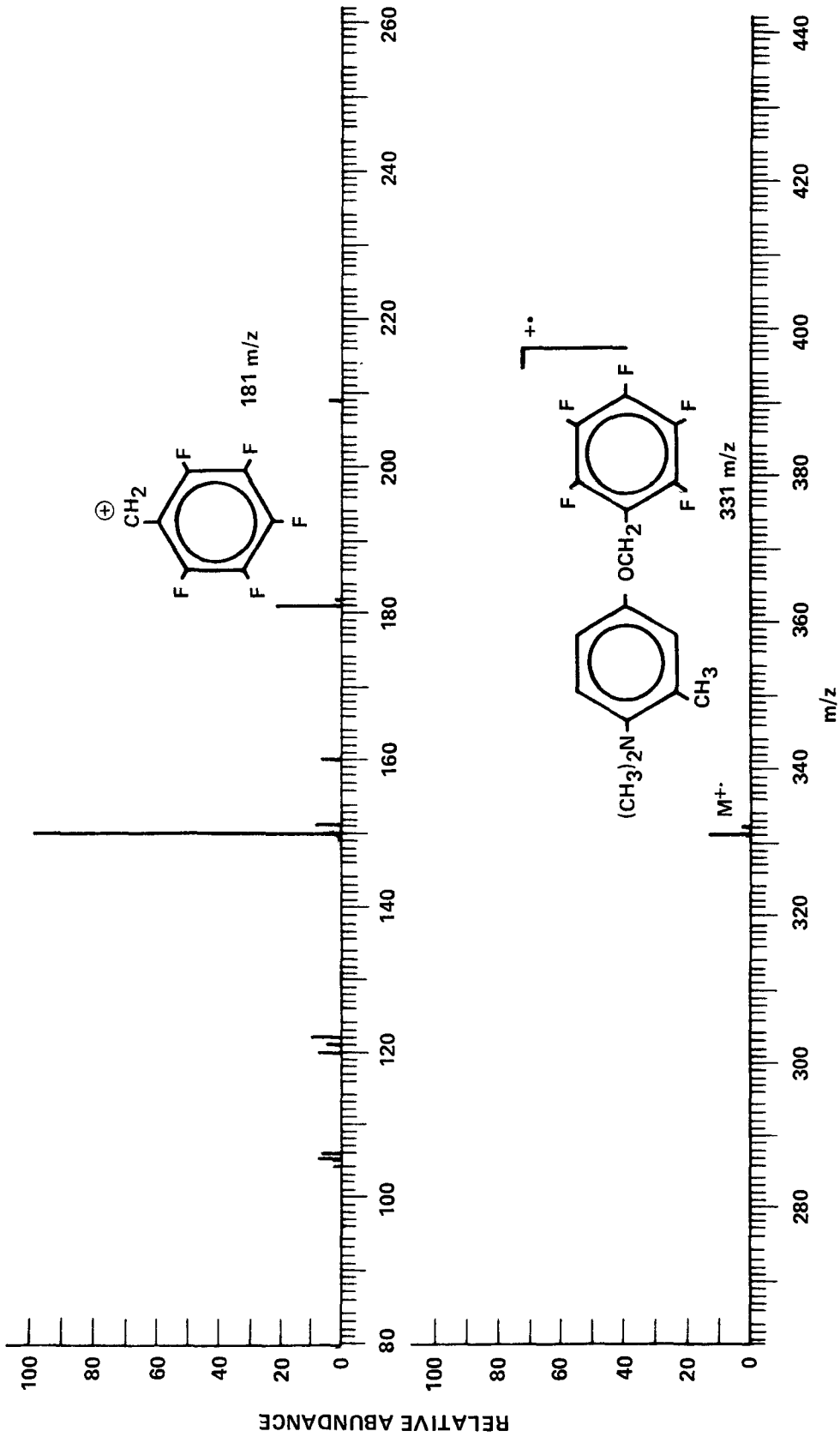
Column Linearity Check of Aminocarb Derivative on OV–17/OV–210.



Column Linearity Check of Aminocarb Derivative on SE–30/OV–210.



Mass Spectrum of Aminocarb PFB Derivative I



Mass Spectrum of Aminocarb PFB Derivative II

DERIVATIZATION LINEARITY

Linear from 100 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
20 ng	33 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
34 ng	100 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

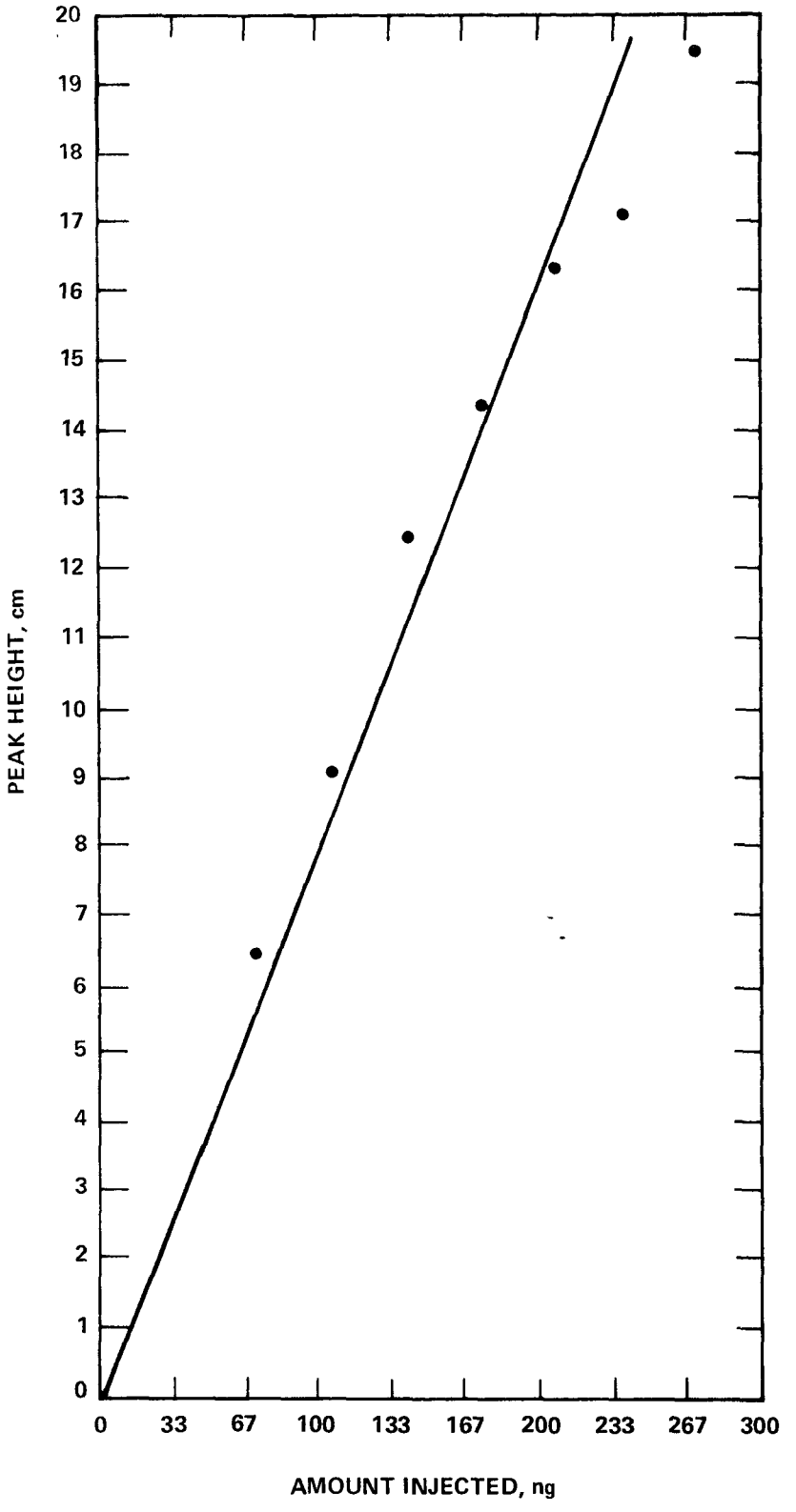
OV-17/OV-210	SE-30/OV-210
2.0	3.0

COMMENTS

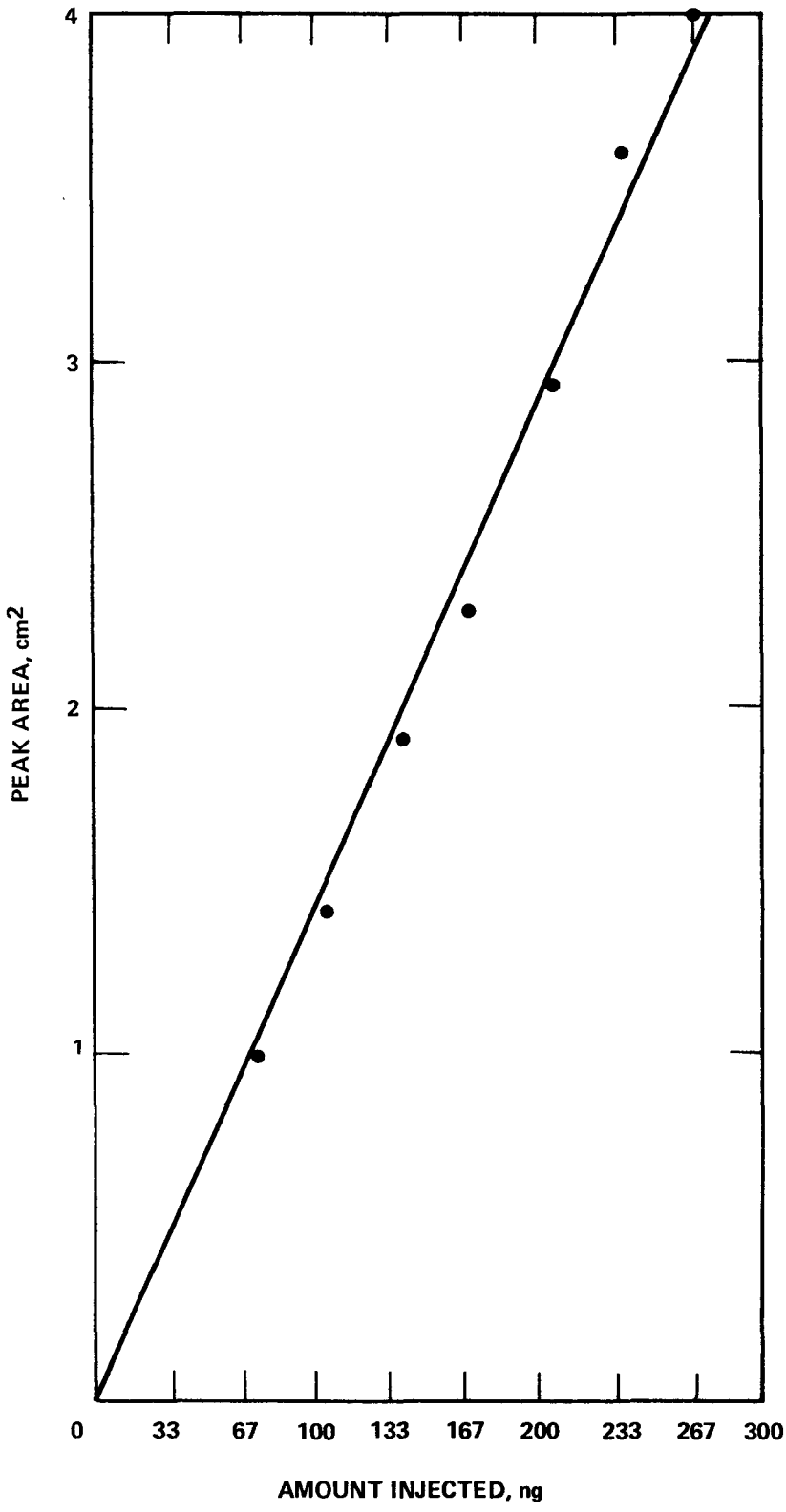
None.

DECAY

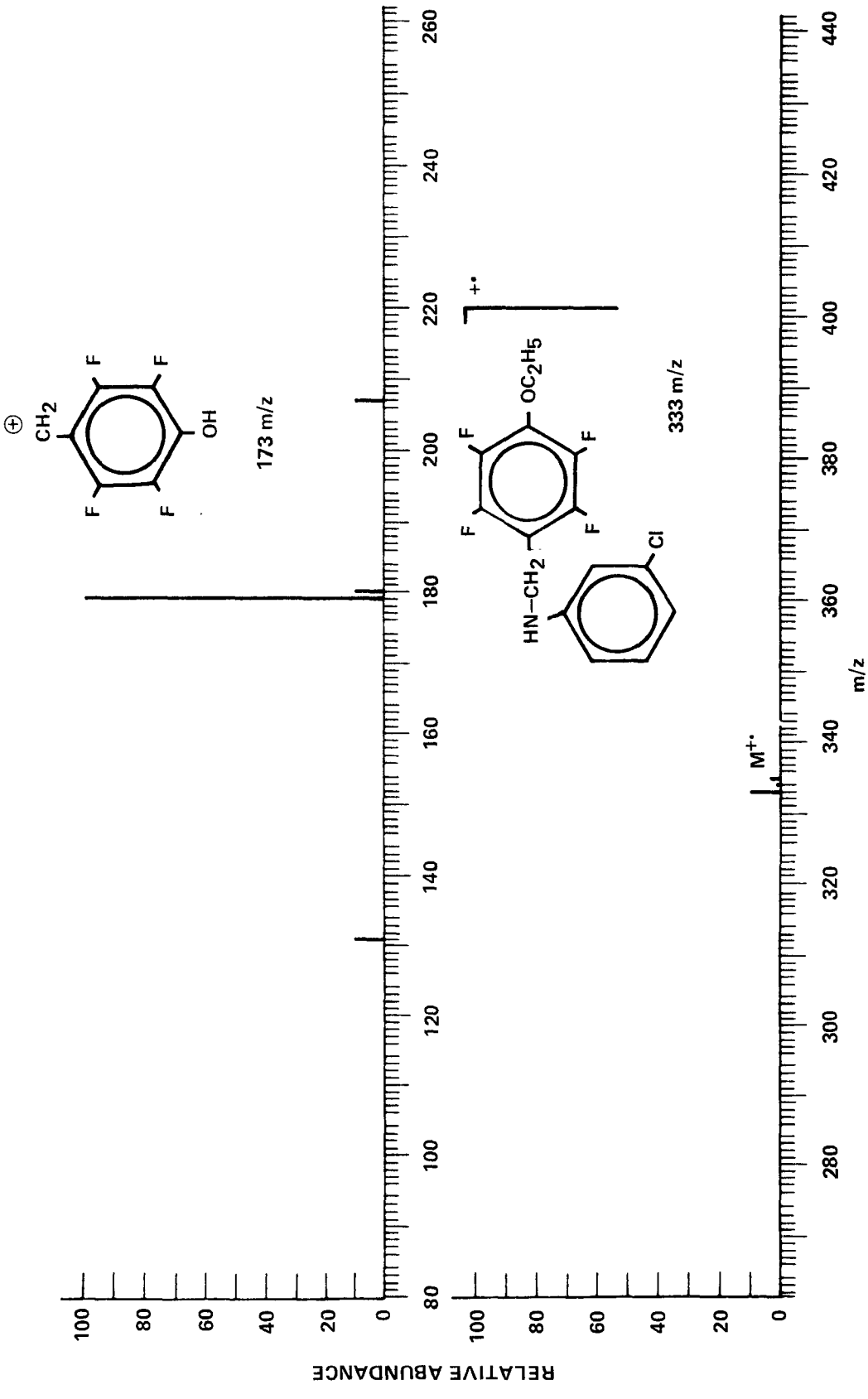
Stable under test conditions.



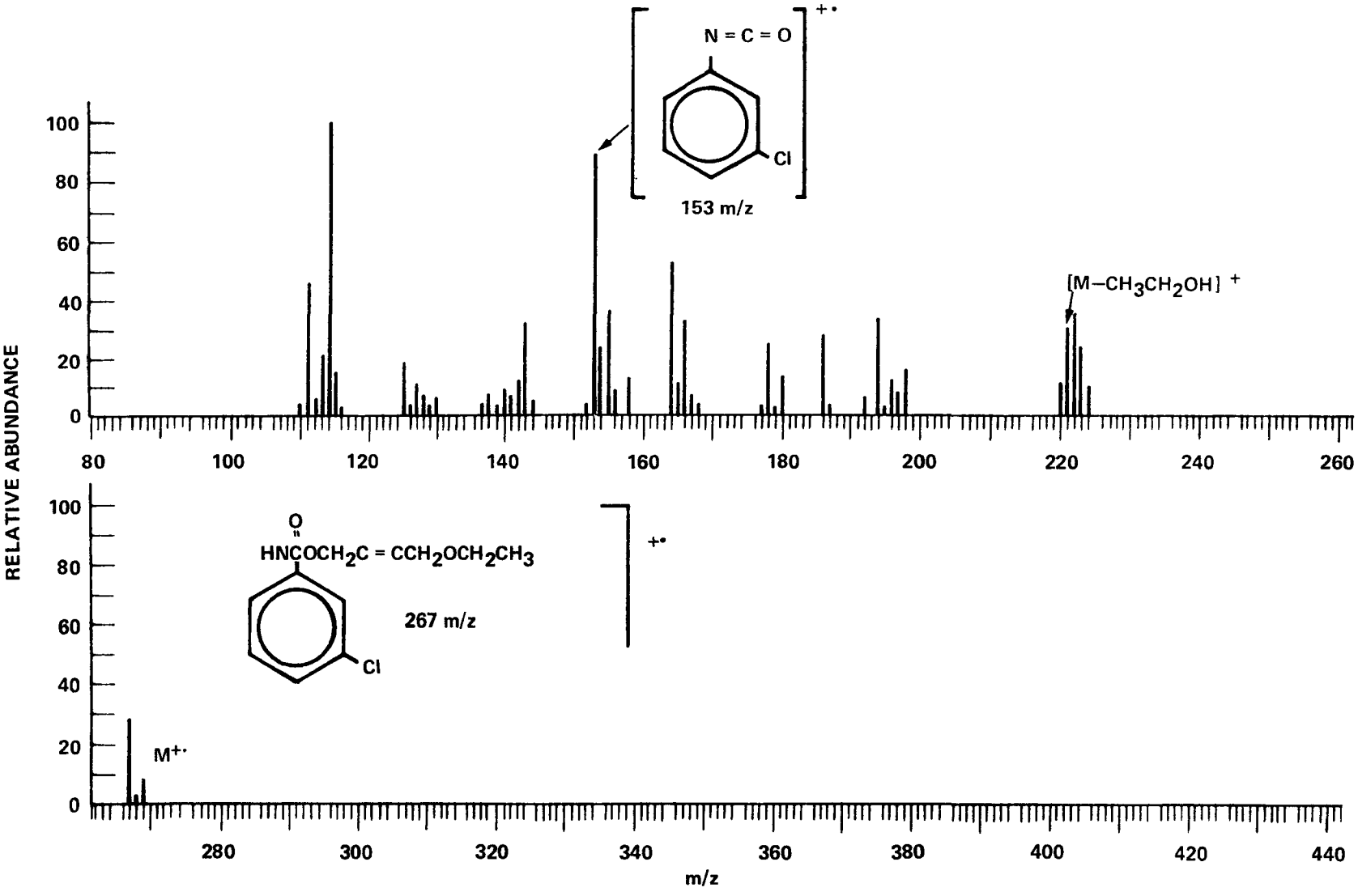
Column Linearity Check of Barban Derivative on OV–17/OV–210.



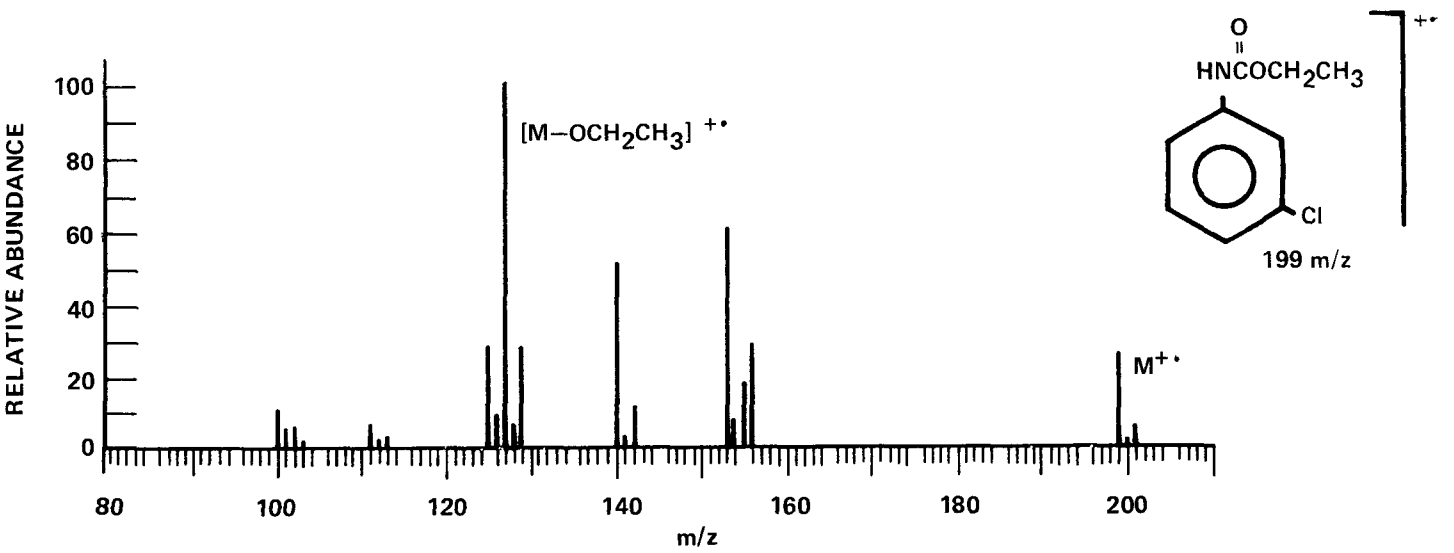
Column Linearity Check of Barban Derivative on SE–30/OV–210.



Mass Spectra of Barban PFB Derivative I



Mass Spectrum of Barban non PFB Derivative I



Mass Spectrum of Barban non PFB Derivative II

BENTHIOCARB

DERIVATIZATION LINEARITY

Linear from 10 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
0.65 ng	0.48 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
1.8 ng	2.0 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

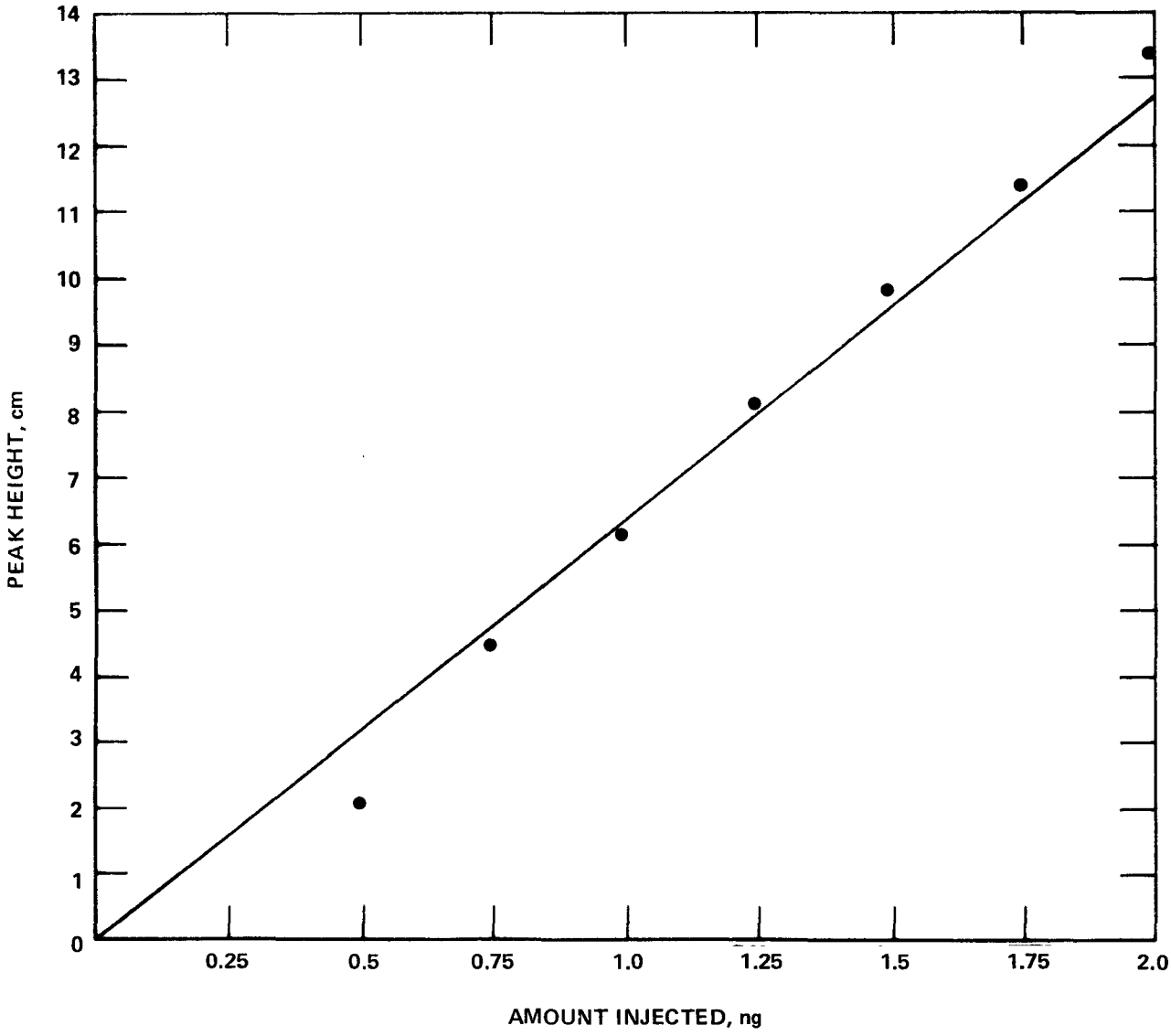
OV-17/OV-210	SE-30/OV-210
0.91	1.00

COMMENTS

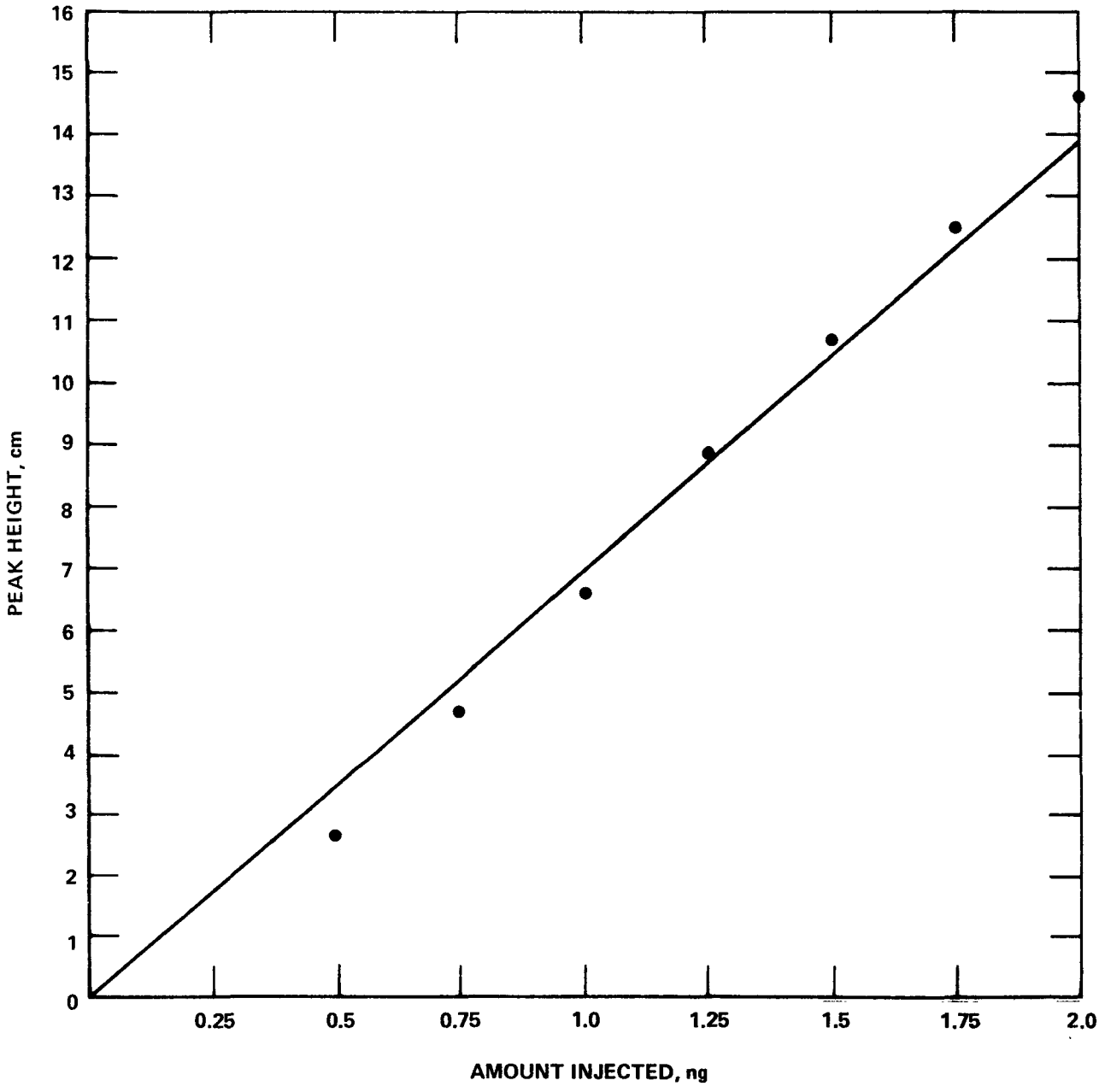
Must be diluted 100 fold due to background interference.

DECAY

Stable under test conditions.



Column Linearity Check of Benthiocarb Derivative on OV–17/OV–210.



Column Linearity Check of Benthiocarb Derivative on SE–30/OV–210.

DERIVATIZATION LINEARITY

Linear from 1 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
0.20 ng	0.18 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
1.0 ng	0.89 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

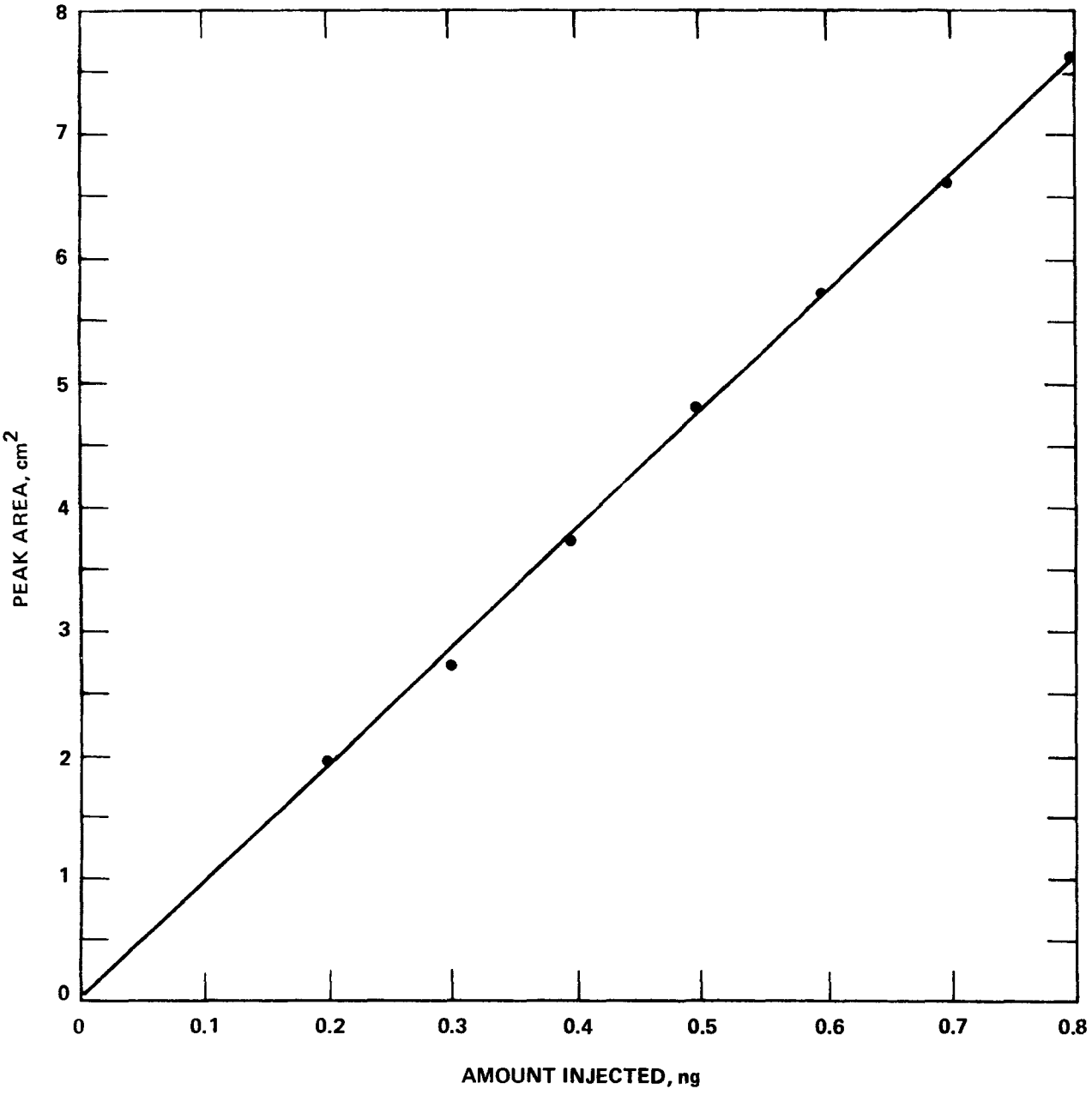
OV-17/OV-210	SE-30/OV-210
4.7	3.6

COMMENTS

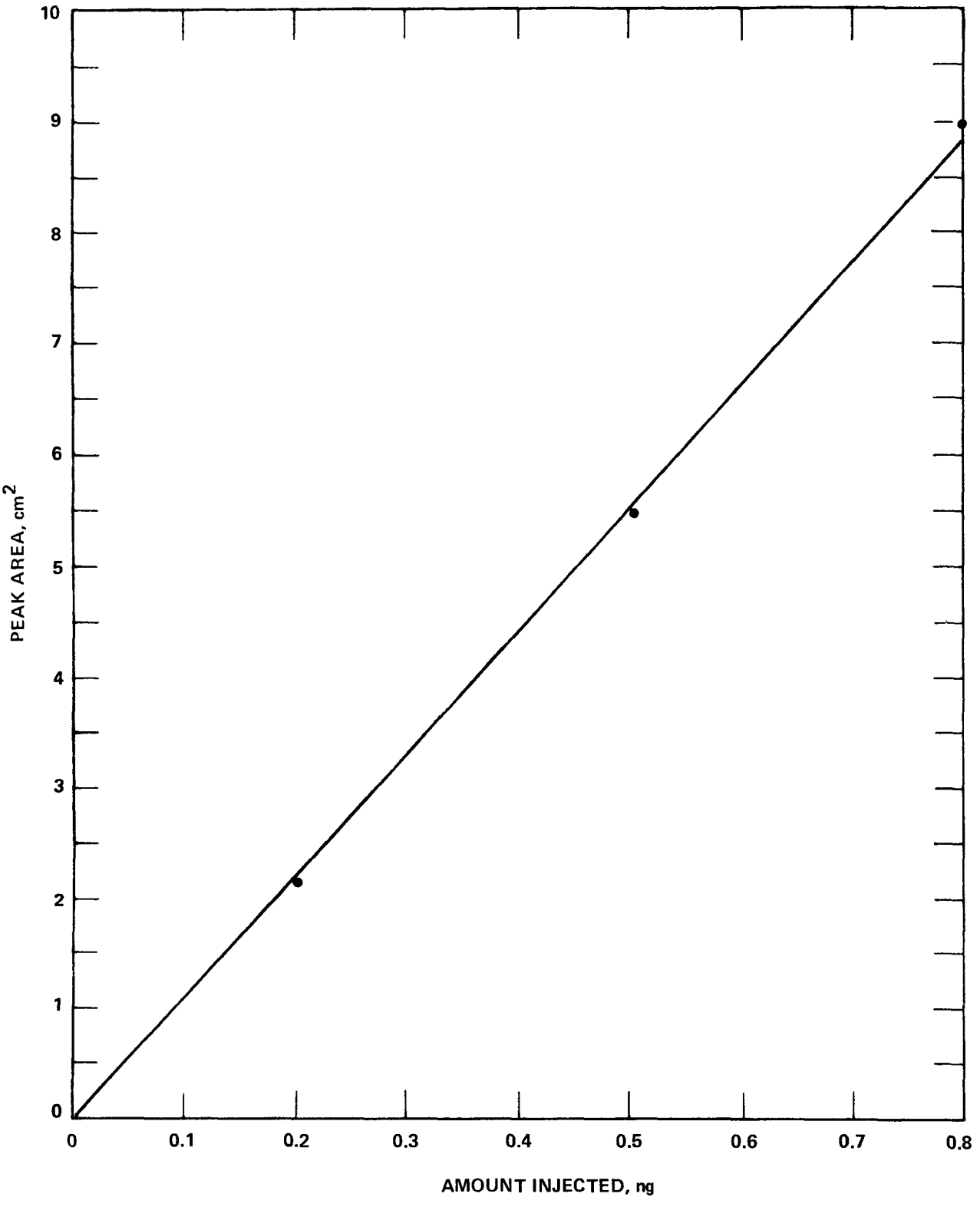
None.

DECAY

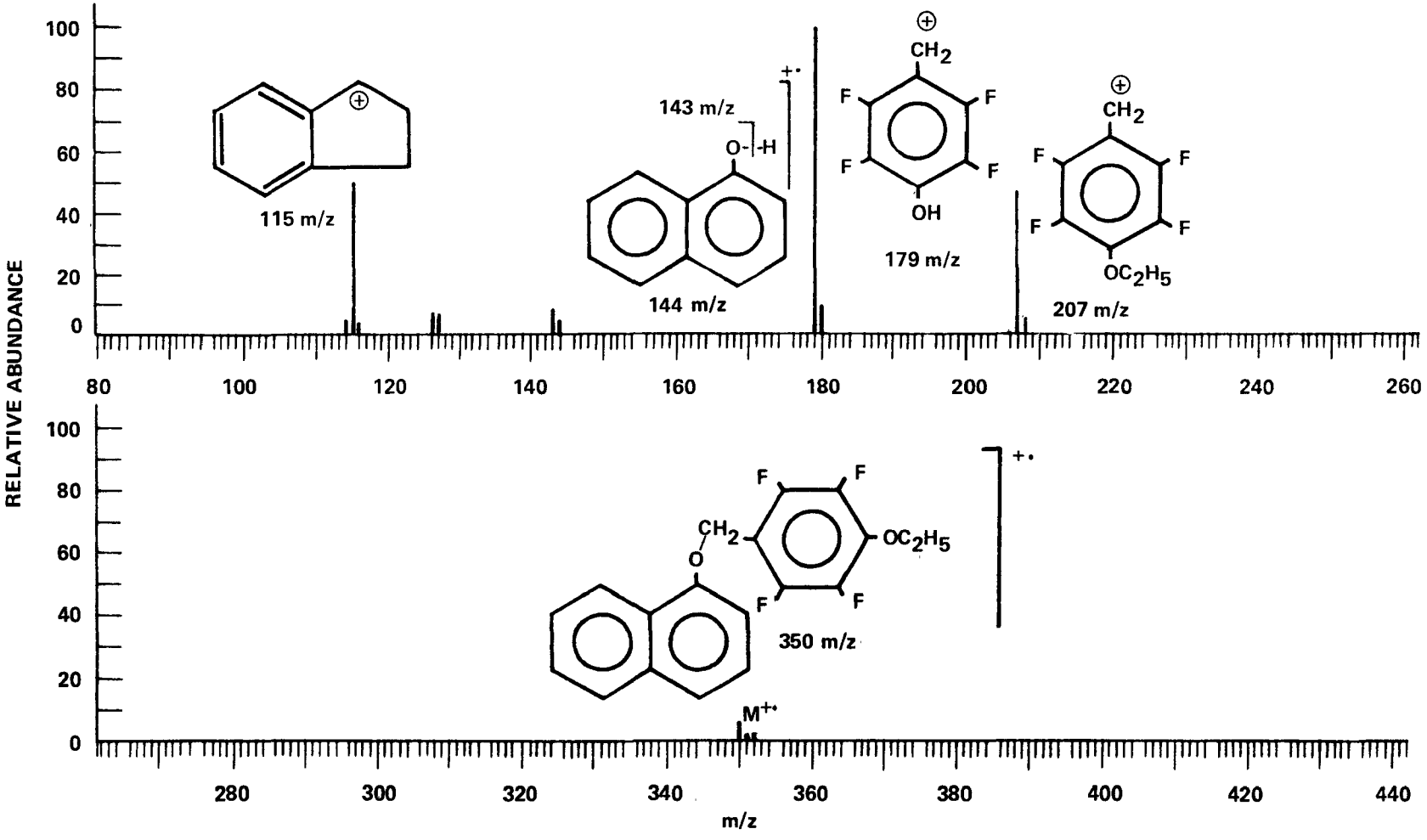
Stable under test conditions.



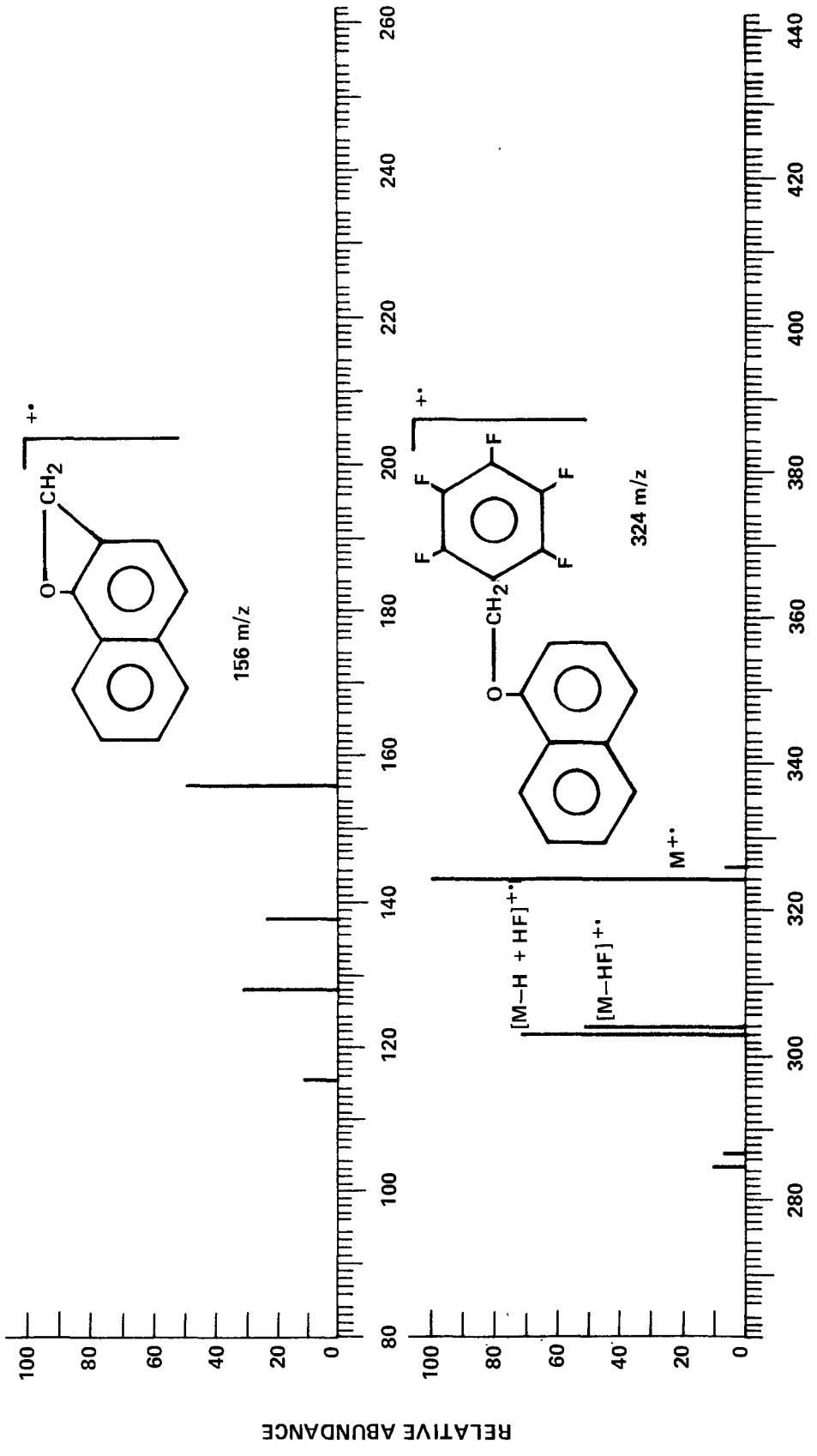
Column Linearity Check of Carbaryl Derivative on OV–17/OV–210.



Column Linearity Check of Carbaryl Derivative on SE–30/OV–210.



Mass Spectrum of Carbaryl PFB Derivative I



Mass Spectrum of Carbaryl PFB Derivative II

CARBOFURAN

DERIVATIZATION LINEARITY

Linear from 2 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
0.70 ng	See comments

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
3.1 ng	

RELATIVE RETENTION TIME (ALDRIN = 1.00)

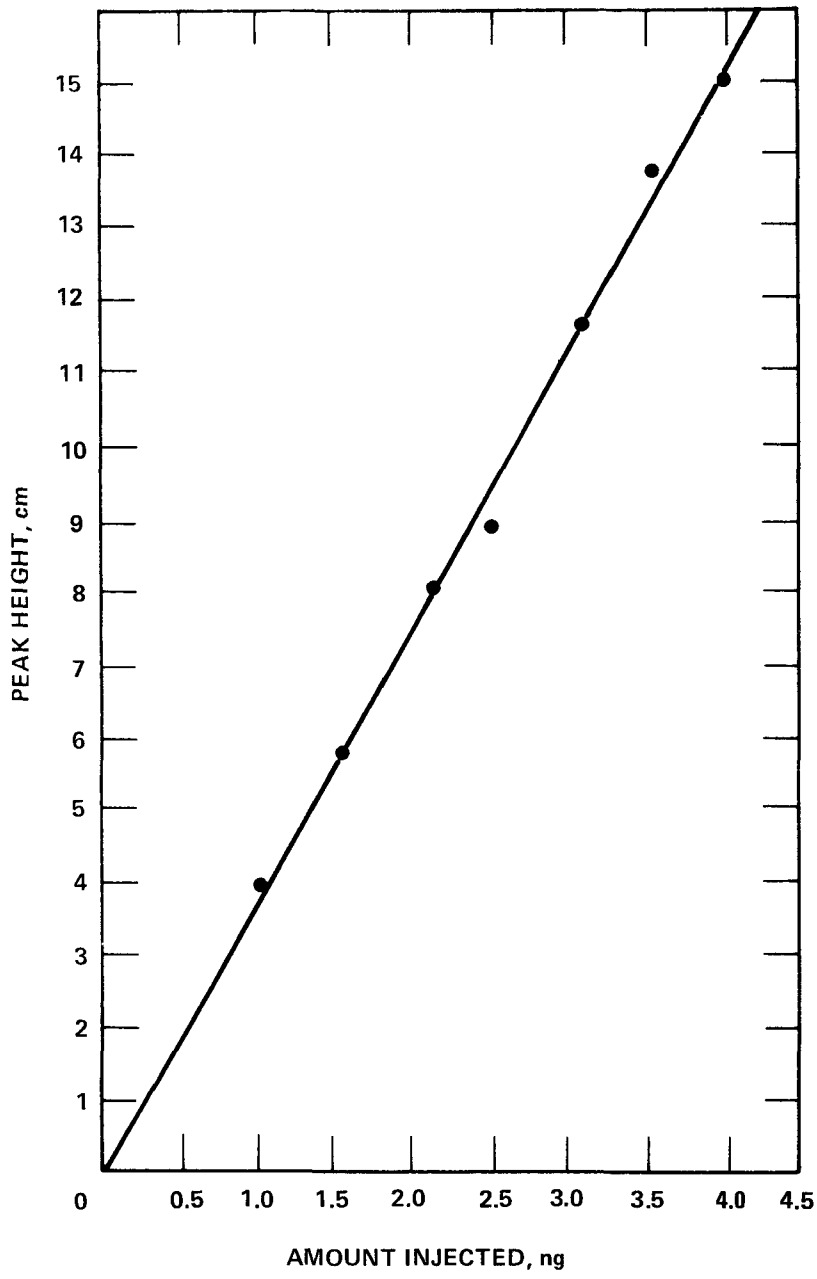
OV-17/OV-210	SE-30/OV-210
2.1	

COMMENTS

Must be diluted 100 fold due to background interference. Characterization was not attempted on the SE-30/OV-210 column due to high background interference.

DECAY

Stable under test conditions.



Column Linearity Check of Carbofuran Derivative on OV–17/OV–210.

DERIVATIZATION LINEARITY

Linear from 0.1 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
0.024 ng	0.024 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
0.15 ng	0.15 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

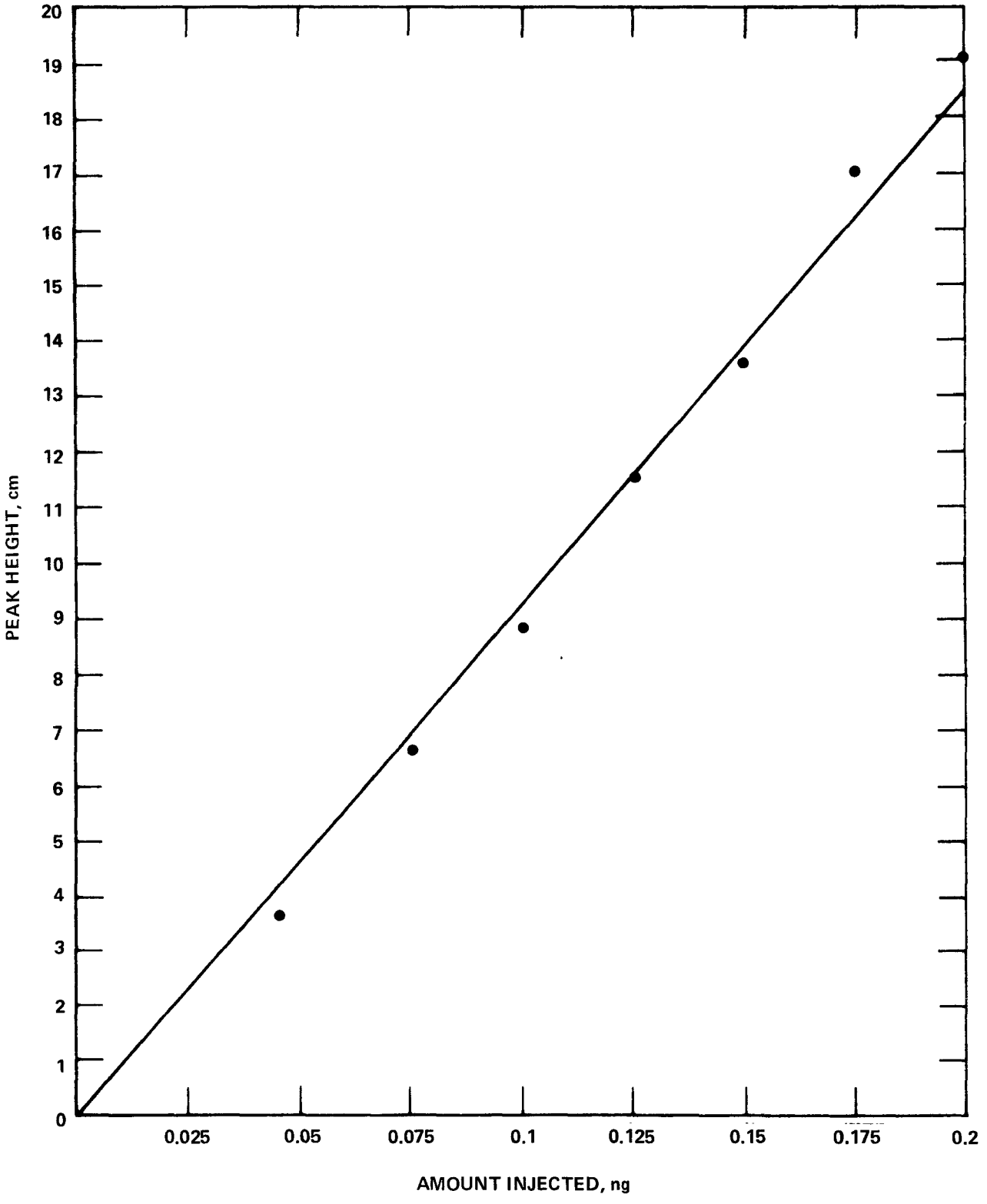
OV-17/OV-210	SE-30/OV-210
0.64	0.62

COMMENTS

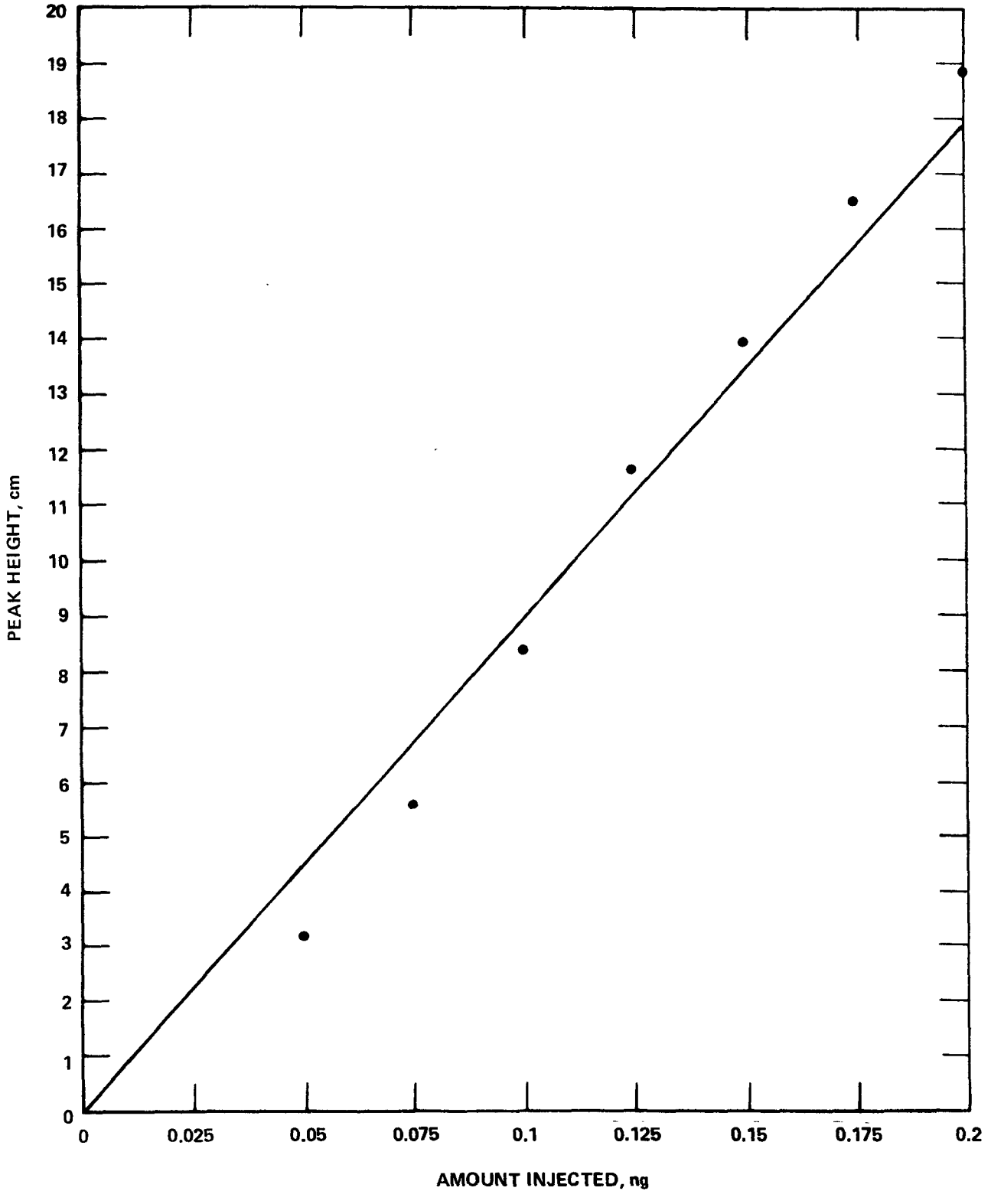
The derivative was difficult to quantitate due to the variability of length of derivatization time. This made decay studies impossible and the error was greatly increased in the other studies.

DECAY

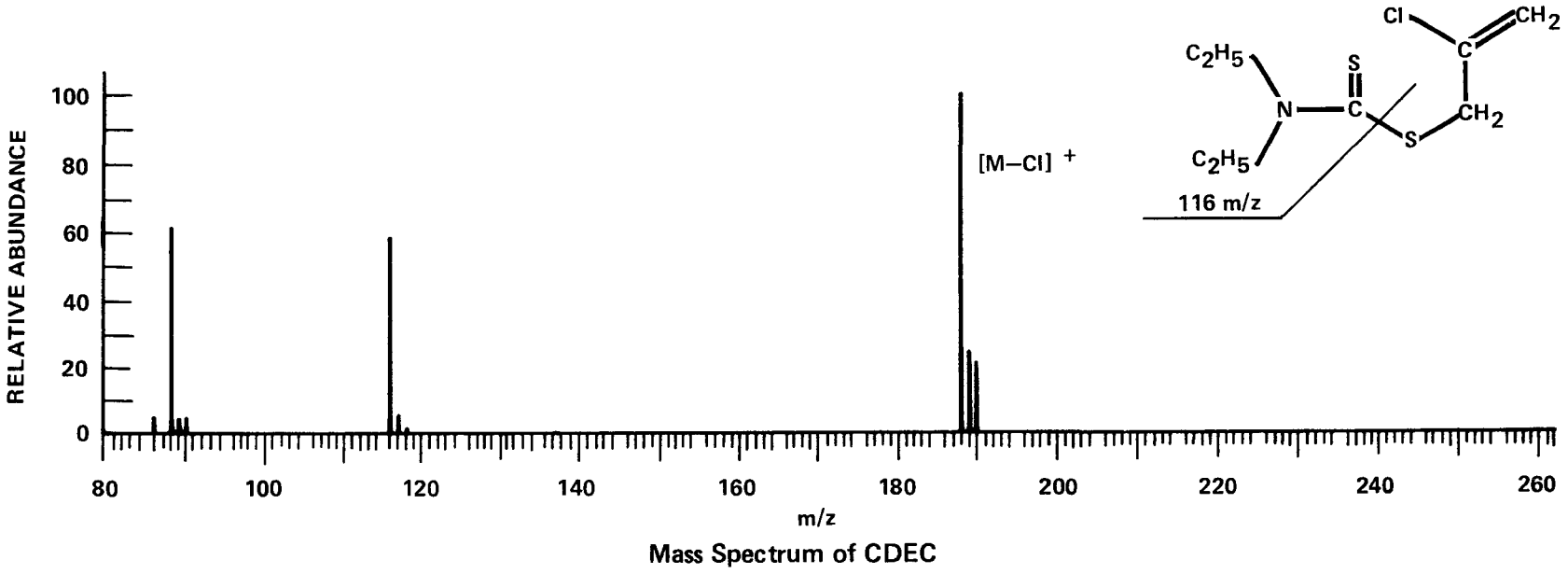
Not applicable.



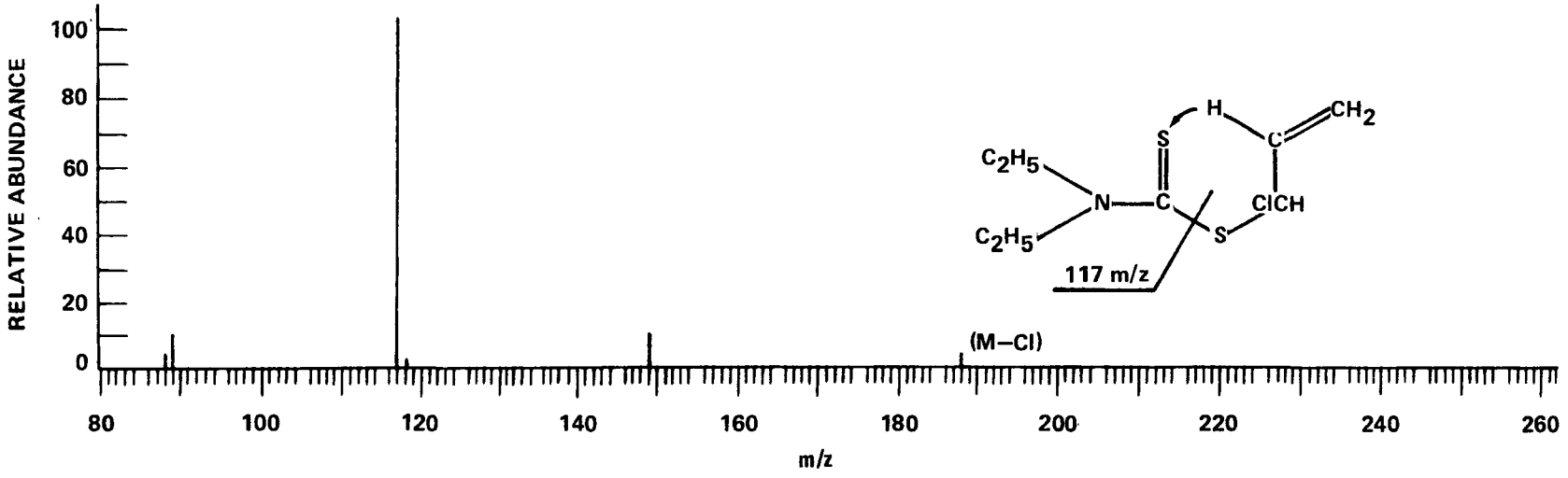
Column Linearity Check of CDEC Derivative on OV–17/OV–210.



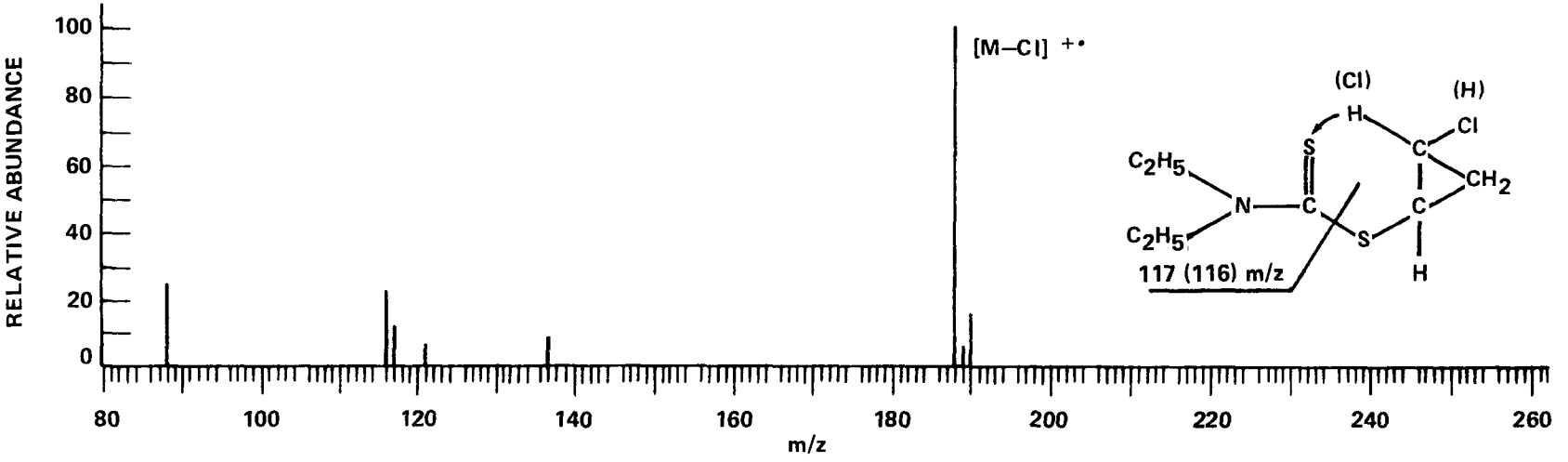
Column Linearity Check of CDEC Derivative on SE–30/OV–210.



Mass Spectrum of CDEC



Mass Spectra of CDEC Rearrangement Product I



Mass Spectrum of CDEC Rearrangement Product II

CHLOROPROPHAM

DERIVATIZATION LINEARITY

Linear from 10 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
0.72 ng	0.72 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
3.1 ng	3.0 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

OV-17/OV-210	SE-30/OV-210
0.39*, 2.9	0.40*, 3.0

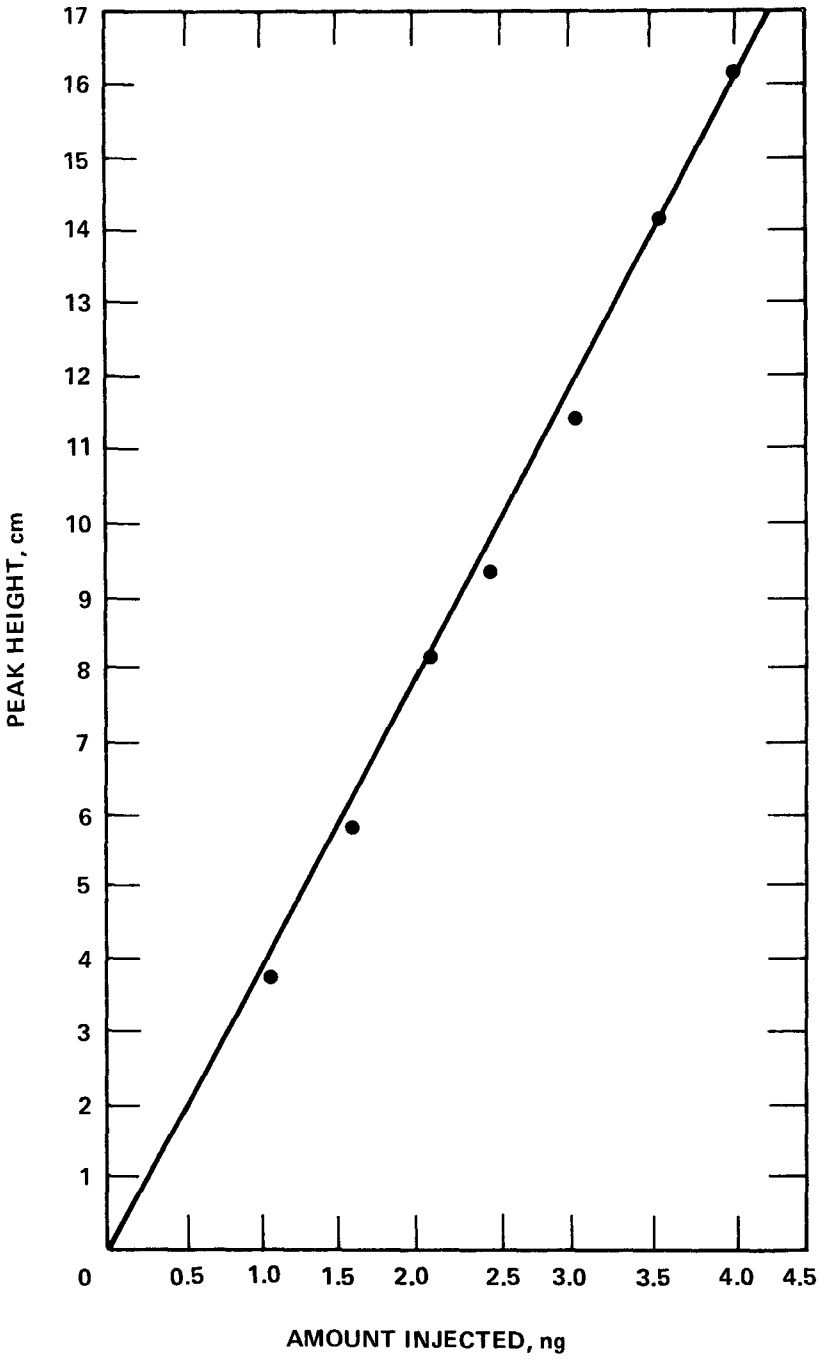
COMMENTS

Must be diluted 100 fold due to background interference.

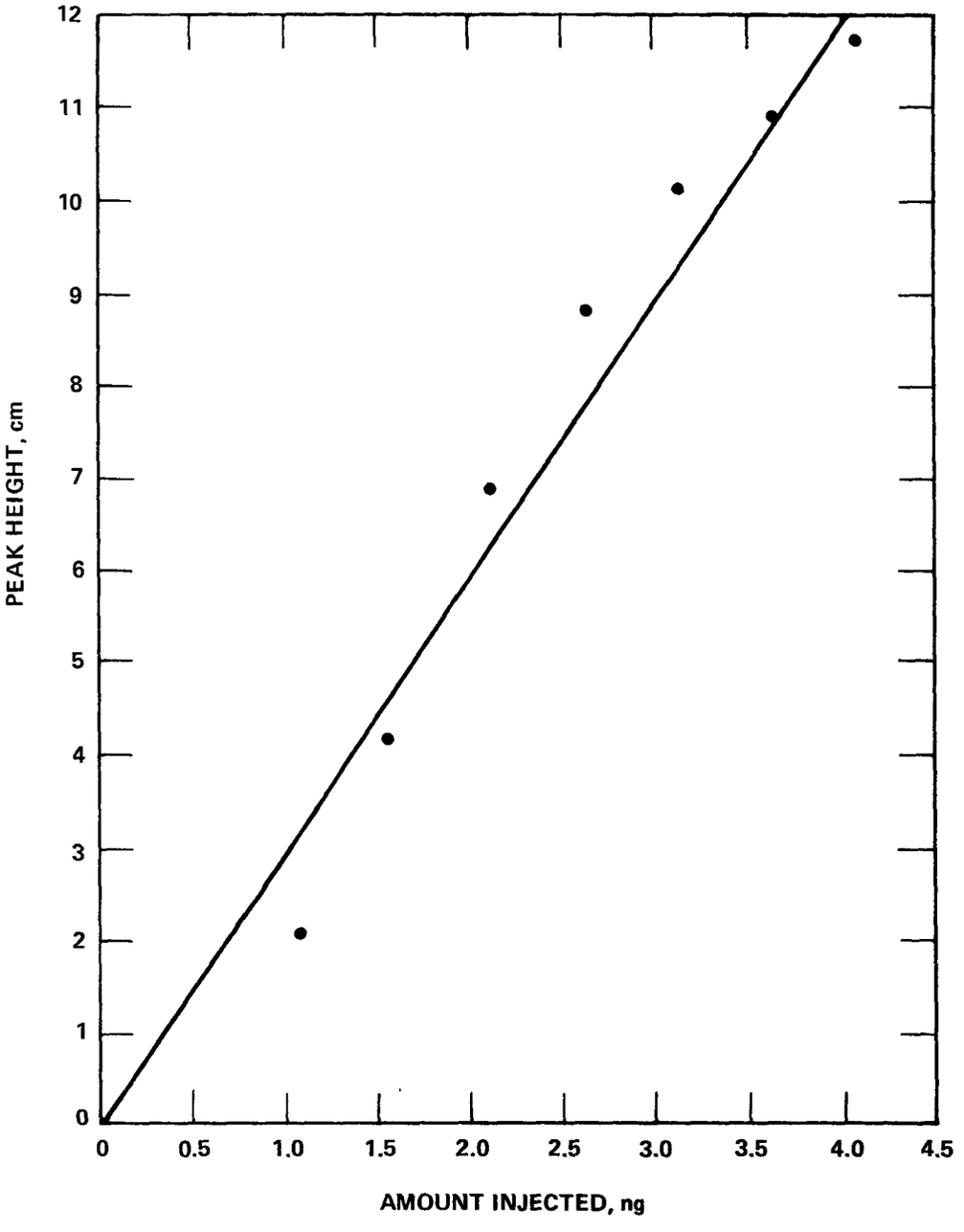
DECAY

Stable under test conditions.

*Major peak



Column Linearity Check of Chlorpropham Derivative on OV–17/OV–210.



Column Linearity Check of Chlorpropham Derivative on SE–30/OV–210.

DERIVATIZATION LINEARITY

Linear from 100 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
6.3 ng	8.4 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
32 ng	42 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

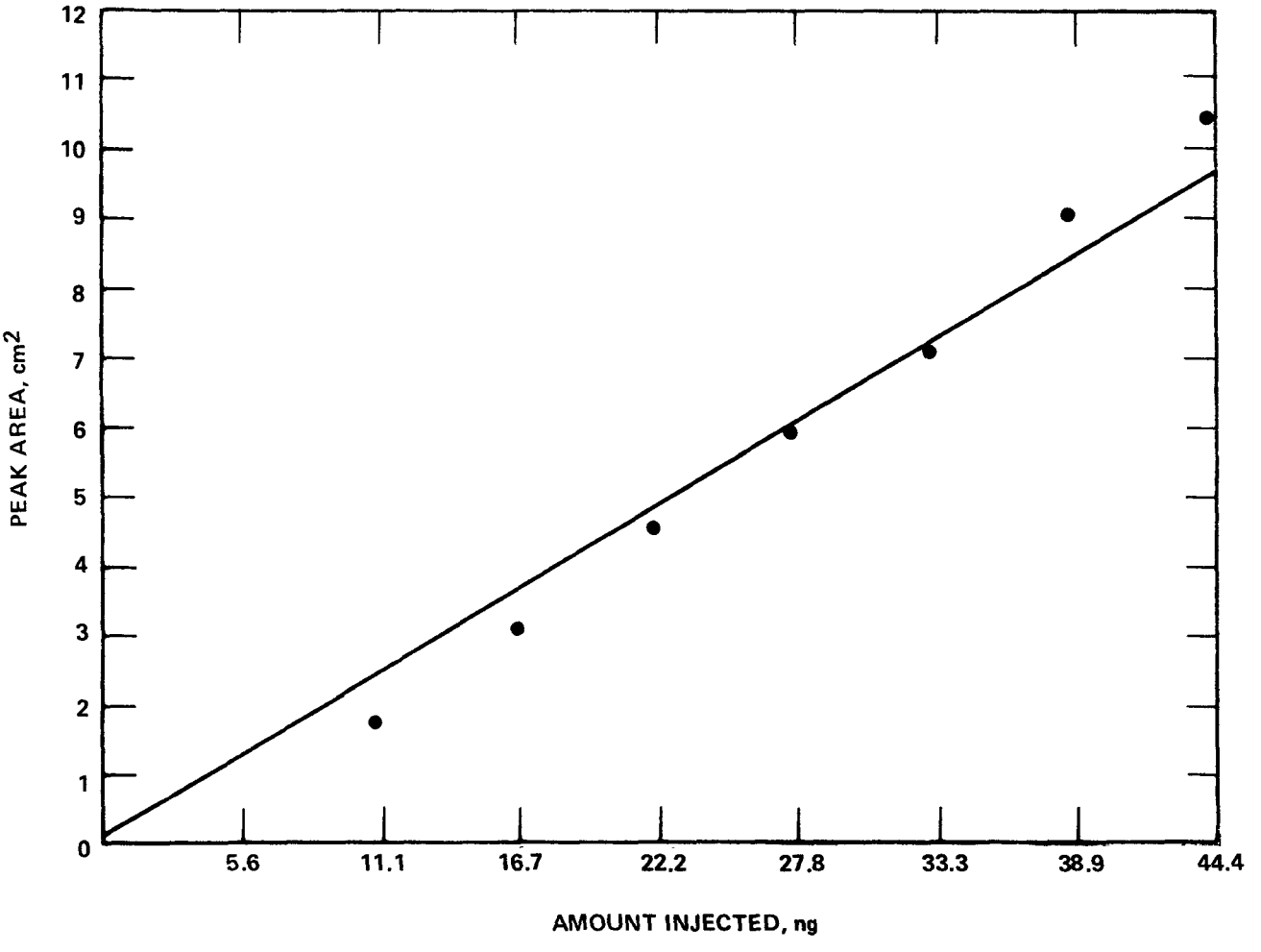
OV-17/OV-210	SE-30/OV-210
2.8	1.8

COMMENTS

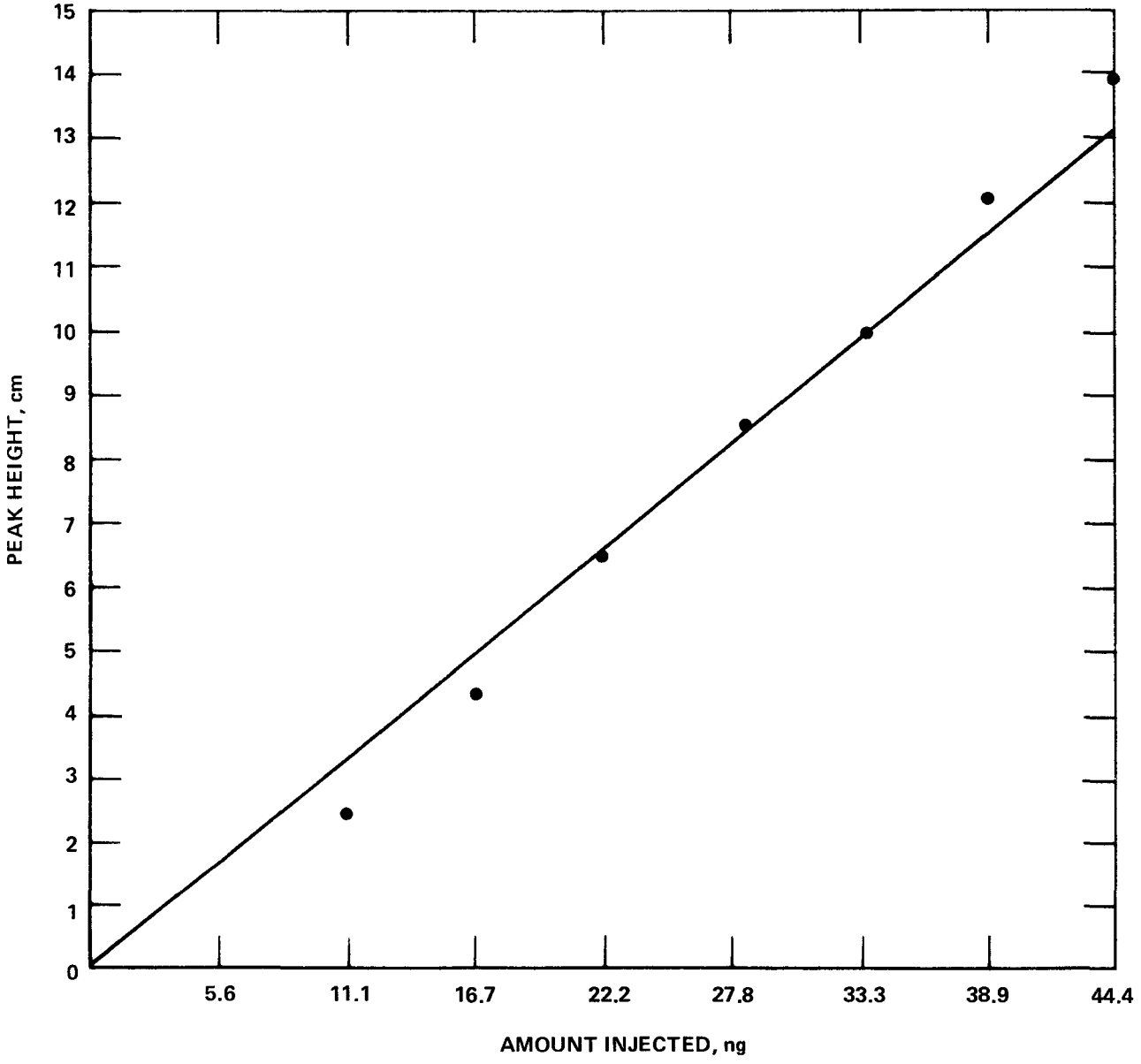
None

DECAY

Stable under test conditions.



Column Linearity Check of Desmedipham Derivative on OV–17/OV–210.



Column Linearity Check of Desmedipham Derivative on SE–30/OV–210.

FORMETANATE, HCL

DERIVATIZATION LINEARITY

Linear from 100 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
4.7 ng	4.1 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
23 ng	20 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

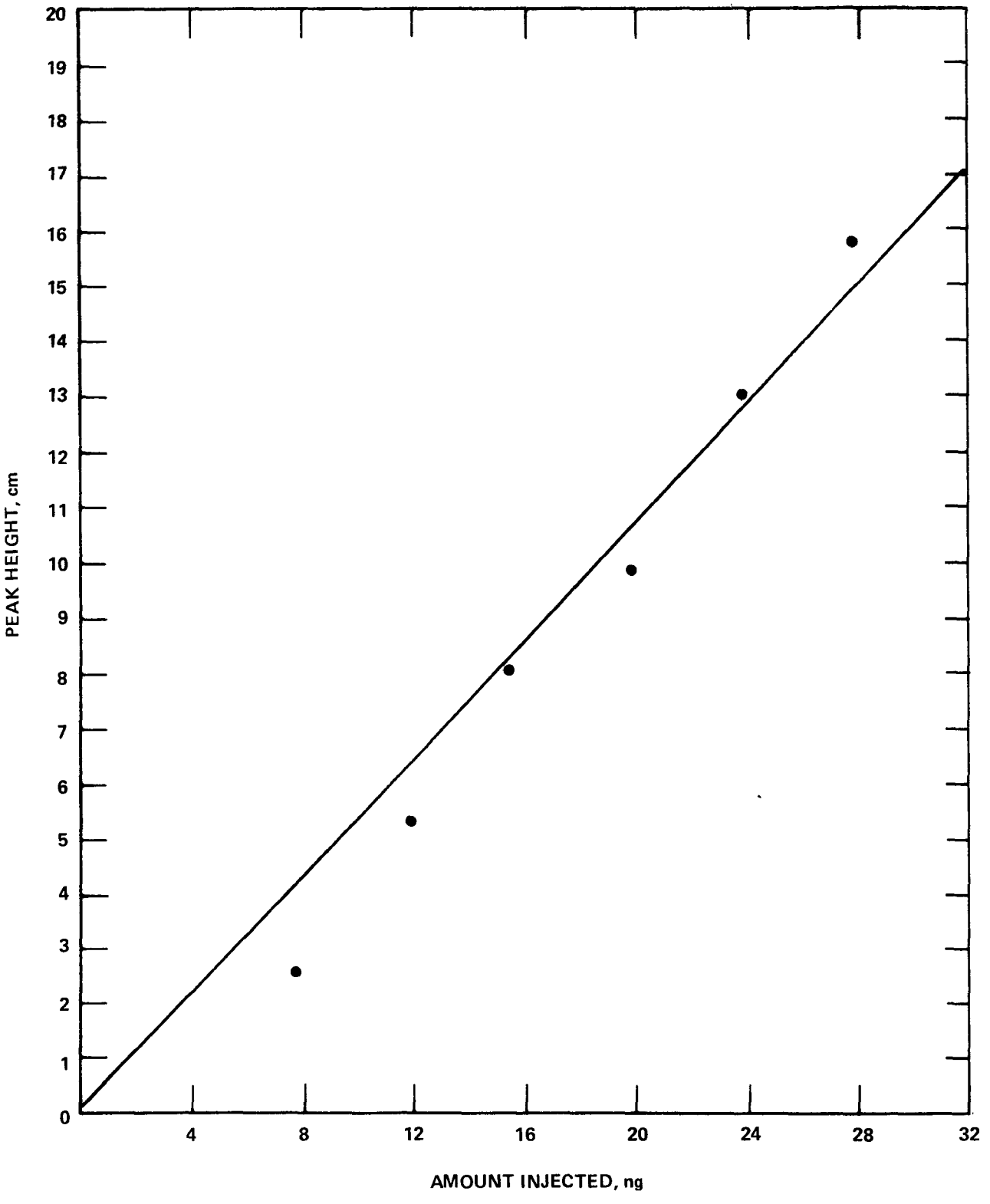
OV-17/OV-210	SE-30/OV-210
1.7	2.2

COMMENTS

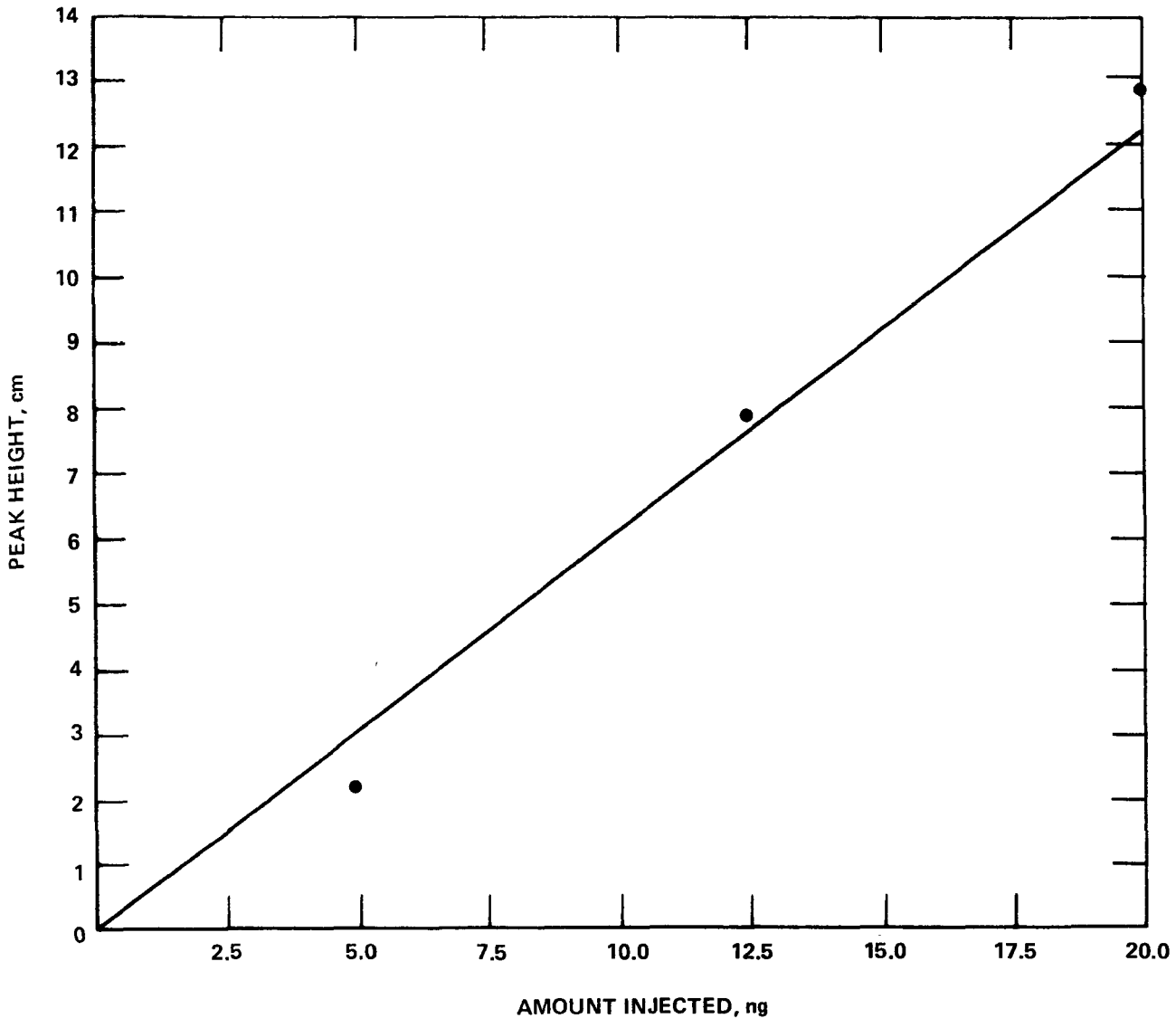
None

DECAY

Stable under test conditions.



Column Linearity Check of Formetanate·HCl Derivative on OV–17/OV–210.



Column Linearity Check of Formetanate·HCl Derivative on SE–30/OV–210.

KARBUTILATE

DERIVATIZATION LINEARITY

Linear from 100 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
9.7 ng	9.9 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
49 ng	49 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

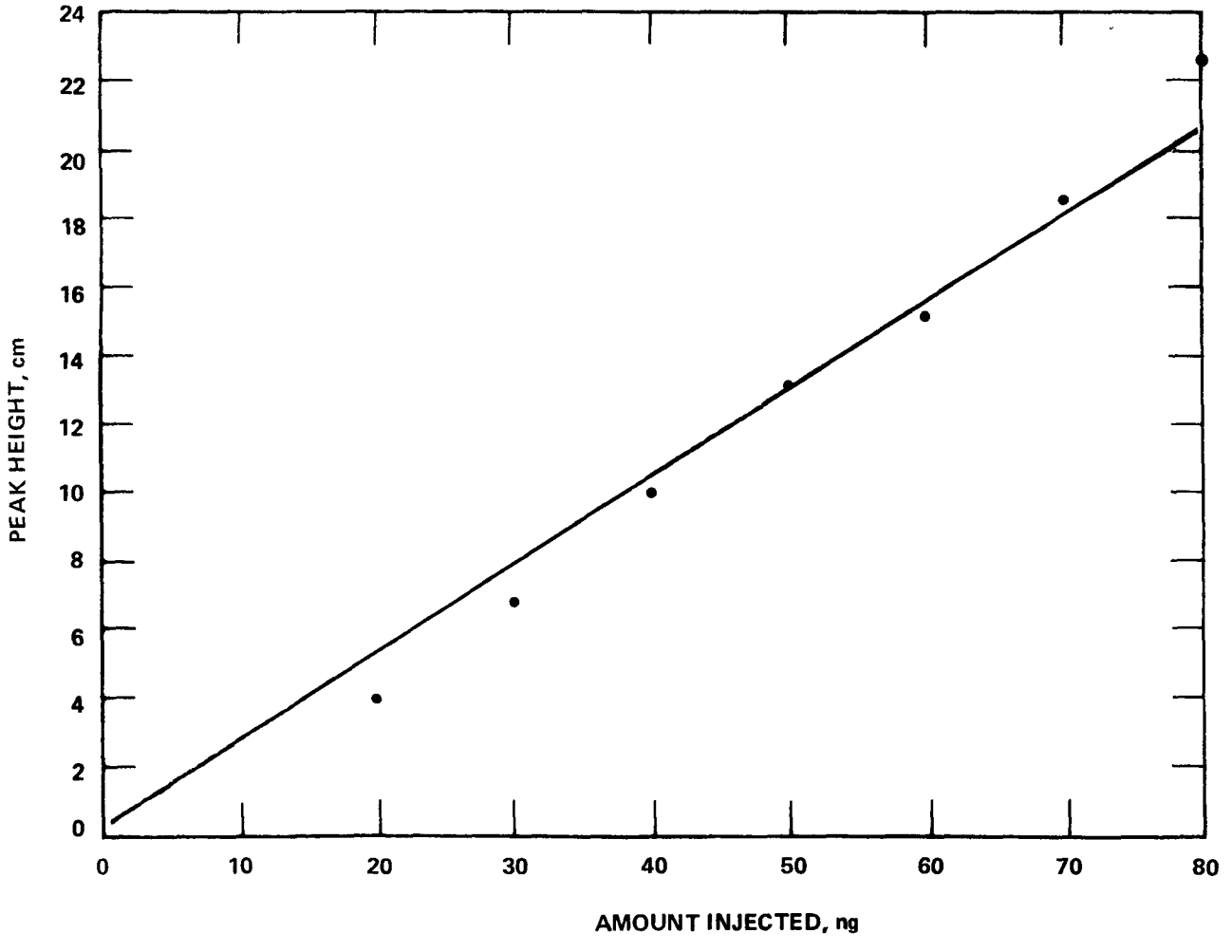
OV-17/OV-210	SE-30/OV-210
2.5	2.1

COMMENTS

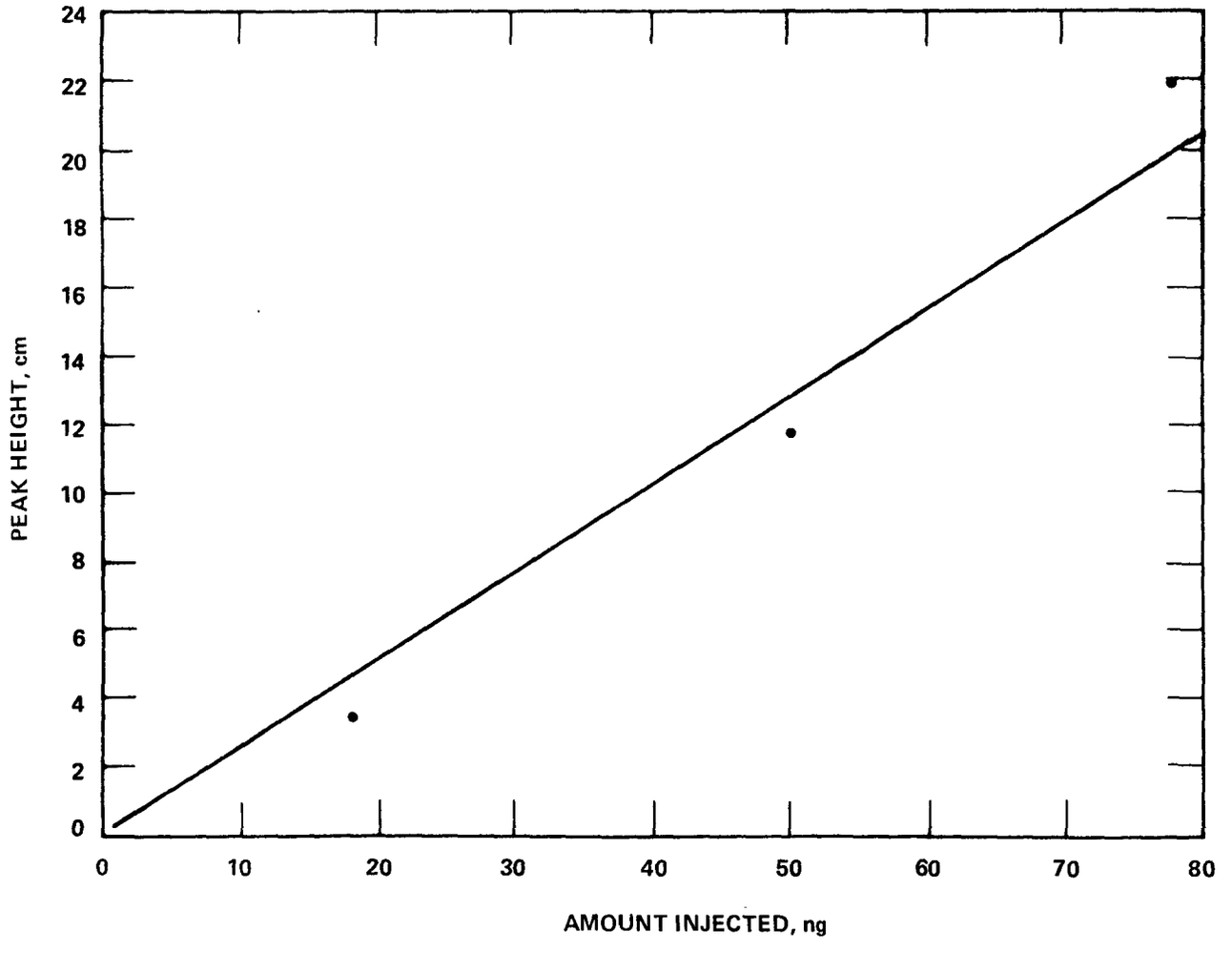
None

DECAY

Stable under test conditions.



Column Linearity Check of Karbutilate Derivative on OV–17/OV–210.



Column Linearity Check of Karbutilate Derivative on SE-30/OV–210.

DERIVATIZATION LINEARITY

Linear from 10 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
0.091 ng	0.096 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
0.46 ng	0.48 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

OV-17/OV-210	SE-30/OV-210
1.2	1.0, 1.2*

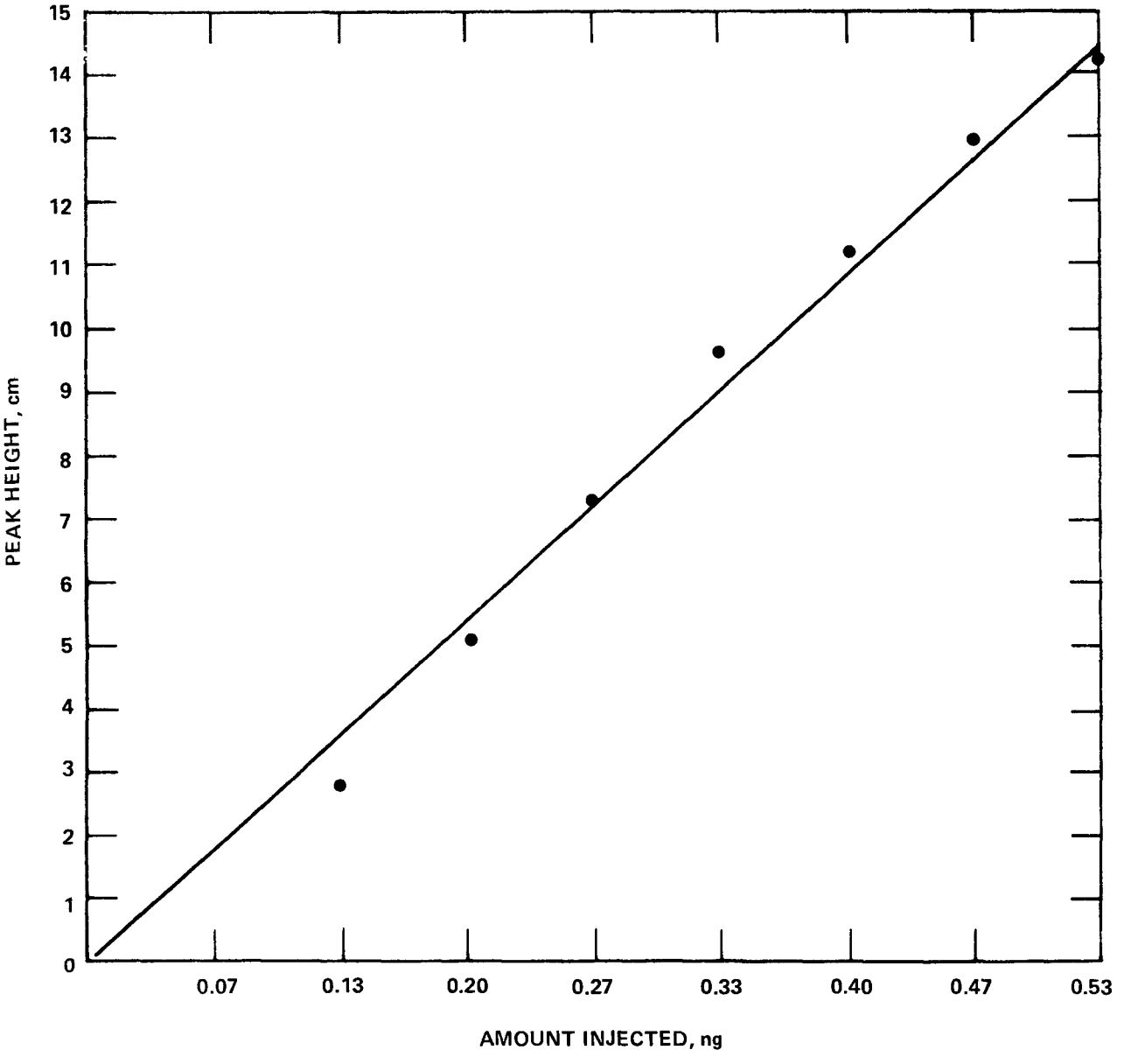
COMMENTS

Confirmation of derivatization linearity below 10 µg was impossible because of background interference.

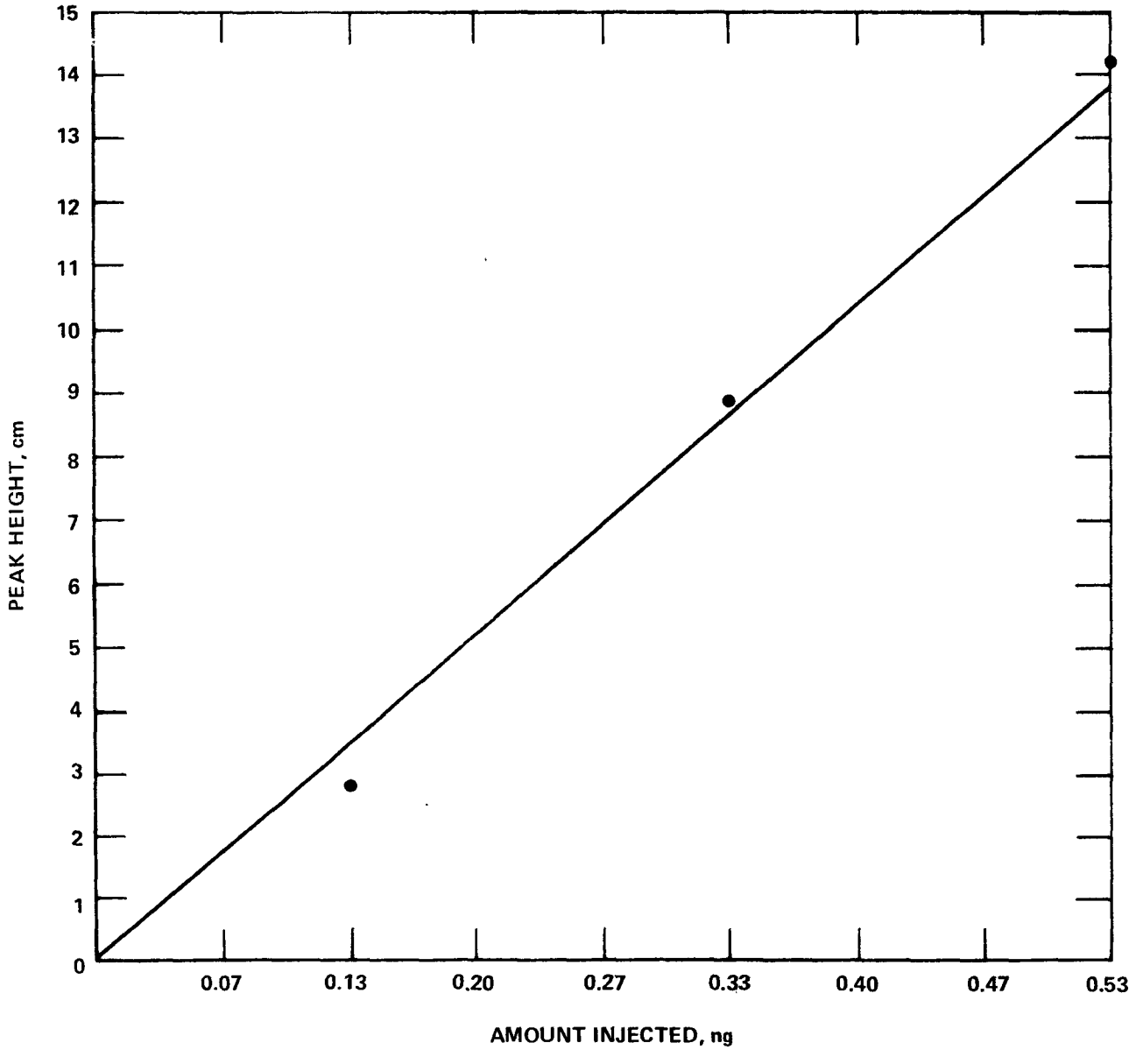
DECAY

Stable under test conditions.

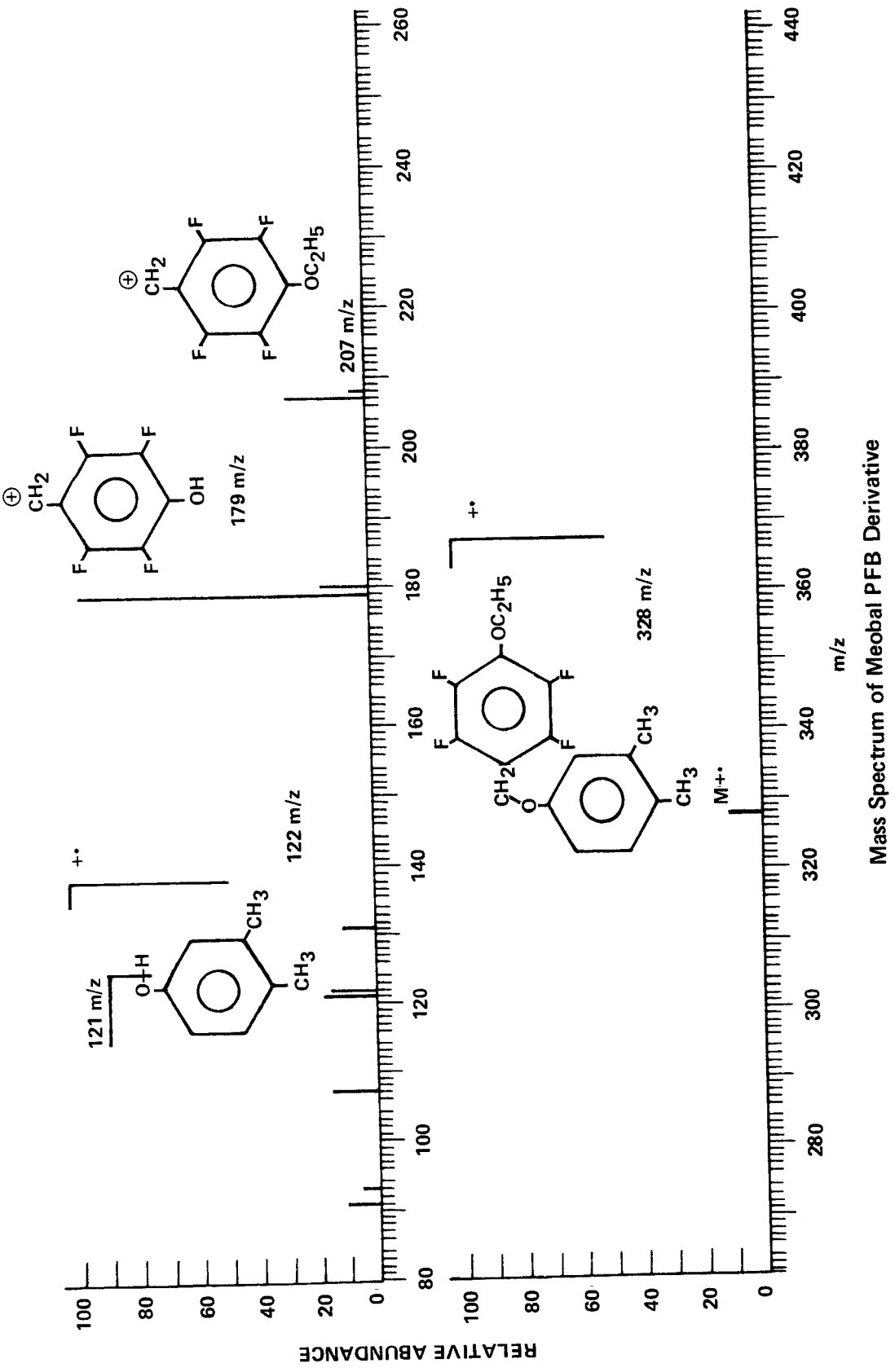
*Major peak



Column Linearity Check of Meobal Derivative on OV–17/OV–210.



Column Linearity Check of Meobal Derivative on SE–30/OV–210.



Mass Spectrum of Meobal PFB Derivative

DERIVATIZATION LINEARITY

Linear from 1 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
0.35 ng	0.30 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
1.8 ng	1.5 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

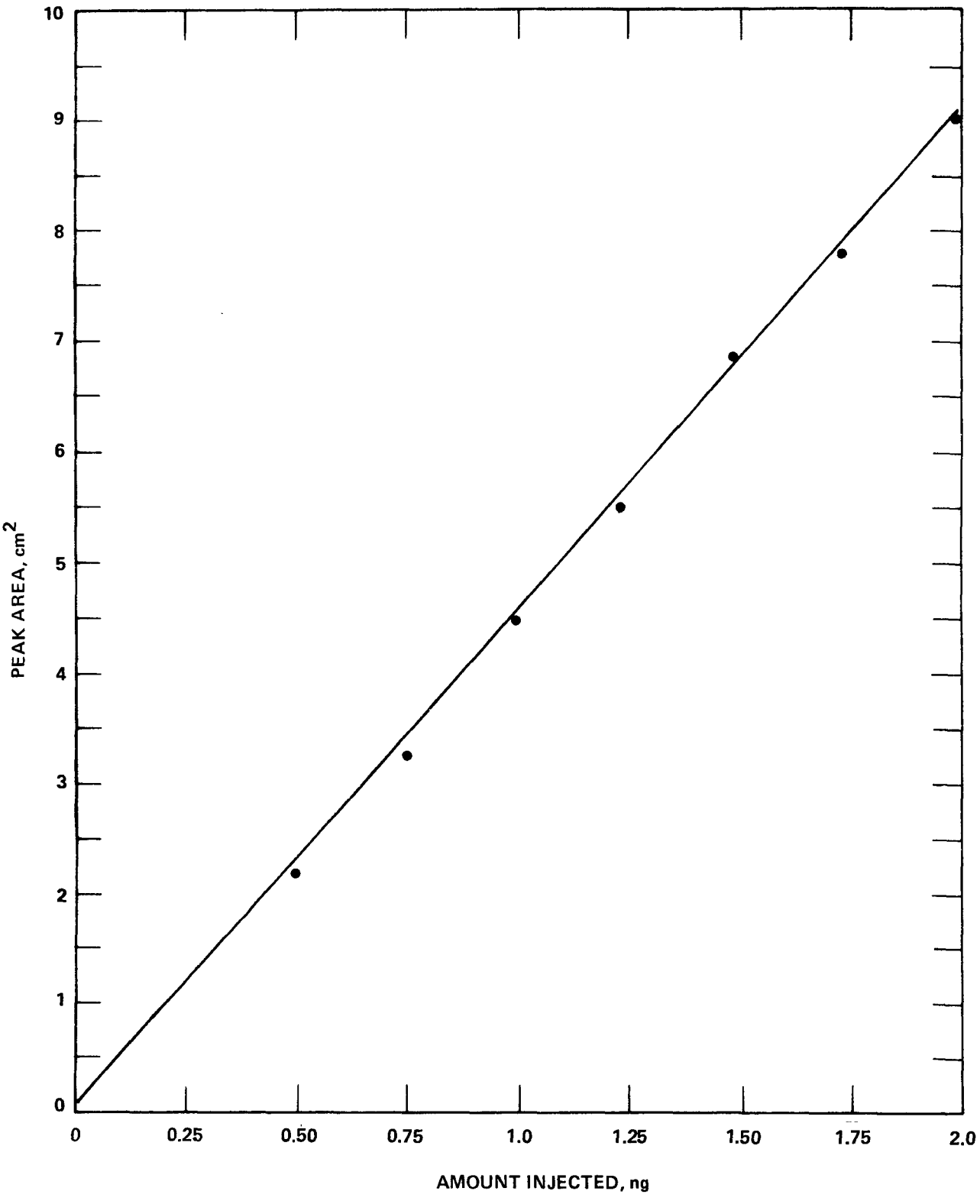
OV-17/OV-210	SE-30/OV-210
3.7	3.1

COMMENTS

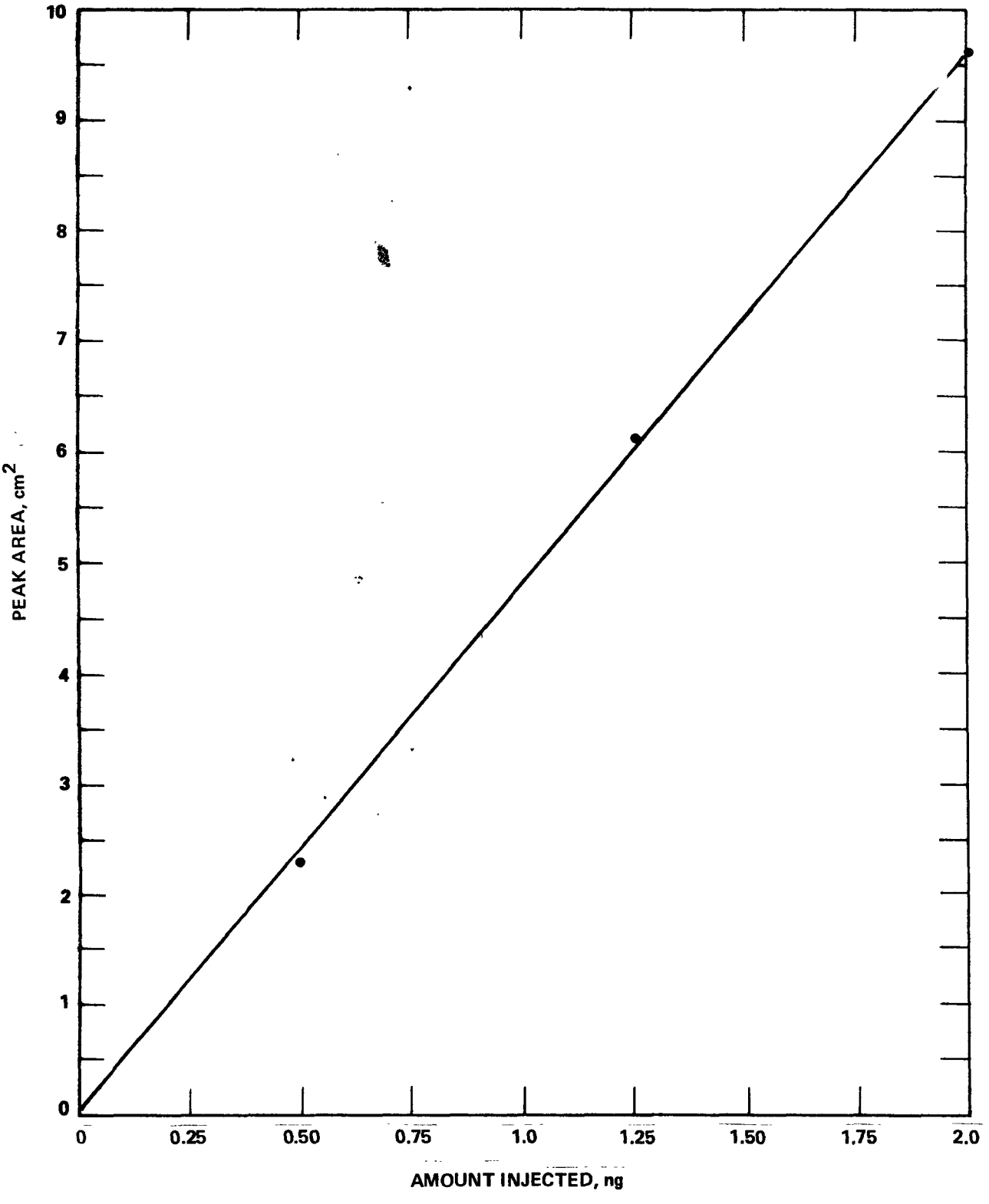
None.

DECAY

Stable under test conditions.



Column Linearity Check of Methiocarb Derivative on OV–17/OV–210.



Column Linearity Check of Methiocarb Derivative on SE–30/OV–210.

DERIVATIZATION LINEARITY

Linear from 1 to 100 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
0.031 ng	0.026 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
0.16 ng	0.13 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

OV-17/OV-210	SE-30/OV-210
0.37, 0.71, 1.3*	0.25, 0.40, 1.5*

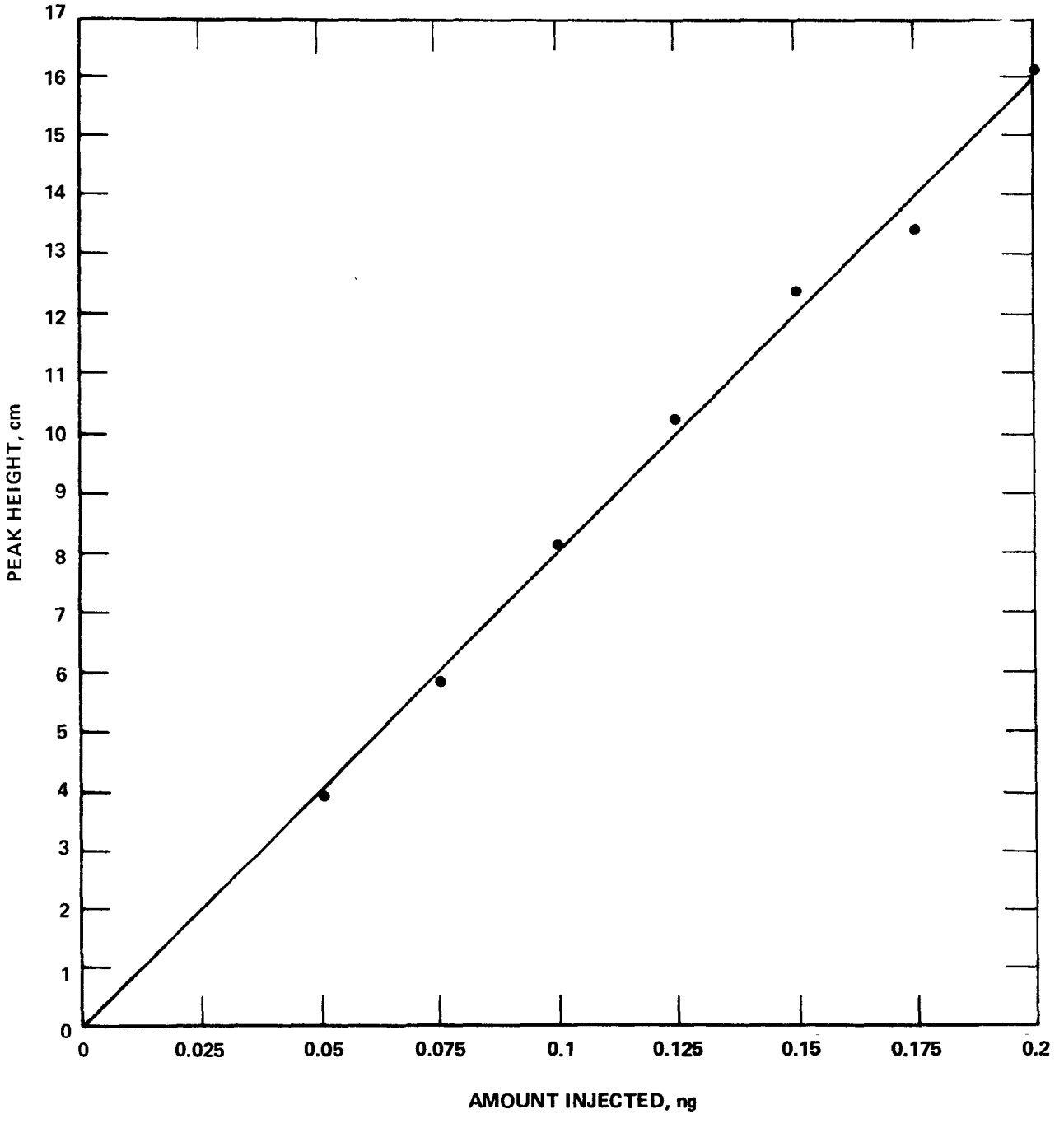
COMMENTS

Measurements were made on the third peak.

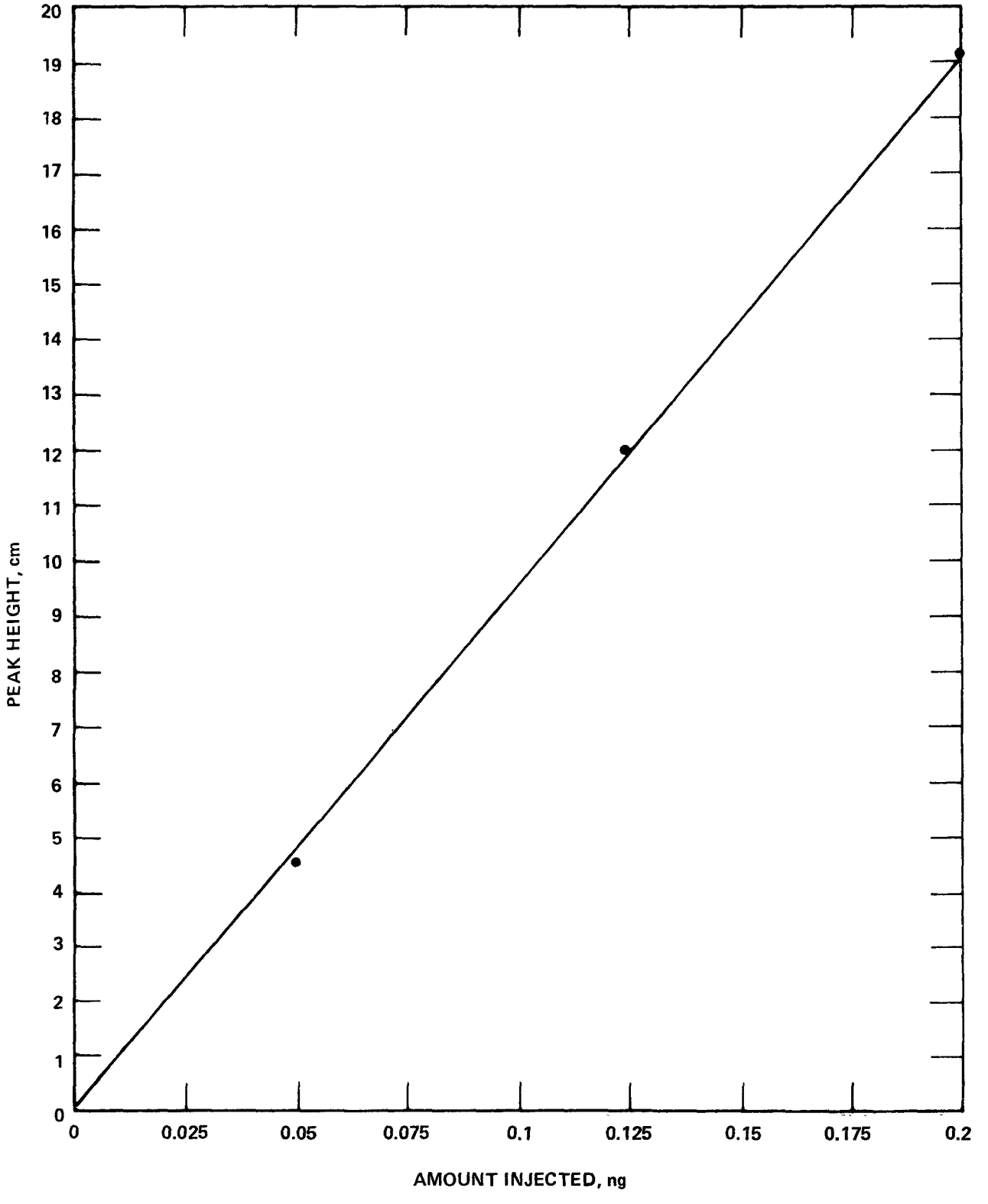
DECAY

Stable under test conditions.

*Major peak



Column Linearity Check of Methomyl Derivative on OV–17/OV–210.



Column Linearity Check of Methomyl Derivative on SE–30/OV–210.

PHENMEDIPHAM

DERIVATIZATION LINEARITY

Linear from 100 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
18 ng	14 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
88 ng	68 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

OV-17/OV-210	SE-30/OV-210
1.8,2.3*, 2.8	1.5, 1.6*, 1.8

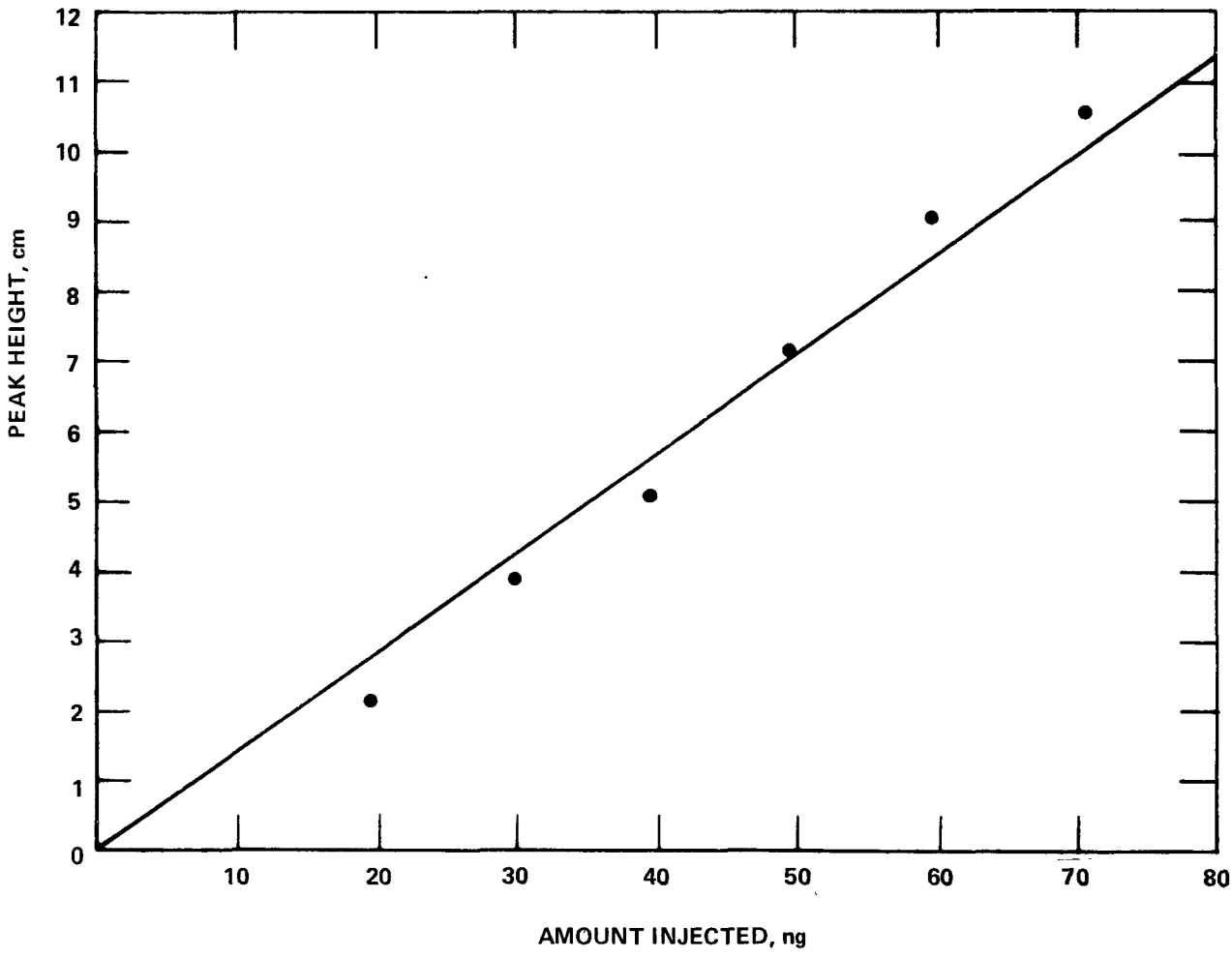
COMMENTS

Measurements were made of the second peak.

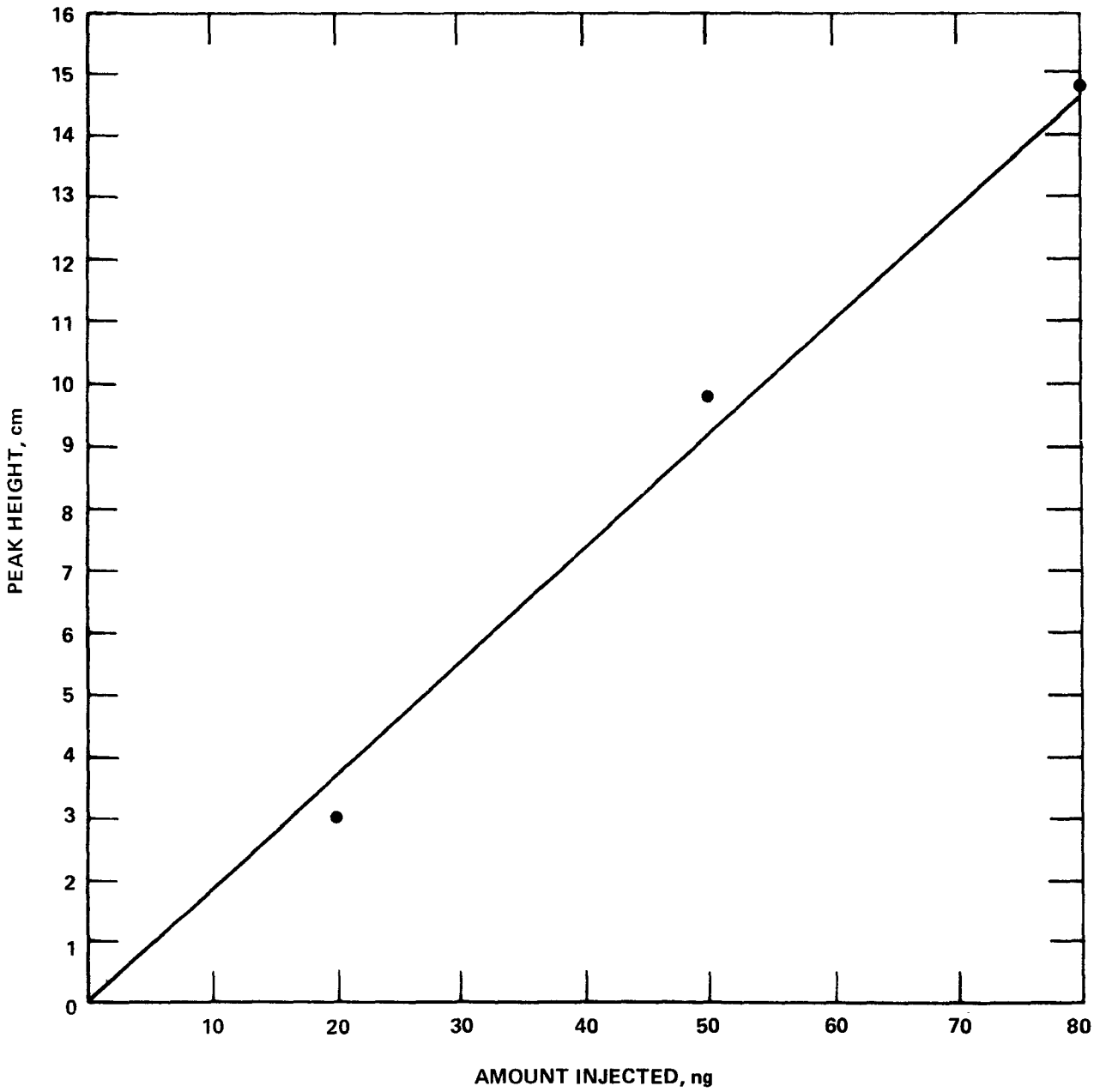
DECAY

Stable under test conditions.

*Major peak



Column Linearity Check of Phenmedipham Derivative on OV–17/OV–210.



Column Linearity Check of Phenmedipham Derivative on SE–30/OV–210.

DERIVATIZATION LINEARITY

Linear from 10 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
0.14 ng	0.14 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
0.68 ng	0.70 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

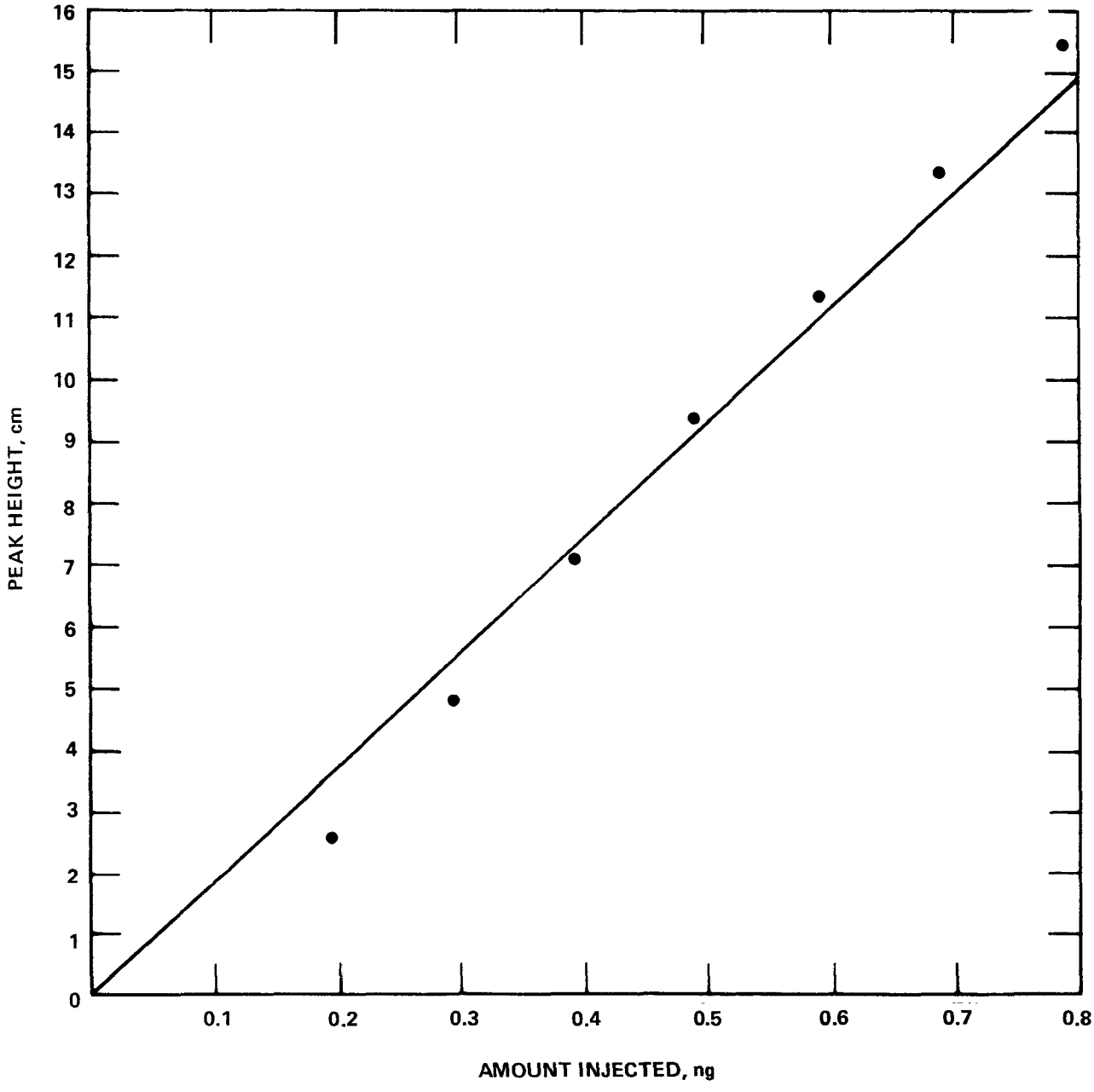
OV-17/OV-210	SE-30/OV-210
1.4	1.4

COMMENTS

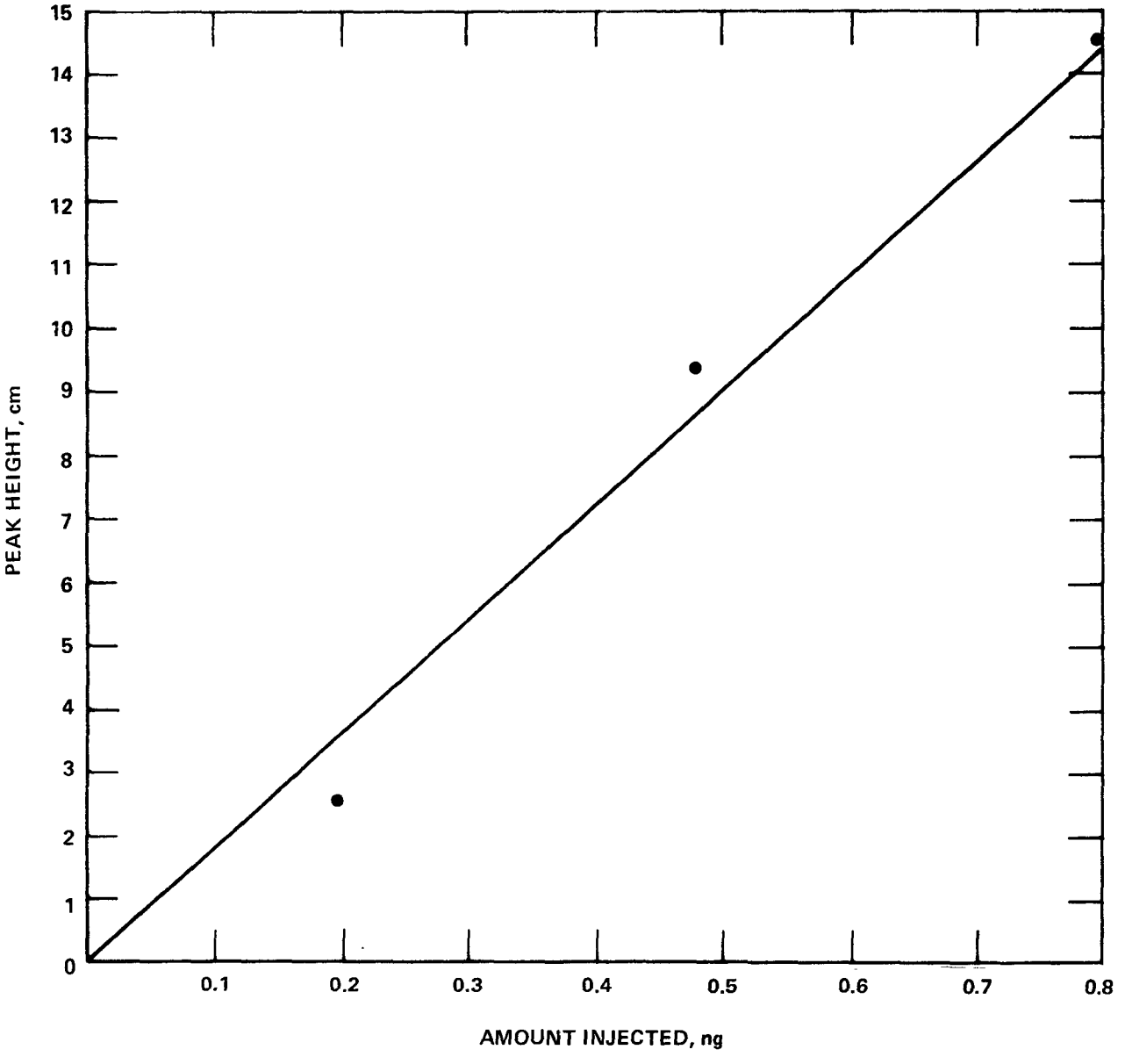
Confirmation of derivatization linearity below 10 µg was impossible because of background interference.

DECAY

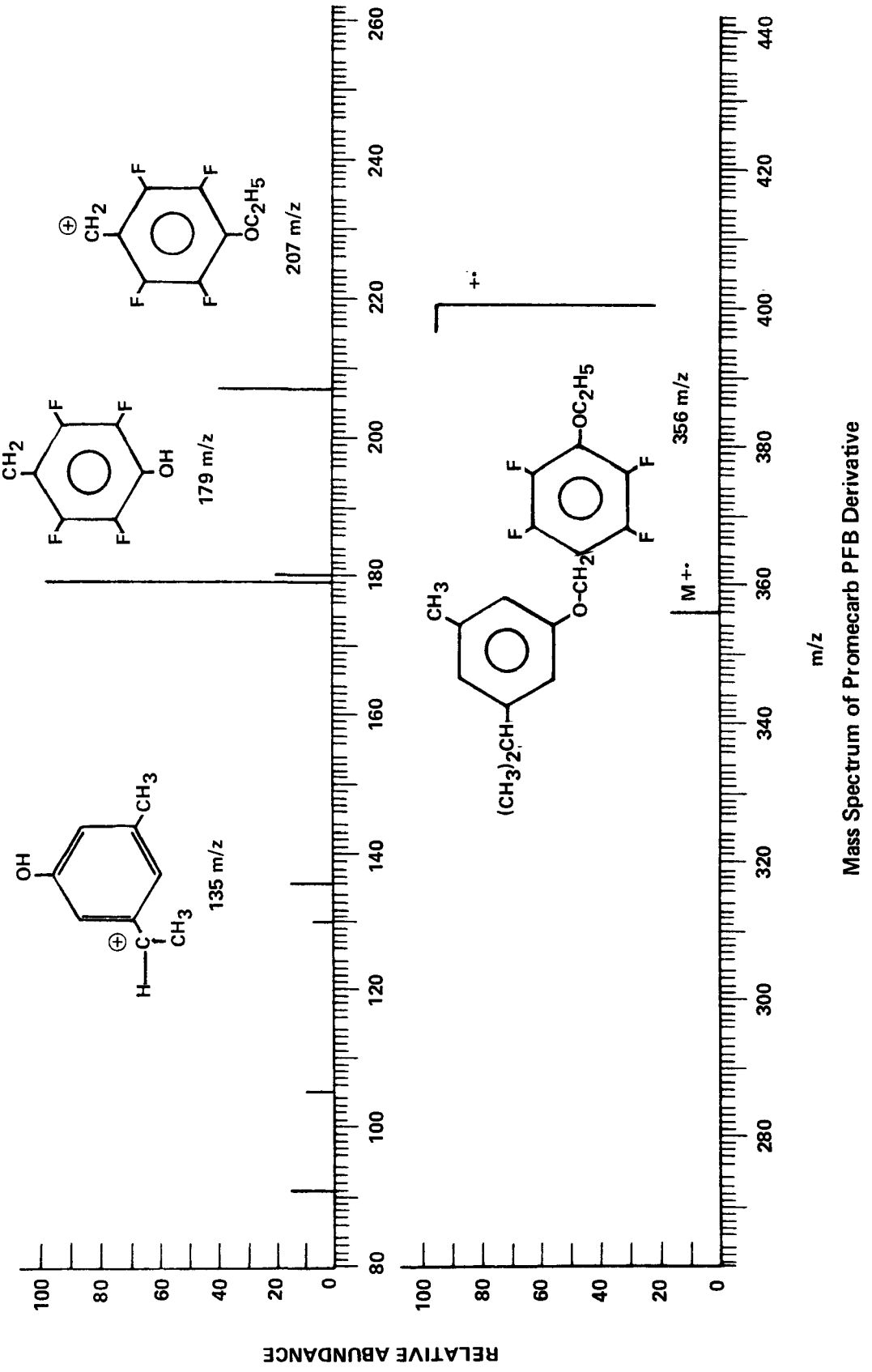
Stable under test conditions.



Column Linearity Check of Promecarb Derivative on OV–17/OV–210.



Column Linearity Check of Promecarb Derivative on SE–30/OV–210.



Mass Spectrum of Promecarb PFB Derivative

PROPOXUR

DERIVATIZATION LINEARITY

Linear from 10 to 1000 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
0.080 ng	0.081 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
0.24 ng	0.24 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

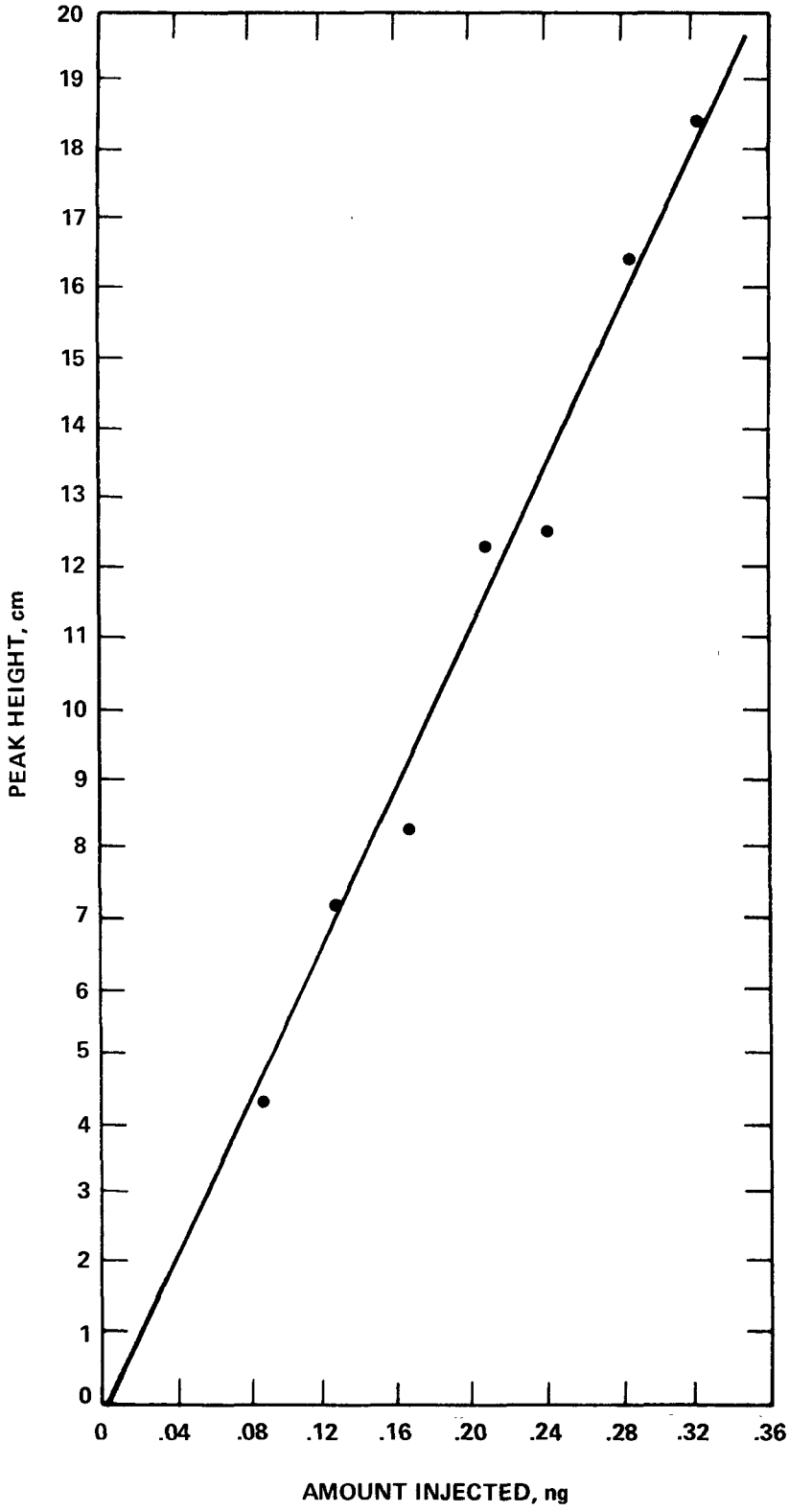
OV-17/OV-210	SE-30/OV-210
1.2	1.2

COMMENTS

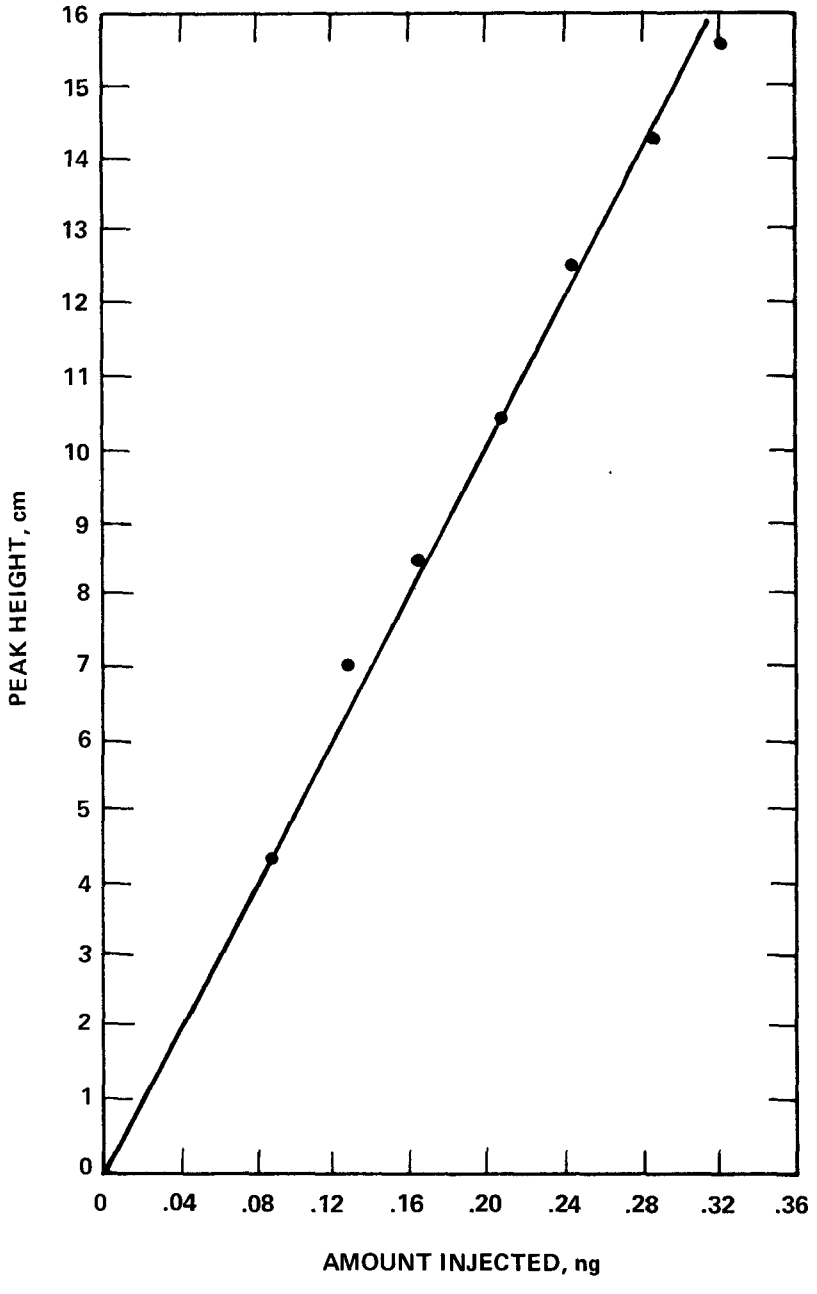
Must be diluted 100 fold due to background interference.

DECAY

Stable under test conditions.



Column Linearity Check of Propoxur Derivative on OV–17/OV–210.



Column Linearity Check of Propoxur Derivative on SE–30/OV–210.

THIOPHANATE METHYL

DERIVATIZATION LINEARITY

Linear from 10 to 100 µg

AMOUNT NEEDED TO PRODUCE 10% FSD

OV-17/OV-210	SE-30/OV-210
0.0087 ng	0.012 ng

AMOUNT NEEDED TO PRODUCE 50% FSD

OV-17/OV-210	SE-30/OV-210
0.044 ng	0.057 ng

RELATIVE RETENTION TIME (ALDRIN = 1.00)

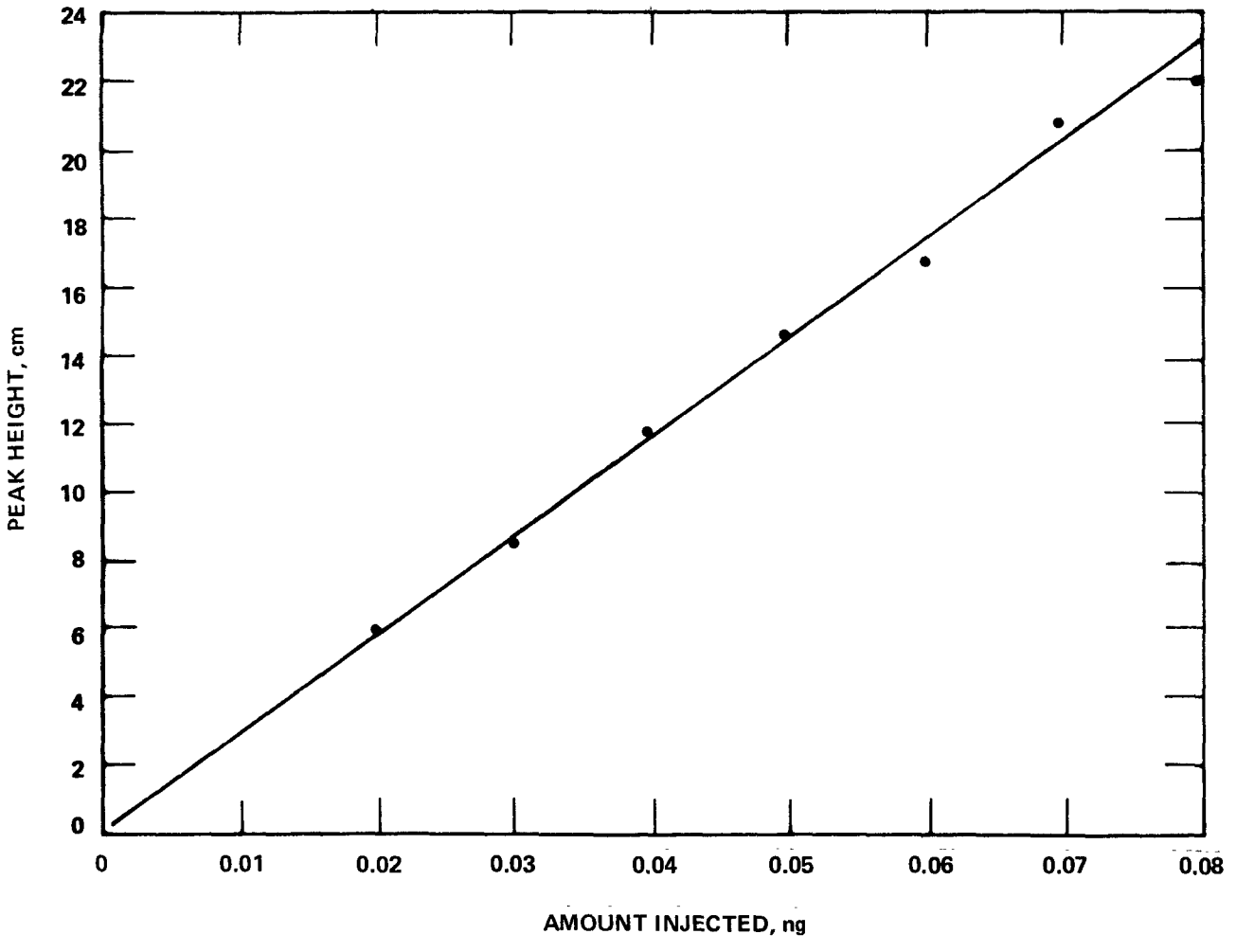
OV-17/OV-210	SE-30/OV-210
3.0	3.3

COMMENTS

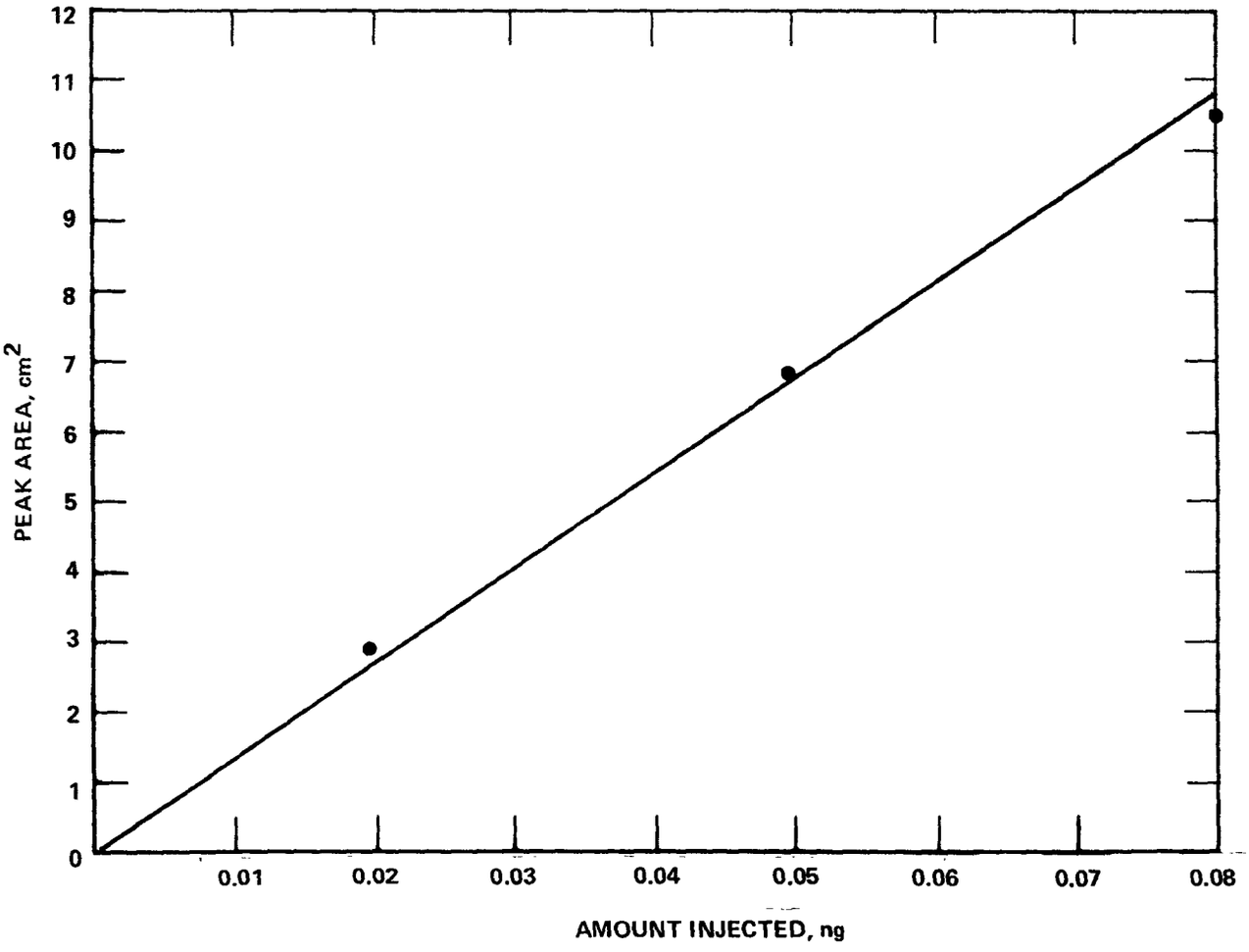
Confirmation of derivatization linearity below 10 µg was impossible because of blank peak interference.

DECAY

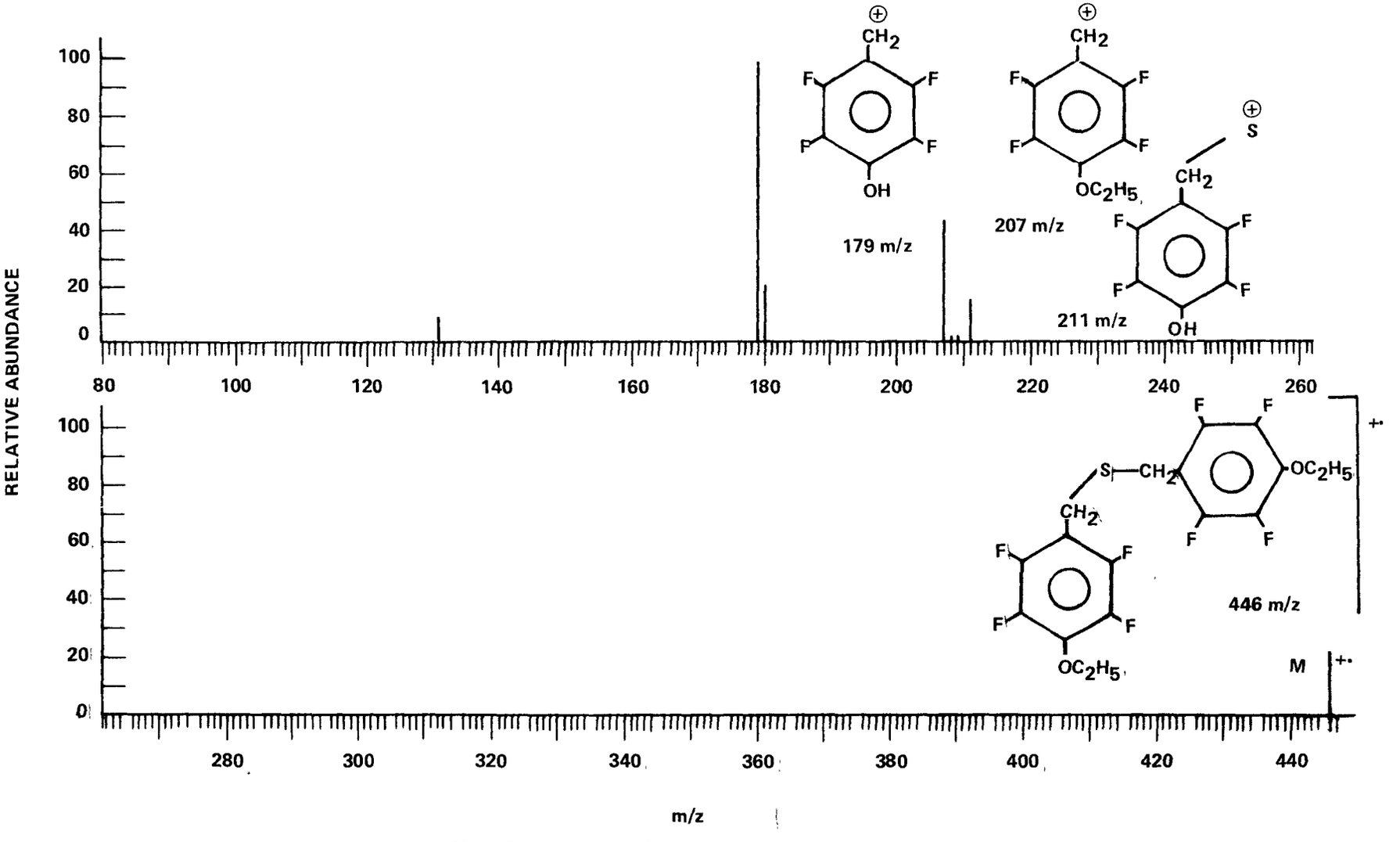
Stable under test conditions.



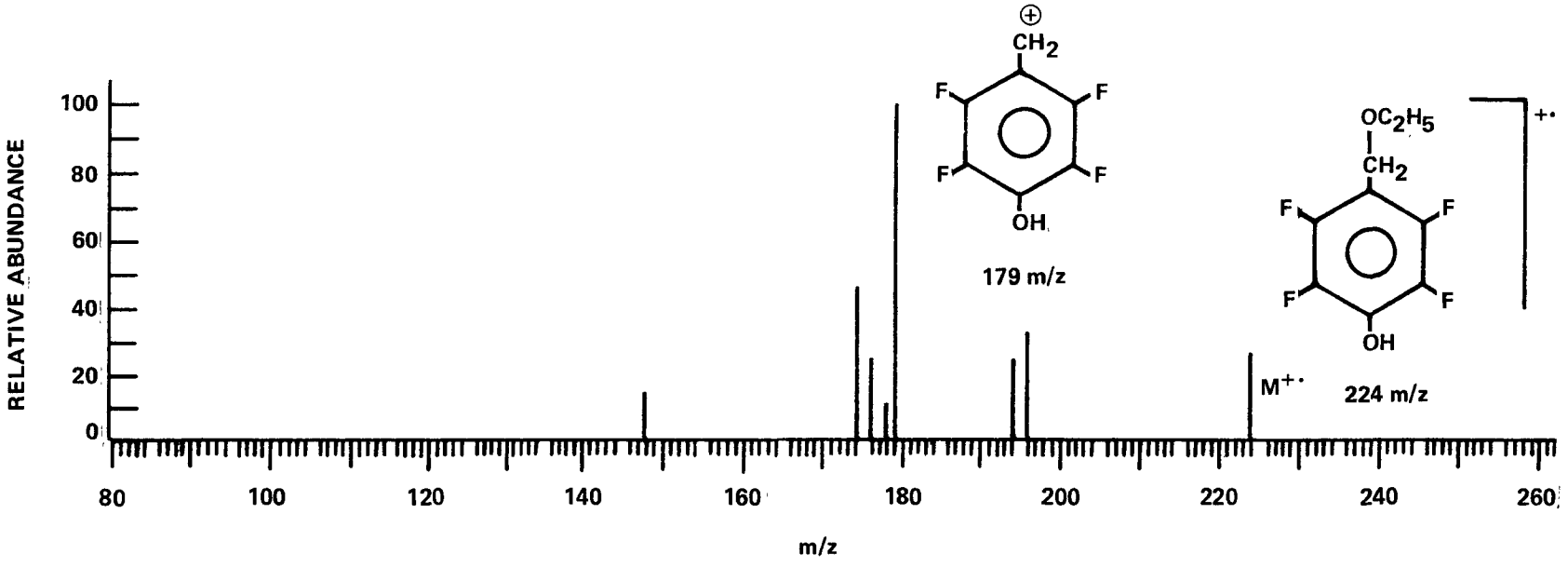
Column Linearity Check of Thiophanate Methyl Derivative on OV–17/OV–210.



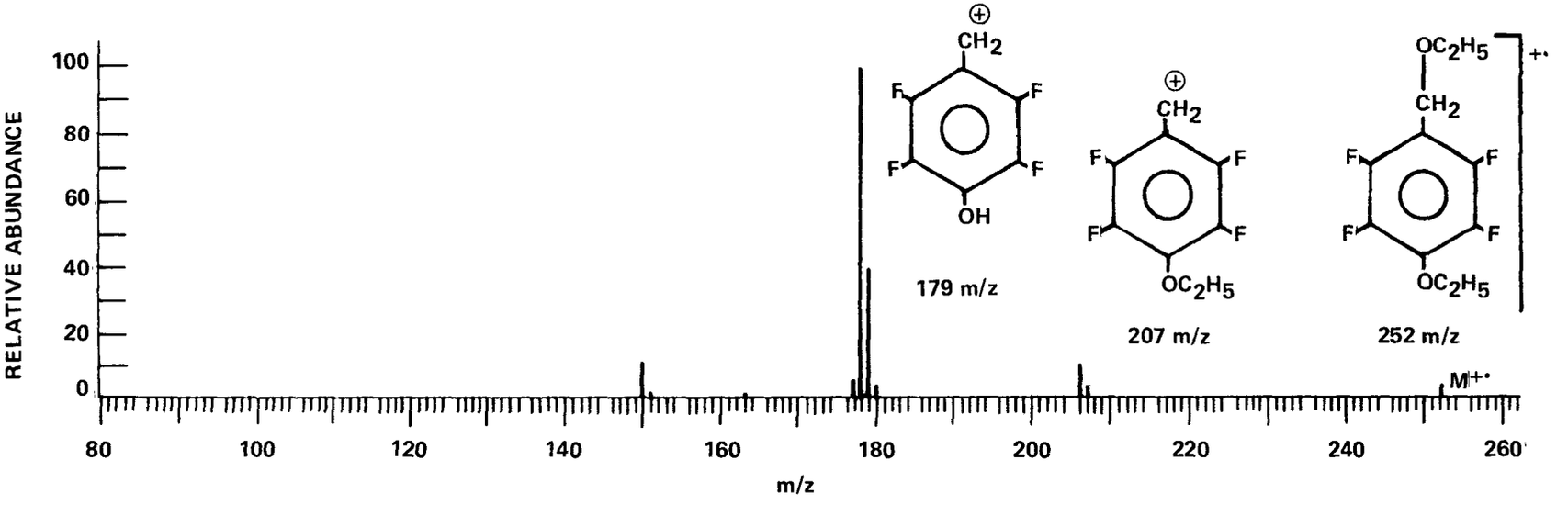
Column Linearity Check of Thiophanate Methyl Derivative on SE–30/OV–210.



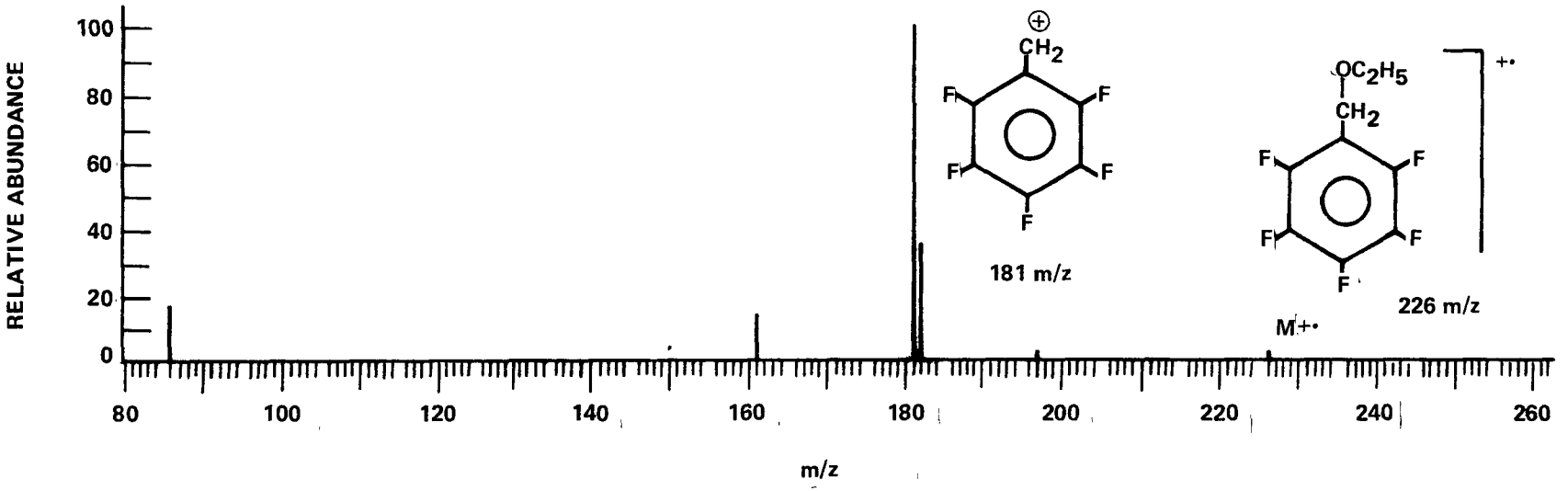
Mass Spectrum of Thiophanate Methyl PFB Derivative



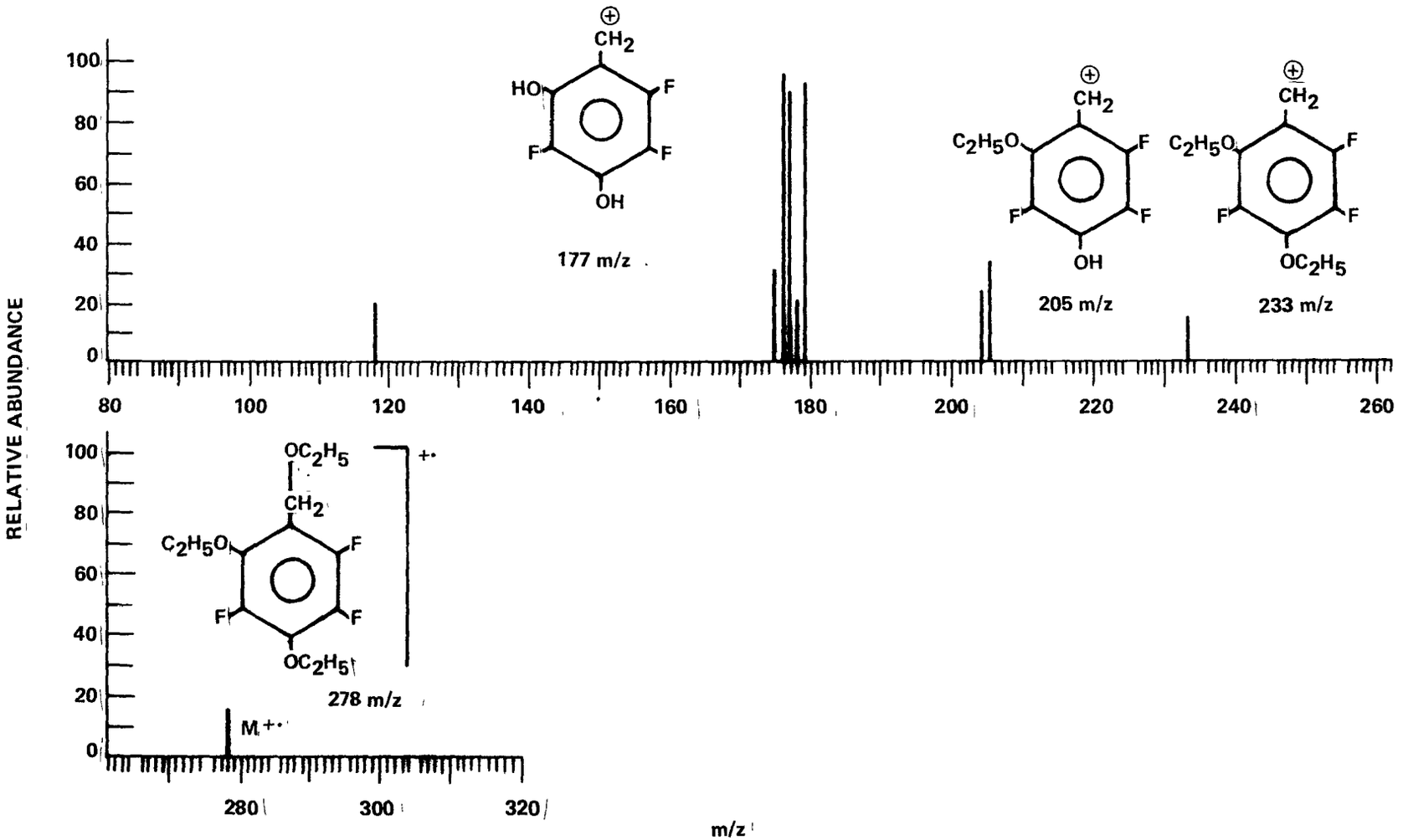
Mass Spectrum of PFB Reagent Blank Product I



Mass Spectrum of PFB Reagent Blank Product II



Mass Spectrum of PFB Reagent Blank Product III



Mass Spectrum of PFB Reagent Blank Product IV

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO
EPA-600/4-79-077		

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	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Merrill D. Jackson, Stephen D. Soileau, G. Wayne Sovocool and Richard A. Sachleben	

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

A procedure was developed for the determinatic[illegible]ce quantities of a broad range of carbamate pesticides. The carbamates w[illegible] d[illegible] and derivatized in a single step, using alkali and α-bromo-2,3,4,5[illegible]orotoluene (PFBB), and were subsequently analyzed using electron captu[illegible]s chromatography. This one step derivatization method created a novel derivative in which one fluorine on the PFB ring was displaced by an ethoxide ion via aromatic nucleophilic substitution.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Method of analysis, pesticide, insecticide, carbamate	Methods Evaluation Methods Development	14B 13B

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