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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A high performance liquid chromatographic method was developed for the analysis of o-chlorobenzylidenemalononitrile and o-chlorobenzaldehyde in soil. After precision and accuracy tests were performed following the USATHAMA QA Plan, soil samples from Camp Simms were extracted and analyzed using the developed method. K		

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TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES	ii
LIST OF TABLES	iii
SUMMARY	iv
I. ANALYTICAL METHOD	1
II. FIELD SAMPLE ANALYSIS	13
A. Sample Preparation and Analysis	13
B. Quality Control	13
C. Results and Discussion	15
APPENDIX A - O-Chlorobenzaldehyde in Soil Precision and Accuracy Data Set	A-1
APPENDIX B - O-Chlorobenzylidenemalononitrile in Soil Precision and Accuracy Data Set	B-1
APPENDIX C - FID Chromatograms, Precision and Accuracy Data Set	C-1



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LIST OF FIGURES

<u>Figure Number</u>		<u>Page</u>
1	Mass Spectrum of 2CBMN	2
2	Peak Height Values for Spectrum of 2CBMN	3
3	GC/MS Chromatogram of CEA	4
4	HPLC Chromatogram of CEA and 2CBMN	9
5	HPLC Chromatogram of CEA and 2CBMN Spiked Soil Sample	10
6	Map of Camp Simms	14
7	HPLC Chromatogram of Field Sample CSS20	16
8	Integrated Spectrum of Field Sample CSS22	17
9	Specific Ion High Resolution Search Field Sample CSS22	18
10	Integrated Spectrum of Field Sample CSS23	19
11	Peak Height Values for Field Sample CSS23	20

LIST OF TABLES

<u>Table Number</u>		<u>Page</u>
1	Camp Simms Field Sample Results by HPLC	15

SUMMARY

A high performance liquid chromatography method for the analysis of o-chlorobenzylidenemalononitrile and o-chlorobenzaldehyde in soils was developed under Task R902.35.01. The precision and accuracy of the developed method was determined from the analysis of forty spiked soil samples over the range of 1-20 parts per million. The detection limit at the 90% confidence level, calculated by the method of Hubaux and Vos, is 2.4 ppm CEA and 1.7 ppm 2CBMN.

Eighteen field samples collected at Camp Simms were extracted and analyzed using this method, as well as a few determinations by gas chromatography and mass spectrometry for verification. No 2CBMN or CEA was detected in any of the field samples.

I. ANALYTICAL METHOD

1. APPLICATION: The method described in this report is for the quantification of o-Chlorobenzylidenemalononitrile (2CBMN) and o-Chlorobenzaldehyde (CEA) in soils using high-performance liquid chromatography.

a. Tested Concentration Range: The tested concentration ranges are 1.2 to 20.0 ppm ($\mu\text{g}/\text{gram}$ of soil) for CEA and 1.2 to 18.2 ppm ($\mu\text{g}/\text{gram}$ of soil) for 2CBMN.

b. Sensitivity: A 50- μL injection of a calibration standard representing 1.05 ppm CEA and 1.25 ppm 2CBMN gives an average integrated response of 48767 units and 60788 units respectively.

c. Detection Limit: The detection limit calculated by the method of Hubaux and Vos from soils is 2.4 ppm CEA and 1.7 ppm 2CBMN at the 90% confidence level.

d. Gas Chromatography/Mass Spectrometry: Data was obtained on 2CBMN by direct probe high resolution mass spectrometry. A fifty μL portion of a 10 ppm calibration standard was dried down to obtain the spectra shown in Figures 1 and 2. CEA was evaluated by gas chromatography/mass spectrometry using a 3% Dextsil column operated at 125°C. An example chromatogram representing 30 ng CEA injected directly is shown in Figure 3.

e. Analysis Rate: After sample preparation, one analyst can analyze 5 samples per hour.

2. CHEMISTRY

a. o-Chlorobenzaldehyde

CAS RN 89-98-5

Hazardous characteristics: Irritant

Melting point: 19°C

Boiling point: 213°C

Flash point: 88°C

Solubility: Alcohol, methylene chloride

b. o-Chlorobenzylidenemalononitrile

CAS RN 40915-55-7

Hazardous characteristics: Irritant, extremely strong lachrymator

MASS SPECTRUM DATA: HCSCEA #3
06/27/80 9:00:00 + 6:00 CALI: HDRAP1 #17
SAMPLE: 10 PPM 2CBMN, 10 PPM CEA
ENHANCED (S 15B IN 1T)

BASE M/E: 188
RI: 1665070.

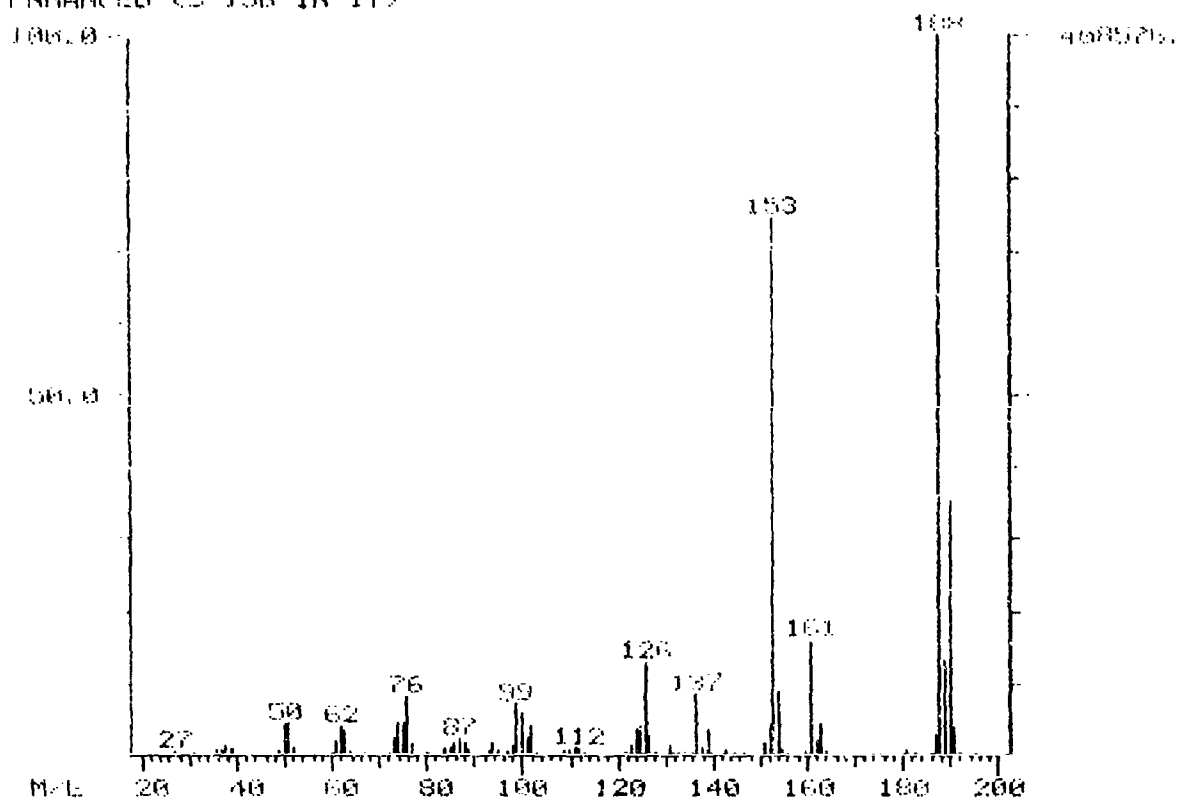


FIGURE 1. Mass Spectrum of 2CBMN

RTO + MASS CHROMATOGRAMS DATA: HCSCEA #1 SCANS 1 TO 15
 06/27/80 9:00:00 CALI: HCSCEA #4
 SAMPLE: 10 PPM 2CBMN, 10 PPM CEA
 RANGE: G 1, 15 LABEL: H 0, 4.0 QUAN: A 0, 1.0 BASE: U 20, 3

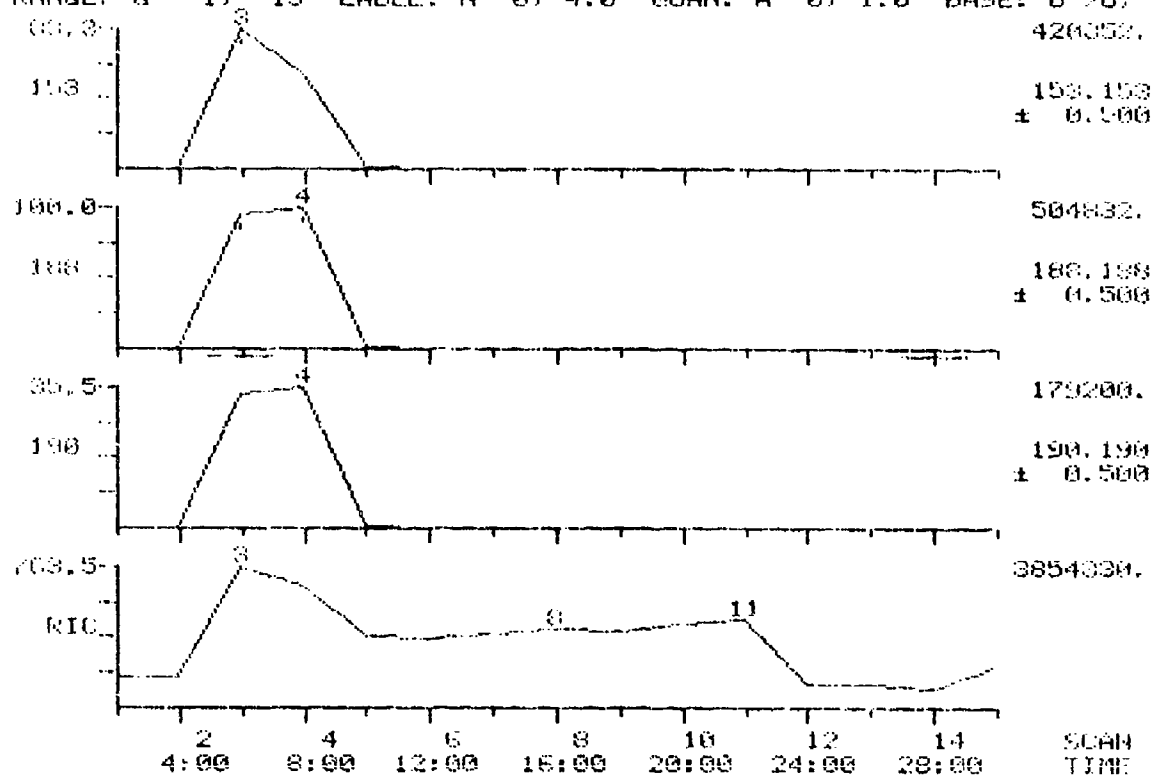


FIGURE 2. Peak Height Values for Spectrum of 2CBMN

CEAC52
M/E 139
CAL100-3UL,10FPMCEA+2CBHN,6/27;DEXSIL,125JSC,1500
3UL,3ONG AREA=46490
AMP.: 00002316

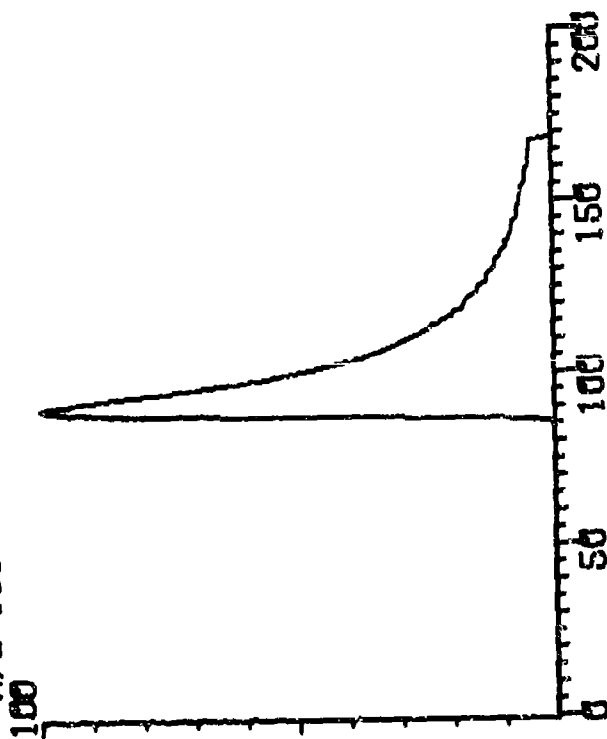


FIGURE 3. GC/MS Chromatogram of CEA

Melting point: 94°C

Boiling point: 310°C

Solubility: Alcohol, methylene chloride

Vapor pressure at 25°C: ~0.7 mg/m³

3. APPARATUS

- a. Instrumentation: Waters Assoc., High Performance Liquid Chromatograph Model 6000A with variable wavelength UV detector.
- b. LC Parameters:
 - (1) Column - μ -Bondapak CN (Waters Associates)
 - (2) Mobile Phase - 20% (v:v) methylene chloride in hexane
 - (3) Flow Rate - 1.0 mL/min
 - (4) System Pressure - Varied from 100 to 450 psi depending upon most recent column flush with methanol
 - (5) Detection - Ultra-violet at 260 nm; 0.01 absorbance units full scale.
 - (6) Injection Volume - 50 μ L into a 2 mL injection loop (Rheodyne Model 7120)
 - (7) Retention Times: O-chlorobenzaldehyde - 235 seconds;
o-chlorobenzylidinemalononitrile - 310 seconds
- c. Hardware/Glassware
 - (1) Soxhlet extraction apparatus: (per sample)
 - a. 250 mL flat-bottom reflux flash, #24/40
 - b. Siphon extractor #24/40 at bottom
 - c. Overhead condenser #45/50
 - (2) 250 mL separatory funnel with Teflon stopcock
 - (3) Steam bath plate
 - (4) Kuderna-Danish apparatus
 - a. 10-mL graduated ampule #24/40
 - b. 500-mL collection flask #24/40
 - c. 3-ball Snyder column #24/40
 - d. Security springs; 2 per ampule
 - (5) 2-mL volumetric flask
 - (6) 10-mL volumetric flask

- (7) three 1-mL volumetric flasks
- (8) 50-mL volumetric flask
- (9) 100- μ L syringe
- (10) Extraction thimbles, Whatman cellulose 35 x 94 mm (ID)
- (11) Clean glass wool

d. Chemicals

- (1) Anhydrous, granular sodium sulfate, ACS grade.
Wash by Soxhlet extraction in methylene chloride overnight;
oven dry.
- (2) Methylene chloride, HPLC grade
- (3) Hexane, HPLC grade
- (4) Methanol, HPLC grade
- (5) o-Chlorobenzaldehyde; Army-205-PA-271
- (6) o-Chlorobenzylidenemalononitrile; Army-1206-PA-272

4. STANDARDS

a. Calibration Standards for Liquid Chromatograph

- (1) Master Stock: Approximately 100 mg CEA and 100 mg 2CBMN are weighted into a tared 1-mL volumetric flask and diluted to 1 mL with methylene chloride.
- (2) Calibration Stock: Dilute 250 μ L of the Master Stock to 50 mL using 20% (v:v) methylene chloride in hexane.
- (3) Working Standards: A minimum of three working calibration standards should be made daily and chromatographed before and after the soil sample extracts. They are made by diluting μ L quantities of calibration stock (2) in 1 mL of 20% methylene chloride in hexane, as shown below.

μ L of Calibration Stock in 1 mL		-----CEA----- μ g/mL ppm*		-----2CBMN----- μ g/mL ppm*	
Cal 1	10	5.00	1.00	5.00	1.00
Cal 2	100	50.00	10.00	50.00	10.00
Cal 3	200	100.00	20.00	100.00	20.00

*ppm value based on 50 grams soil

b. Spiking Standards

- (1) CEA Spike: Weigh out approximately 100 mg CEA and dilute to 1 mL with methylene chloride.
- (2) 2CBMN Spike: Weight out 125 mg 2CBMN and dilute to 1 mL with methylene chloride.
- (3) Spike Levels. Field samples are air dried overnight and separated into 50 gram portions. Spiked samples are prepared by injecting μ L quantities of CEA spike (1) and 2CBMN spike (2) into each 50-gram sample as shown below.

Level	μ L CEA (1) 50 grams soil	ppm Value	μ L 2CBMN (2) 50 grams soil	ppm Value
A	0	0	0	0
B	0.5	1.0	0.5	1.25
C	4	8.0	2	5.0
D	6	12.0	4	10.0
E	8	16.0	6	15.0
F	10	20.0	8	20.0

5. SAMPLE PREPARATION

a. Extraction: One Soxhlet extraction apparatus is required for each of the 10 samples prepared on a daily basis. Transfer entire soil sample to an extraction thimble and cover the top with glass wool to prevent sample loss. Add ~200 mL of methylene chloride to the flat-bottom reflux flask and connect the three-tier Soxhlet together. Set heating unit at an appropriate setting and allow the Soxhlets to extract overnight (or ~6-8 hours). Make sure the condenser hoses are secure and the water flow is sufficient.

b. Drying: In a 250-mL separatory funnel with a glass wool plug and Teflon stopcock add ~20 grams of clean sodium sulfate. Pass the soil extract through the sodium sulfate by adding small quantities to the separatory funnel and collecting the dried extract in an appropriate container dropwise until the entire sample has eluted. Rinse the

sulfate 3 times with a small amount of methylene chloride and add the washes to the dried sample.

c. Concentrating: One Kuderna-Danish (K-D) set-up is required for each soil extract. Connect the 10-mL ampule to the collection flask and secure the connection with 2 springs. Add the methylene chloride to the collection flask and connect the 3-ball Snyder column. Concentrate the samples using steam to less than 2 mL with rinsing, and remove from heat.

d. Final Sample Preparation: Transfer the concentrated extract to a 2-mL volumetric flask and dilute to 2 mL with methylene chloride. Then transfer the entire 2 mL sample to a 10-mL volumetric and dilute to mark with hexane. This will give a 20% solvent mix to resemble the mobile phase used during analysis.

e. Analysis: A series of instrument calibration standards is prepared, as outlined above, and analyzed during the same time period as the soil extracts. Curves are established by plotting concentration in mg/mL versus peak area. All calibration standards and samples should be analyzed in duplicate. In addition, after the first day of the program, one sample from the previous day is analyzed in duplicate to monitor day-to-day response. Chromatograms of calibration standards and spiked soil samples used to generate precision and accuracy data are shown in Figures 4 and 5 respectively. CEA elutes in approximately 4 minutes and 2CBMN elutes in approximately 5 minutes using the conditions outlined in this report.

6. CALCULATION: Read the concentration, in mg/mL, corresponding to the sample peak area from the standard curve. Multiply the mg found by 10 to obtain the total mg in the final extract volume of 10 mL. This is equivalent to mg per 50 grams, since 50 grams of soil was extracted initially. To obtain part-per-million values (mg/kg) multiply the mg/50 g by 20.

For these validation studies, the ppm levels (spiked versus Found) were plotted by the method of Hubaux and Vos to obtain detection limits, precision and accuracy of the method. The results of the precision and

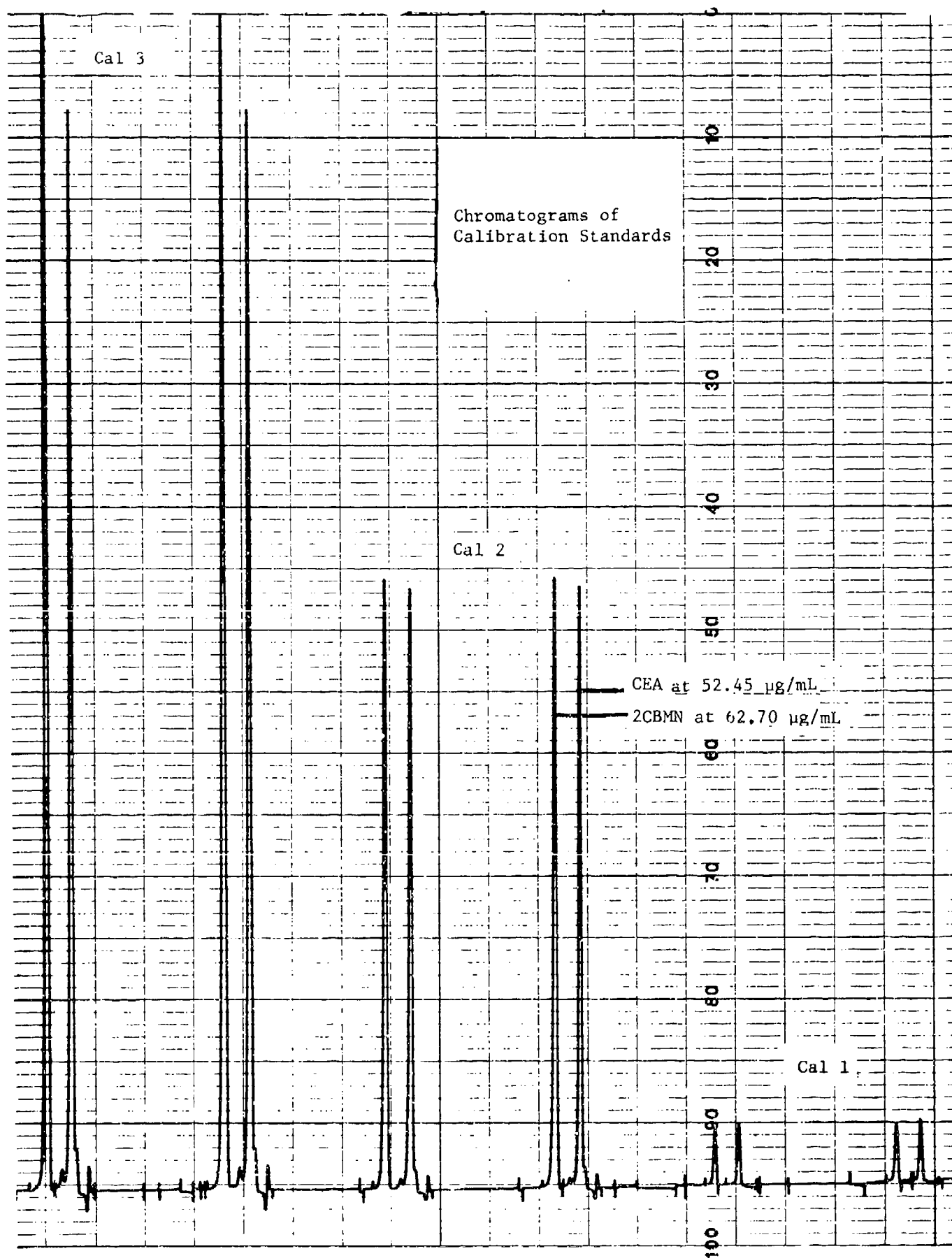


FIGURE 4. HPLC Chromatogram of CEA and 2CBMN

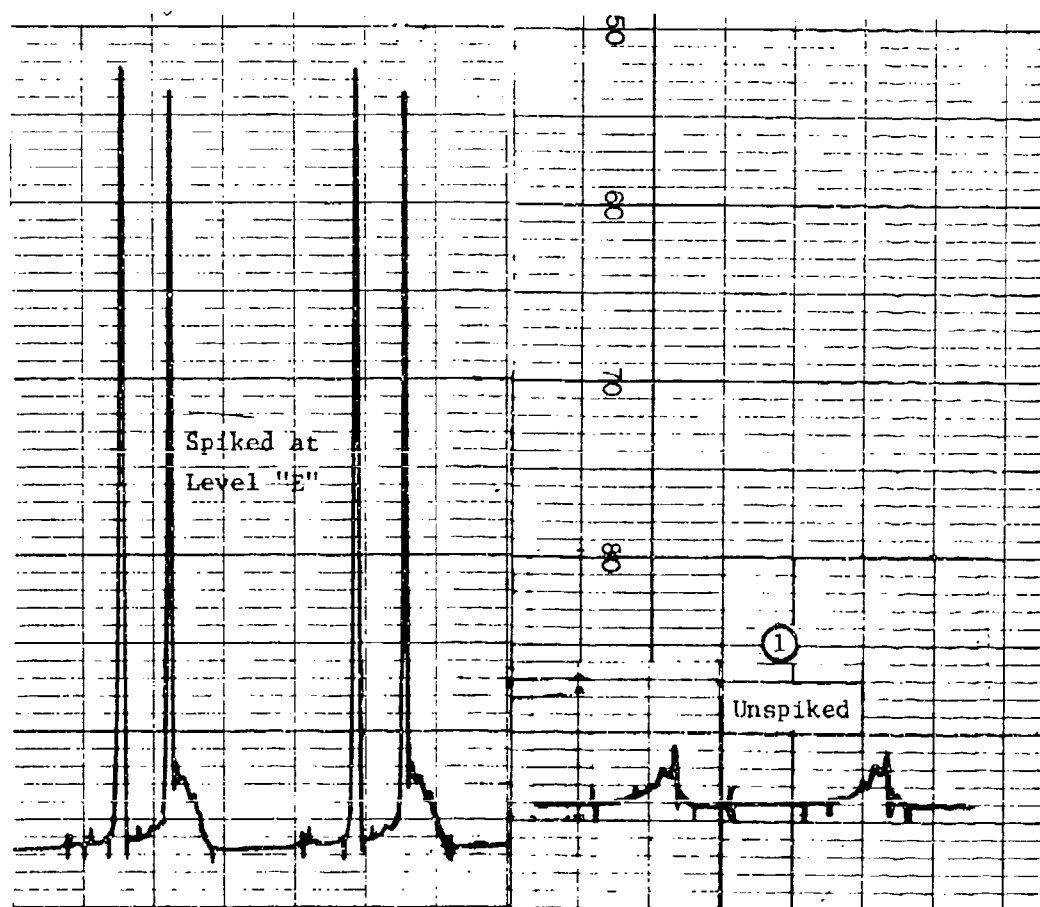


FIGURE 5 HPLC Chromatogram of CEA and 2CBMN
Spiked Soil Sample

accuracy tests for CEA and 2CBMN may be found in Appendices A and B respectively.

7. REFERENCE: NIOSH Manual of Analytical Methods, Volume 5, pp. 304-1 to 304-10. Date issued: 4/79.

II. FIELD SAMPLE ANALYSIS

This section of the report summarizes experiments performed on soil samples collected at Camp Simms and analyzed for o-chlorobenzylidenemalononitrile (2CBMN) and o-chlorobenzaldehyde (CEA). Samples were analyzed initially by high performance liquid chromatography (HPLC). Field samples were collected by USATHAMA personnel in a 50' x 150' area shown on the map in Figure 6. A total of eighteen samples were collected and shipped to Arthur D. Little, Inc., for analysis. Of the samples without any interference present, not more than 2 ppm of 2CBMN or CEA was present based on detection limits calculated by the method of Hubaux and Vos. Two field samples were also analyzed by high resolution mass spectrometry and gas chromatography/mass spectrometry to confirm these results. Finally, six field samples were analyzed by gas chromatography/flame ionization detection which confirmed the absence of any CEA in these samples. Details of each of these experiments may be found on the following pages.

A. Sample Preparation and Analysis

All samples were extracted and analyzed by the method described earlier in this report. Briefly, 50 g samples were extracted overnight in Soxhlet extractors with methylene chloride, followed by Kuderna-Danish concentration to a final volume of 10 mL. After drying with sodium sulfate, the extracts were analyzed by reverse phase HPLC using a μ -Bondapak CN column and UV detection at 260 nm. The mobile phase, flowing at 1.0 mL/min, was 20% methylene chloride in hexane.

B. Quality Control

The submitted field samples were analyzed in conjunction with a complete, quantitative set of QC spiked soil samples prepared as part of the ongoing method validation effort for CEA and 2CBMN. Complete QC data may be found in Appendices A and B. The detection limit at the 90% confidence level, calculated as outlined in the USATHAMA QA protocol of May 1980, is 2.4 ppm CEA and 1.7 ppm 2CBMN.

C. Results and Discussion

The results of the HPLC analysis of submitted field samples are shown in Table 1. For several of the samples, an asterisk has been placed in the column under CEA due to an interference problem encountered during the analysis which obscured the CEA peak. An example chromatogram of a sample with the interference is shown in Figure 7.

In order to identify the interference and to ascertain whether any 2CBMN or CEA was present in the samples, two samples were analyzed by both high resolution mass spectrometry to detect the 2CBMN and by gas chromatography/mass spectrometry to detect the CEA. No 2CBMN or CEA was detected in either sample. The spectra obtained are shown in Figures 8-11. From these analyses, no predominant organic species emerged which could explain the interference encountered during the HPLC analyses, suggesting that the interference was an analytical problem rather than an environmental problem.

Based on information gained during the GC/MS analysis, it was decided to analyze the extracted field samples which showed an interfering peak by gas chromatography using a flame ionization detector. While this method is not as sensitive as the HPLC method, the CEA peak was not obscured. "Limited analysis" quality control as defined in the USATHAMA QC Plan of May 1980 was performed in conjunction with these analyses. The detection limit at the 90% confidence level for the GC/FID method is 14.6 ppm CEA. No CEA was detected in field samples CSS10, 16, 17, 20, 22, or 23. The chromatograms, data and Hubaux and Vos plots are shown in Appendix C.

TABLE 1

Camp Simms Field Sample Results by HPLC

<u>Sample No.</u>	<u>ppm OCE</u>	<u>ppm CS</u>
CSS01	ND	ND
CSS02	ND	ND
CSS03	ND	ND
CSS08	ND	ND
CSS09	ND	ND
CSS10	ND	ND
CSS14	ND	ND
CSS15	ND	ND
CSS16	*	ND
CSS17	*	ND
CSS18	----broken in transport----	
CSS19	ND	ND
CSS20	*	ND
CSS21	ND	ND
CSS22	*	ND
CSS23	*	ND
CSS24	*	ND
CSS25	ND	ND

ND = None detected

x(d) = 2.4 ppm CEA

x(d) = 1.7 ppm 2CBMN

* = Interference present

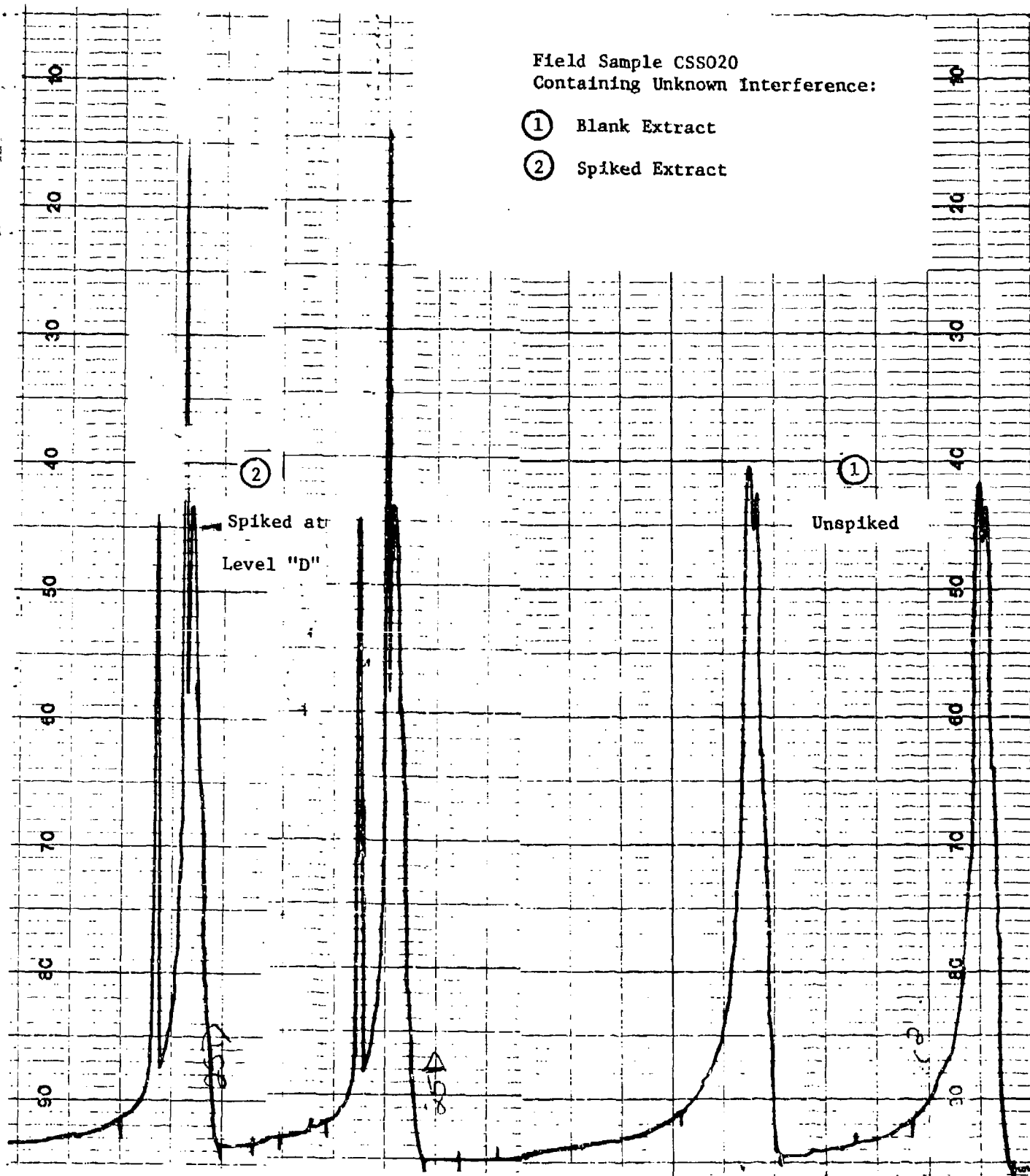


Figure 7 HPLC Chromatogram
of Field Sample CSS20.

100% SPECTRUM DATA: HFGUSS22A #13 Base File: 52
 01:10:00 (4:29:00 + 26:00) CALI: HFGUSS22A #14 RIC: 641400
 Sample: Field CSS 2
 01:10 #20 SUMMED - #1 TO #5 X2.50

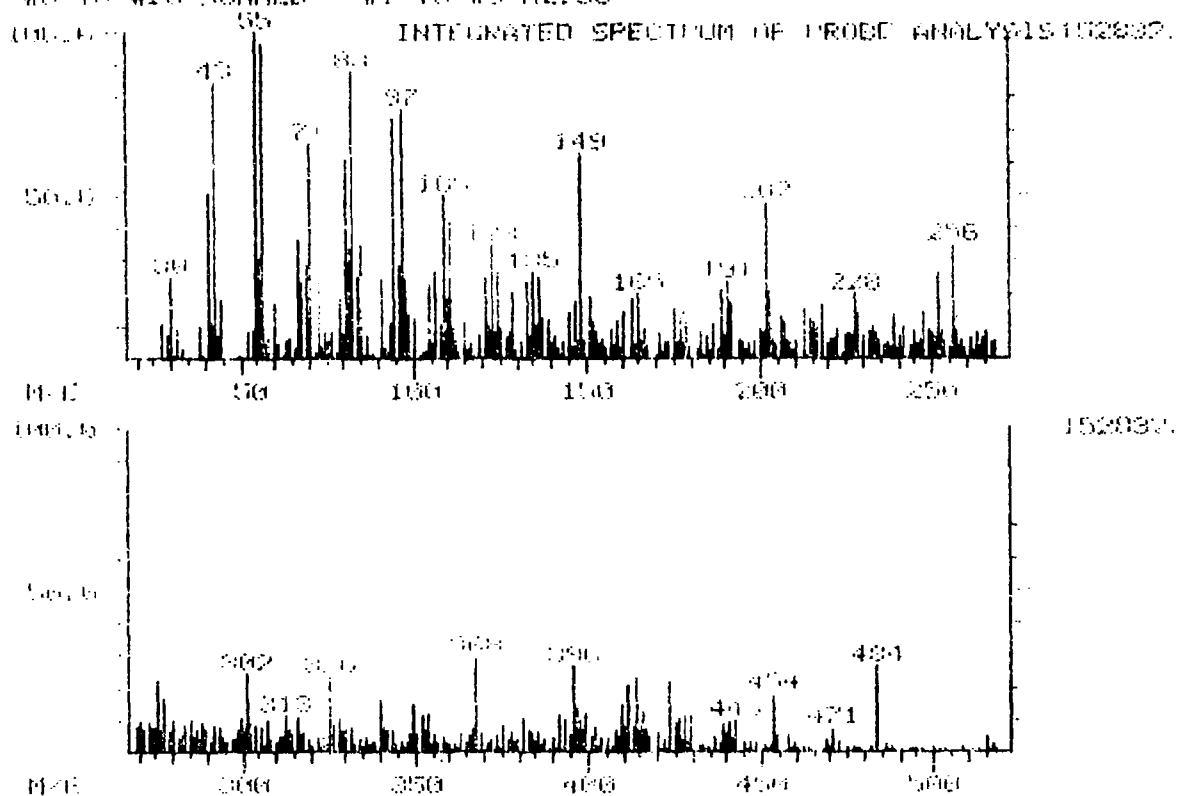


Figure 8. Integrated Spectrum of
 Field Sample CSS22.

100% ACCURACY, 100% TIME
 08:00:00 10:29:00
 100% 100% 100%

100% 100% 100%
 100% 100% 100%

100% 100% 100%
 100% 100% 100%

100% 100% 100%
 100% 100% 100%

100%
 100%
 100%

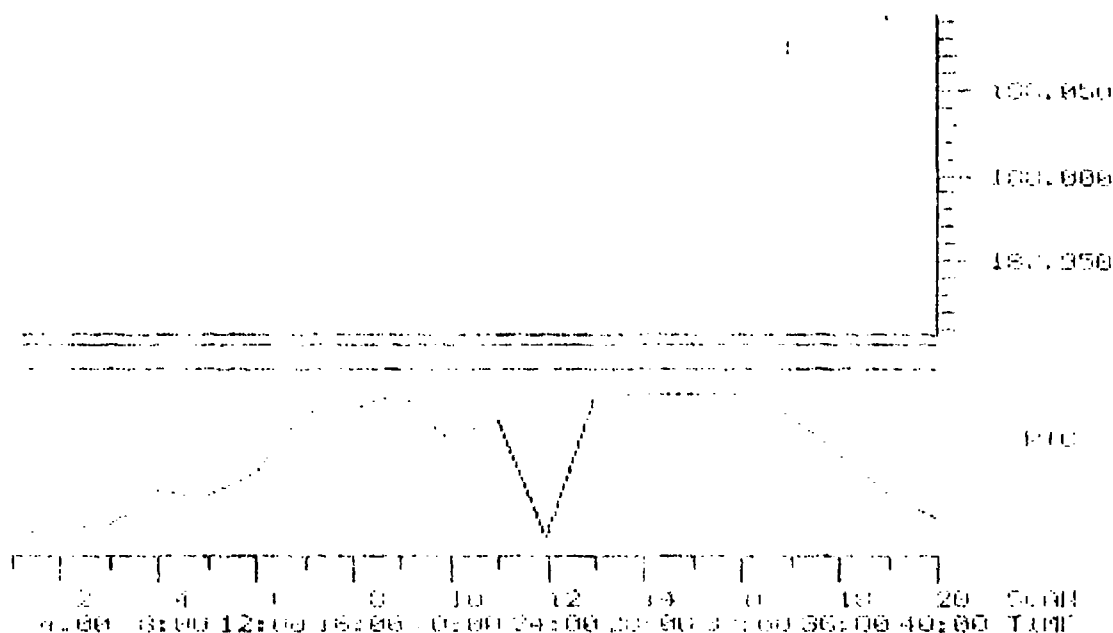


Figure 9 Specific Ion High Resolution
 Search Field Sample CSS22.

MASS SPECTRUM DATA: HCSS23 #6 BASE M/L: 209
 06/27/80 11:11:00 + 12:00 CALI: HCSS23 #3 RIC: 1083890.
 SAMPLE: ARMY
 #3 TO #10 SUMMED - #1 TO #2 X3.00

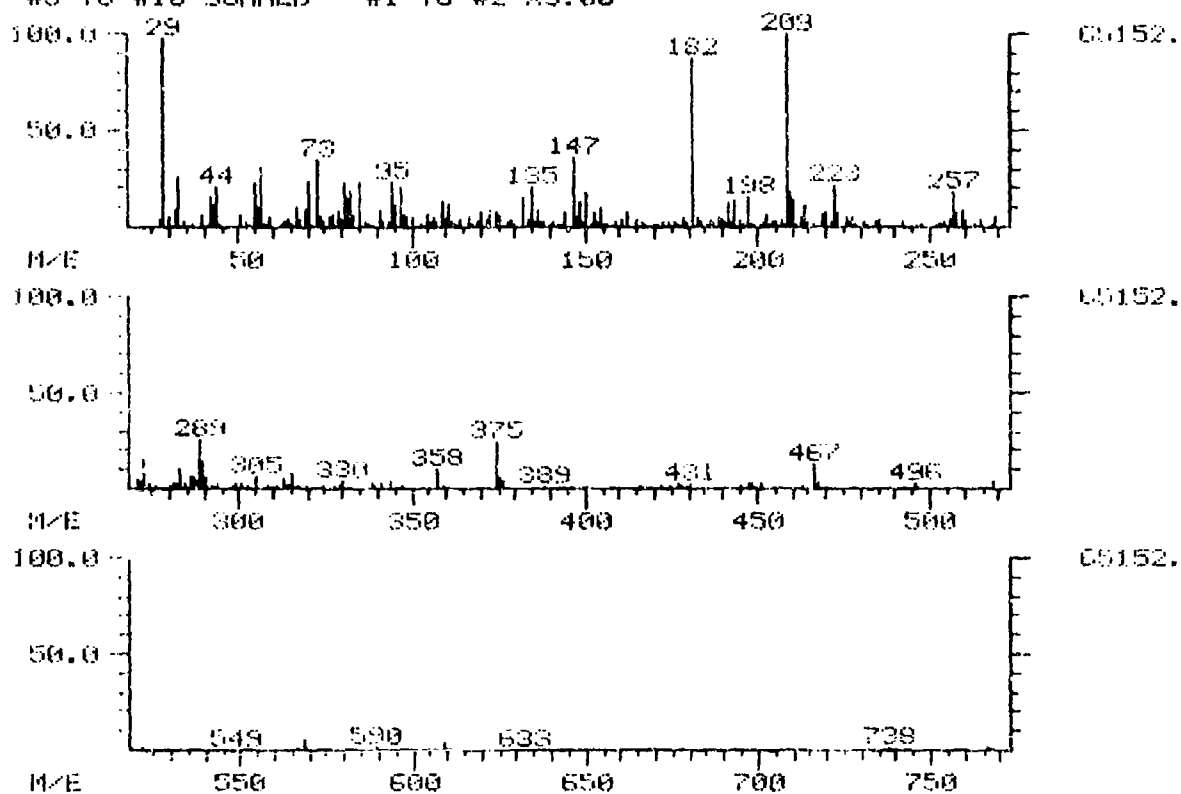


Figure 10 Integrated Spectrum of Field Sample CSS23.

NIC + MASS CHROMATOGRAMS DATA: HCSS23 #1 SCANS 1 TO 10
 05/27/80 11:11:00 CALI: HCSS23 #3
 SAMPLE: ARMY
 RANGE: G 1, 10 LABEL: N 0, 4.0 QUAN: A 0, 1.0 BASE: U 20, 3

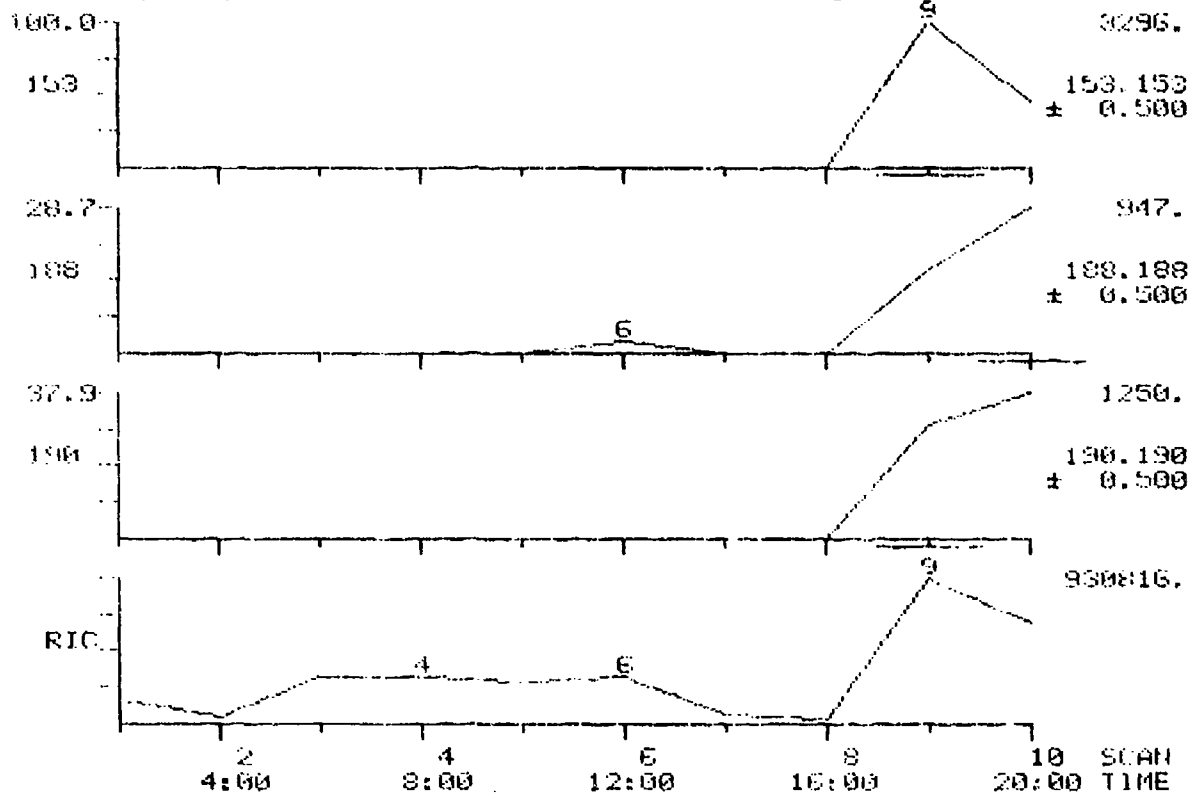


Figure 11 Peak Height Values for
 Field Sample CSS23.

APPENDIX A

Precision and Accuracy Data Set
of o-Chlorobenzaldehyde in soil
Analyzed by the HPLC Method Developed
under Task R902.35.01

CEA P&A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.15
 12
 20
 8
 16
 1.15
 12
 20
 8
 16

1.15
 12
 20
 8
 16
 1.15
 12
 20
 8
 16

8
 16
 1.15
 12
 20
 8
 16
 1.15
 12
 20

8
 16
 1.15
 12
 20
 8
 16
 1.15
 12
 20

MEAN= 11.43 SD= 6.59600500692

PEAK AREA

0.495
 13.5
 19.6
 6.57
 14.6
 0.077
 13.7
 24
 6.98
 15.7

0.494
 10.9
 18
 6.39
 15
 0.374
 13.7
 24.1
 7.04
 17.6

6.95
 15.6
 0.426
 11.4
 17.0
 0.6
 19.4
 0.626
 12.3
 19.0

7.47
 14.6
 0.761
 9.94
 18.9
 9.8
 18.8
 0.788
 13.4
 23.4

MEAN= 11.499525 SD= 7.27830508935

NO. OF PAIRS 40
 NO. RUNS 4 TOTAL X-Y 40 NO. CONCENTR 5

INTERCEPT= -0.800534157559
 SLOPE= 1.0761206612
 R= 0.973240414108
 MEAN SQR DEV OF POINTS FROM REGRESSION= 2.65891730041
 D.F.= 30
 ENTER 2 TAIL P LEVEL (USUALLY .1, EACH CONFID BAND IS
 .05 SO TOTAL P= .1)
 .1
 t= 1.68595113285
 y(c)= 0.509269298529
 x(d)= 2.35551258249

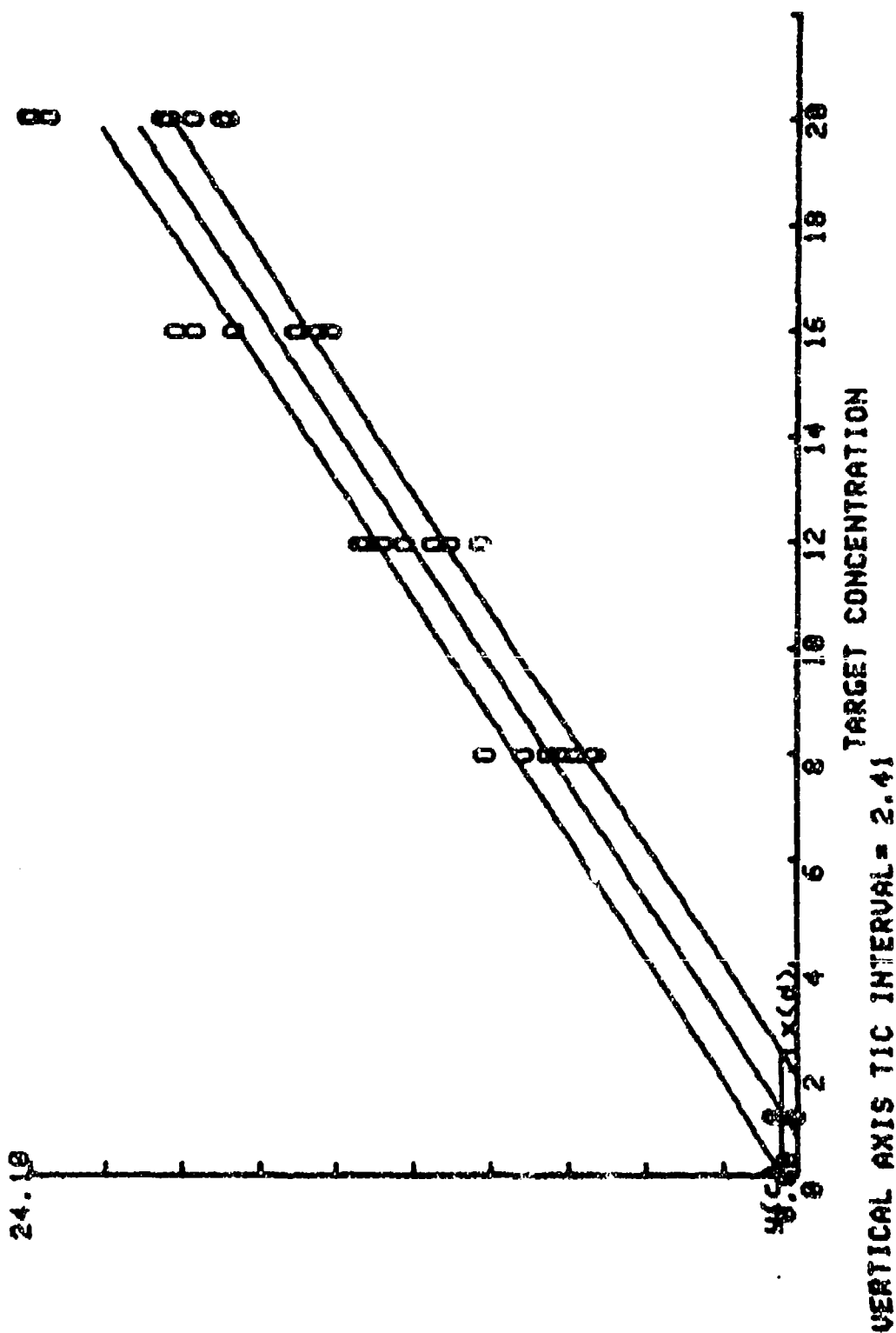
CEA P&A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.15	1.15	8	16	8	16
12	12	16	1.15	16	1.15
20	20	1.15	12	12	20
8	8	20	20	8	20
16	16	8	16	16	16
1.15	1.15	1.15	1.15	1.15	1.15
12	12	12	12	12	12
20	20	20	20	20	20
8	8	8	8	8	8
16	16	16	16	16	16

FOUND CONCENTR

1.203993302451	1.20296376069	7.68550819228	7.68550819228
13.280969047	10.0720831063	14.3111592527	14.3111592527
18.9574783693	17.470656252	1.45107720152	1.45107720152
6.84917075127	6.60190326307	9.90078983591	9.90078983591
14.3111592527	14.602064702	18.306993693	18.306993693
0.81546074636	1.09145210189	9.85069290065	9.85069290065
13.4748218117	13.4748218117	10.2140673107	10.2140673107
23.046239192	23.1391655743	1.47616732475	1.47616732475
7.23016091004	0.02933500691	12.8243371353	12.8243371353
15.3333494583	17.0909507227	22.4086000298	22.4086000298

CEA P&A PART 2: EVALUATION OF PPM SPIKE US PPM RECOVERED
 COMBINED DATA ALL RUNS
 PEAK AREA



CEA PLA PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.15 8 12 16
 20

MEAN= 11.43 SD= 7.28179236177

FOUND CONCENTRATION

1.21330182073 7.78308069373 12.1784987781 15.9954499325
 19.979668575

MEAN= 11.43 SD= 7.28322313442

NO. OF PAIRS 5
 NO. RUNS 4 TOTAL X-Y 40 NO. CONCENTR 5

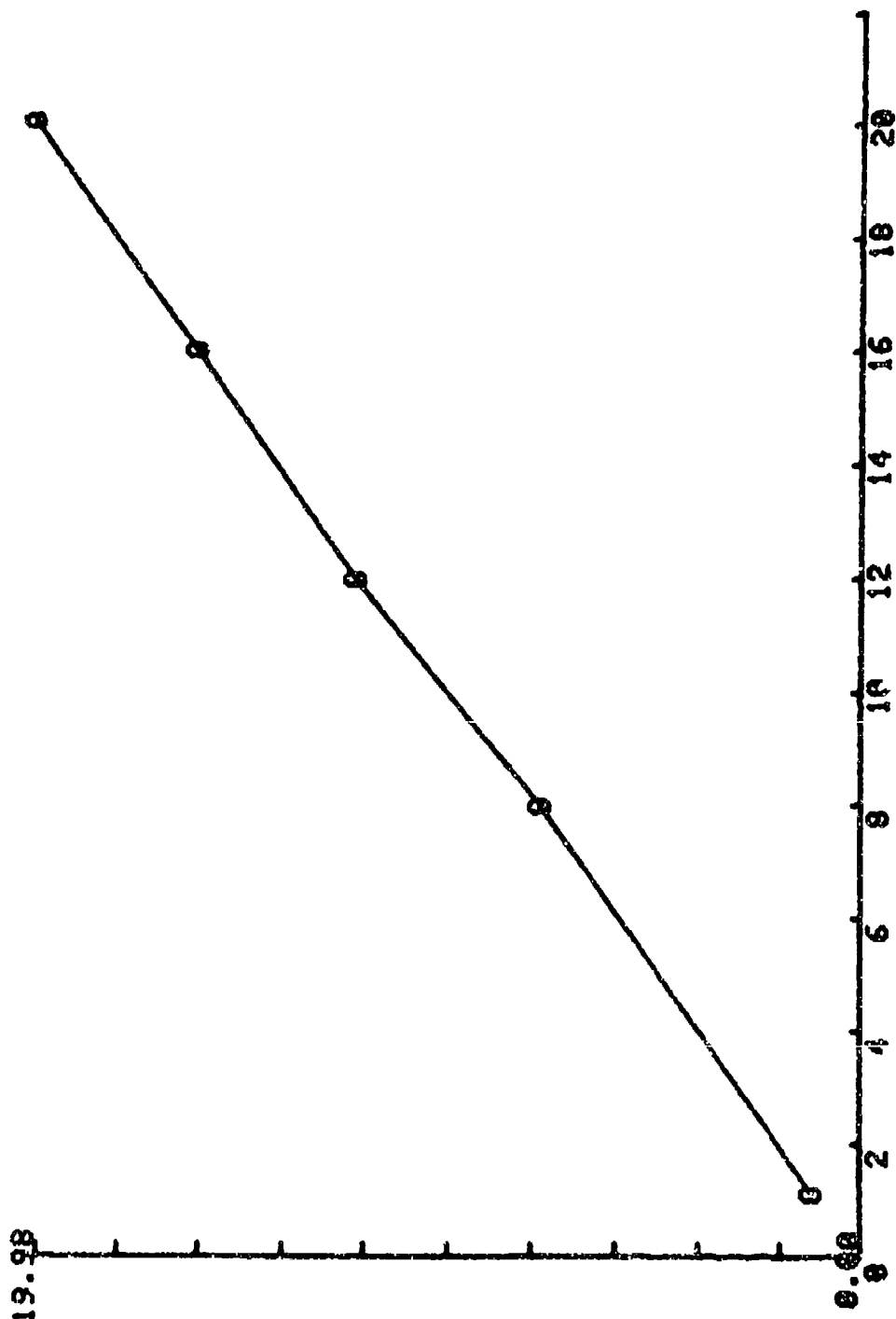
INTERCEPT= -2.195300605E-13

SLOPE= 1

R= 0.999003552271

MEAN SQR DEV OF POINTS FROM REGRESSION= 0.0277856343067

CEA P1A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 FOUND CONCENTRATION



VERTICAL AXIS TIC INTERVAL = 1.9979668575

CEA P1A PART 2: EVALUATION OF PPM SPIKE US PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.13	8	12	16
20			

MEAN= 11.43 SD= 7.28179236177

STANDARD DEVIATION

0.0004298274227	0.483561636412	0.300061024162	0.67388791209
0.945246264698			

MEAN= 0.520637332957 SD= 0.320815847868

NO. OF PAIRS 3
 NO. RUNS 4 TOTAL X-Y 40 NO. CONCENTR 5

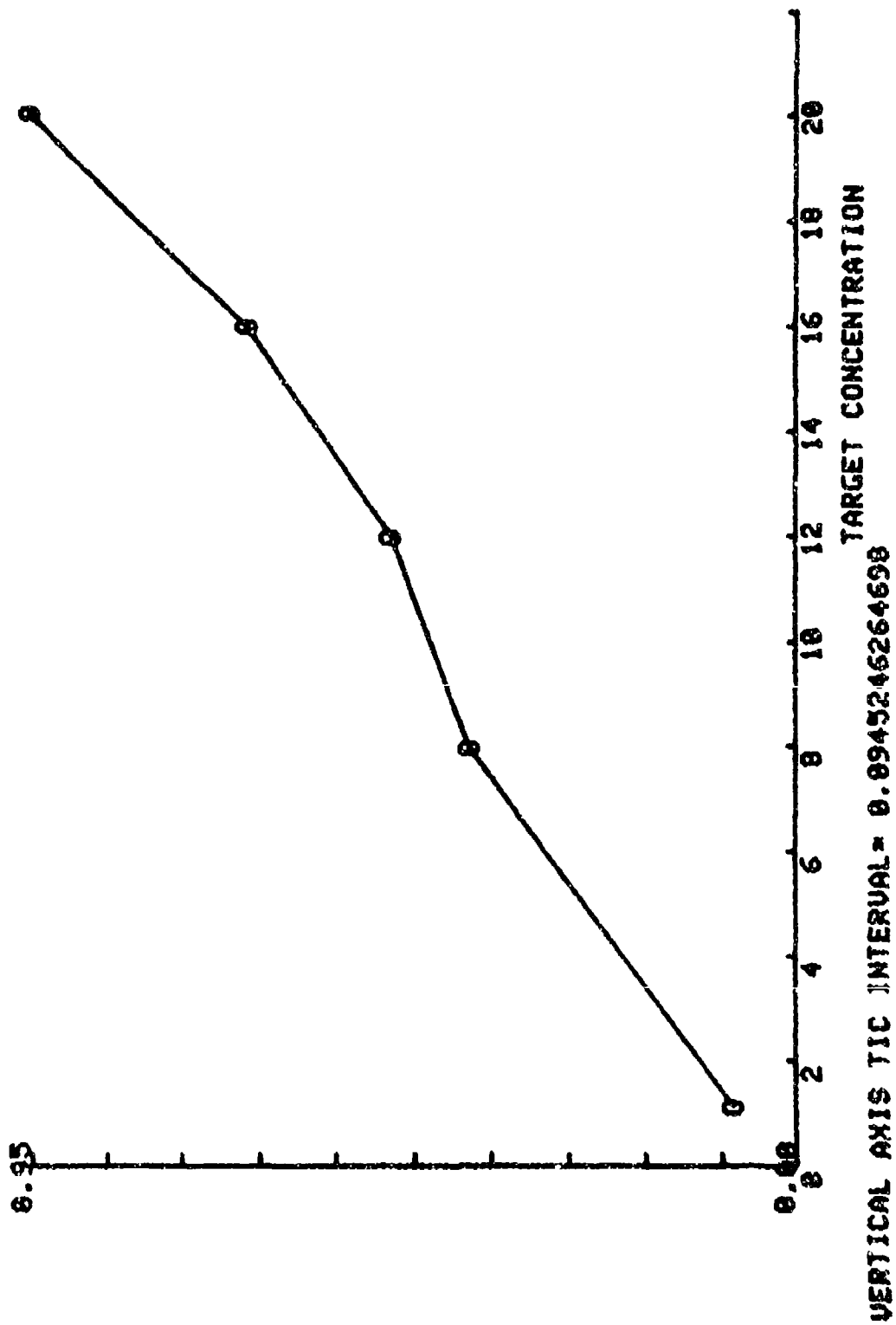
INTERCEPT= 0.0219145164052

SLOPE= 0.0436327923492

R= 0.998363454121

MEAN SQR DEV OF POINTS FROM REGRESSION= 0.00263156706017

CEA PEA PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 STANDARD DEVIATION



CEA P&A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.15	8	12	16
20			

MEAN= 11.43 SD= 7.28179236177

PERCENT INACCURACY

5.58458615007	-2.71148822842	1.48748981751	-0.0284379221983
-0.101657125008			

MEAN= 0.830082418392 SD= 3.01787774603

NO. OF PAIRS 5

NO. RUNS 4 TOTAL X-Y 48 NO. CONCENTR 5

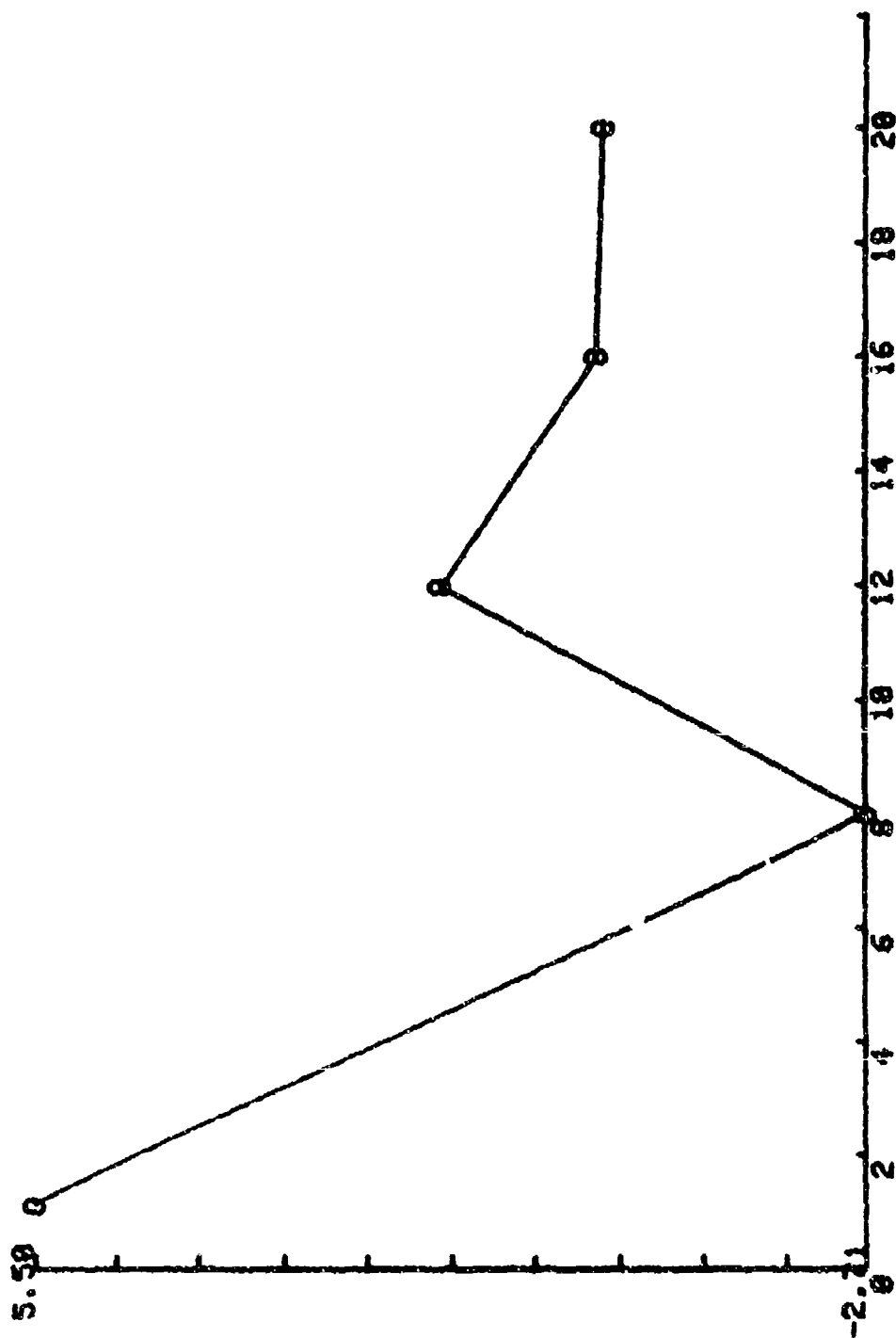
INTERCEPT= 3.38659813045

SLOPE= -0.223665466496

R= -0.539681492885

MEAN SQR DEV OF POINTS FROM REGRESSION= 8.60659461286

CEA P&A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 PERCENT INACCURACY



TARGET CONCENTRATION

VERTICAL AXIS TIC INTERVAL = 0.821599497849

CEA P&A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.15 8 12 16
 28

MEAN= 11.43 SD= 7.28179236177

PERCENT IMPRECISION

6.62980409847 5.18511424874 4.10609742033 4.21299753953
 4.73104076351

MEAN= 4.97205081412 SD= 1.02164206200

NO. OF PAIRS 5

NO. RUNS 4 TOTAL X-Y 40 NO. CONCENTR 5

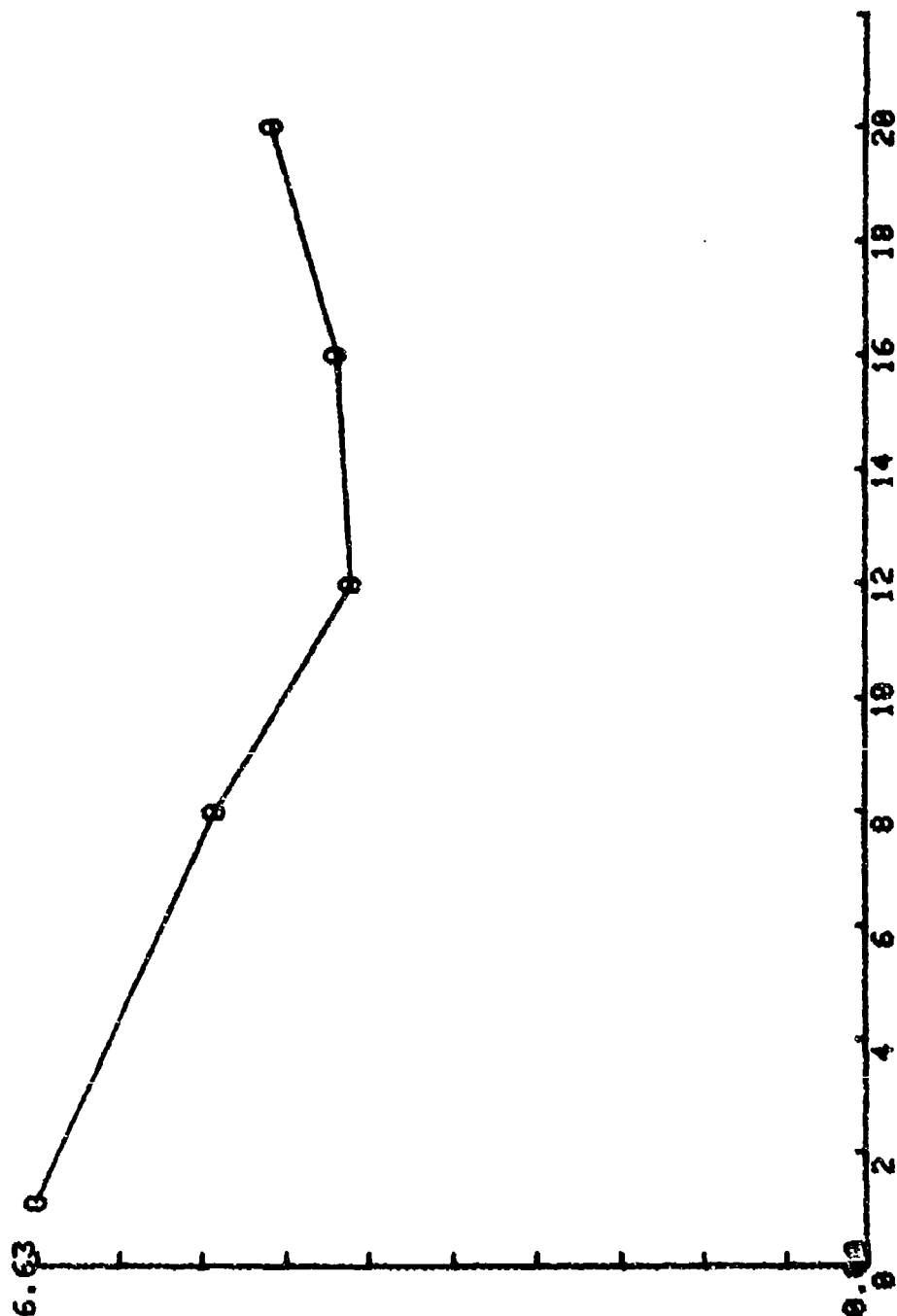
INTERCEPT= 6.2550173813

SLOPE= -0.112175552702

R= -0.79953548621

MEAN SQR DEV OF POINTS FROM REGRESSION= 0.502035221016

CEA P&A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 PERCENT IMPRECISION



TARGET CONCENTRATION

VERTICAL AXIS TIC INTERVAL = 0.662900409847

CEA P&A PART 2: EVALUATION OF PPM SPIKE US PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.15	8	12	16
20			
MEAN= 11.43 SD= 7.28179236177			
PERCENT RECOVERY			
105.50450615	97.2885111716	101.487489018	99.9715620778
99.898342875			

MEAN= 100.830082418 SD= 3.01787774603

NO. OF PAIRS 5

NO. RUNS 4 TOTAL X-Y 40 NO. CONCENTR 5

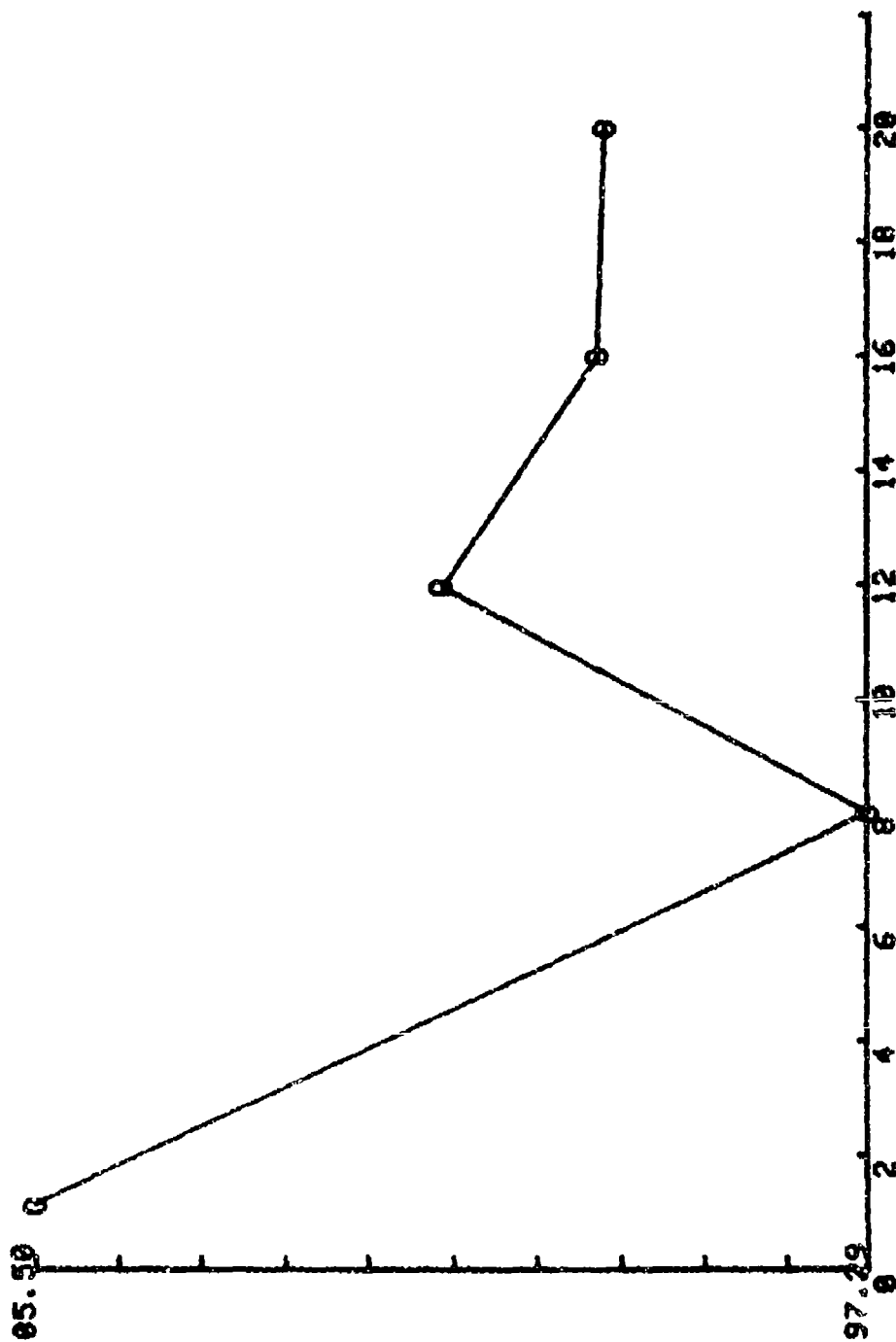
INTERCEPT= 103.38659013

SLOPE= -0.223666466497

R= -0.339681492884

MEAN SQR DEV OF POINTS FROM REGRESSION= 8.60659461209

CEA P&A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 PERCENT RECOVERY



TARGET CONCENTRATION

VERTICAL AXIS TIC INTERVAL = 0.821599497849

APPENDIX B

Precision and Accuracy Data

Set of o-Chlorobenzylidenemalononitrile
in soil. Analyzed by the HPLC method

Developed under Task R902.35.01

208NN P&P PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.16	1.16	4.54	4.54
9.1	9.1	13.6	13.6
18.2	18.2	1.16	1.16
4.54	4.54	9.1	9.1
13.6	13.6	18.2	18.2
1.16	1.16	4.54	4.54
9.1	9.1	13.6	13.6
18.2	18.2	1.16	1.16
4.54	4.54	9.1	9.1
13.6	13.6	18.2	18.2

MEAN= 9.32 SD= 6.18774969416

PEAK AREA

1.5	1.31	4.73
9.54	8.49	13.5
17.6	16.1	6.814
5.43	5.66	18
15.4	15.8	21.6
8.296	8.523	4.67
8.73	9.37	14
18.3	18.7	9.16
5.19	5.21	18.2
13.9	14.3	28.2

MEAN= 9.786525 SD= 6.81938347461

NO. OF PAIRS 40
 NO. RUNS 4 TOTAL X-Y 40 NO. CONCENTR 5

INTERCEPT= -0.400207073014
 SLOPE= 1.00520026543
 R= 0.904750027563
 MEAN SQR DEV OF POINTS FROM REGRESSION= 1.44394301165
 D.F.= 38
 ENTER 2 TAIL P LEVEL (USUALLY .1, EACH CONFID BAND IS
 .05 SO TOTAL P= .1)
 .1
 t= 1.60595113205
 y(c)= 0.516016039133
 x(d)= 1.66375063406

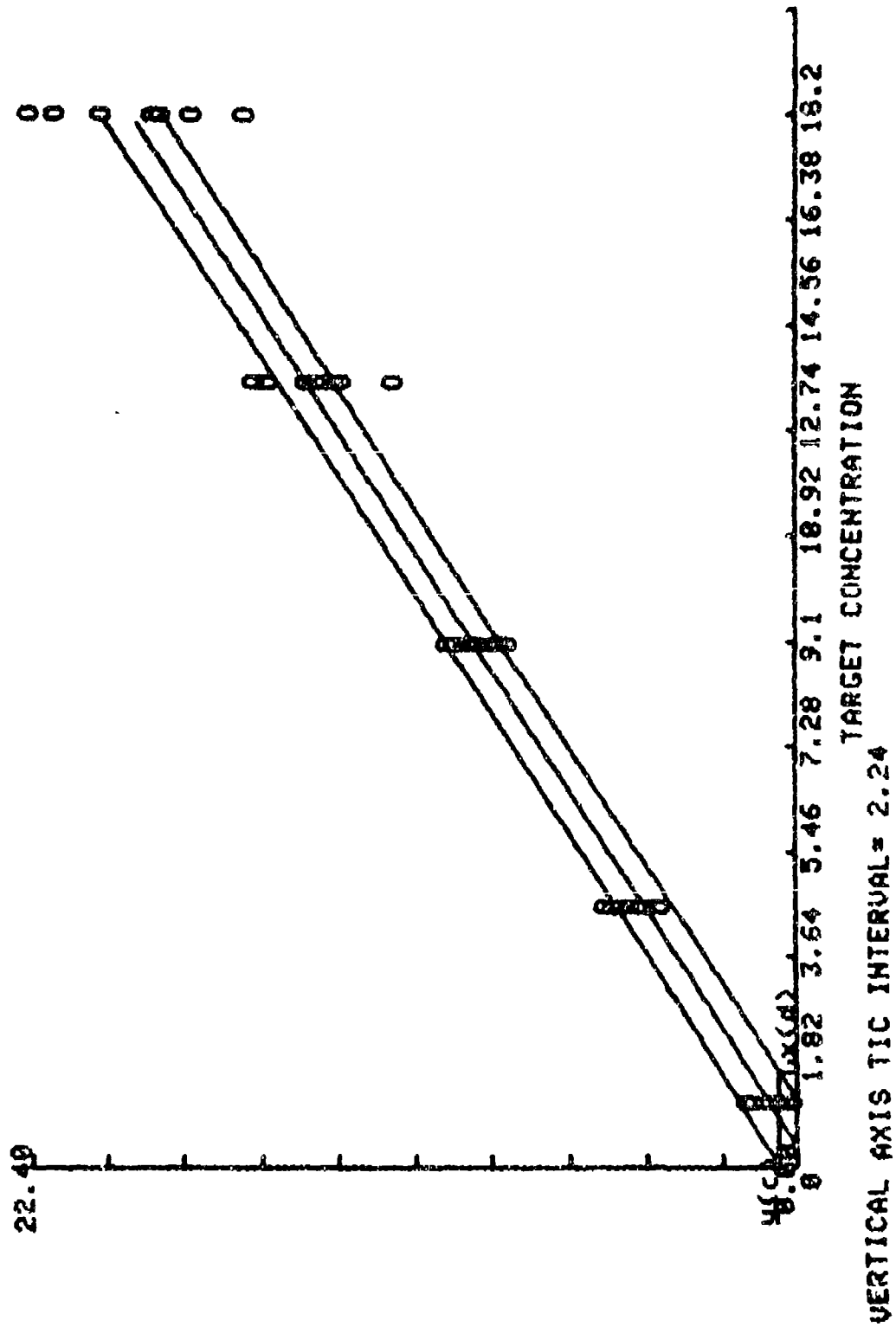
2CBM P&R PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.16	1.16	4.54	4.54
9.1	9.1	13.6	13.6
18.2	18.2	1.16	1.16
4.54	4.54	9.1	9.1
13.6	13.6	18.2	18.2
1.16	1.16	4.54	4.54
9.1	9.1	13.6	13.6
18.2	18.2	1.16	1.16
4.54	4.54	9.1	9.1
13.6	13.6	18.2	18.2

FOUND CONCENTR

1.75833573357	4.1356018503	4.73452548386
9.16656037219	12.6311032371	12.815387432
16.5932134283	1.11057679035	1.12624094692
5.37952016615	8.53999410939	9.59041402055
14.566097204	20.2788973271	20.2788973271
0.548944002025	4.50417024019	4.67924022538
0.42020930268	11.248971775	13.2760979194
17.4224923055	0.515330840693	0.523631629465
5.15037913223	9.00991080649	9.77469821549
13.1839550219	21.0160341069	10.9089079625

20BMN P1.9 PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 PEAK AREA



2CBM P&A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.16	4.54	9.1	13.6
18.2			

MEAN= 9.32 SD= 6.8310906089

FOUND CONCENTRATION

1.01555525234	4.91996145502	8.96384775775	13.2760979194
18.4245376135			

MEAN= 9.32 SD= 6.83729299731

NO. OF PAIRS 5

NO. RUNS 4 TOTAL X-Y 40 NO. CONCENTR 5

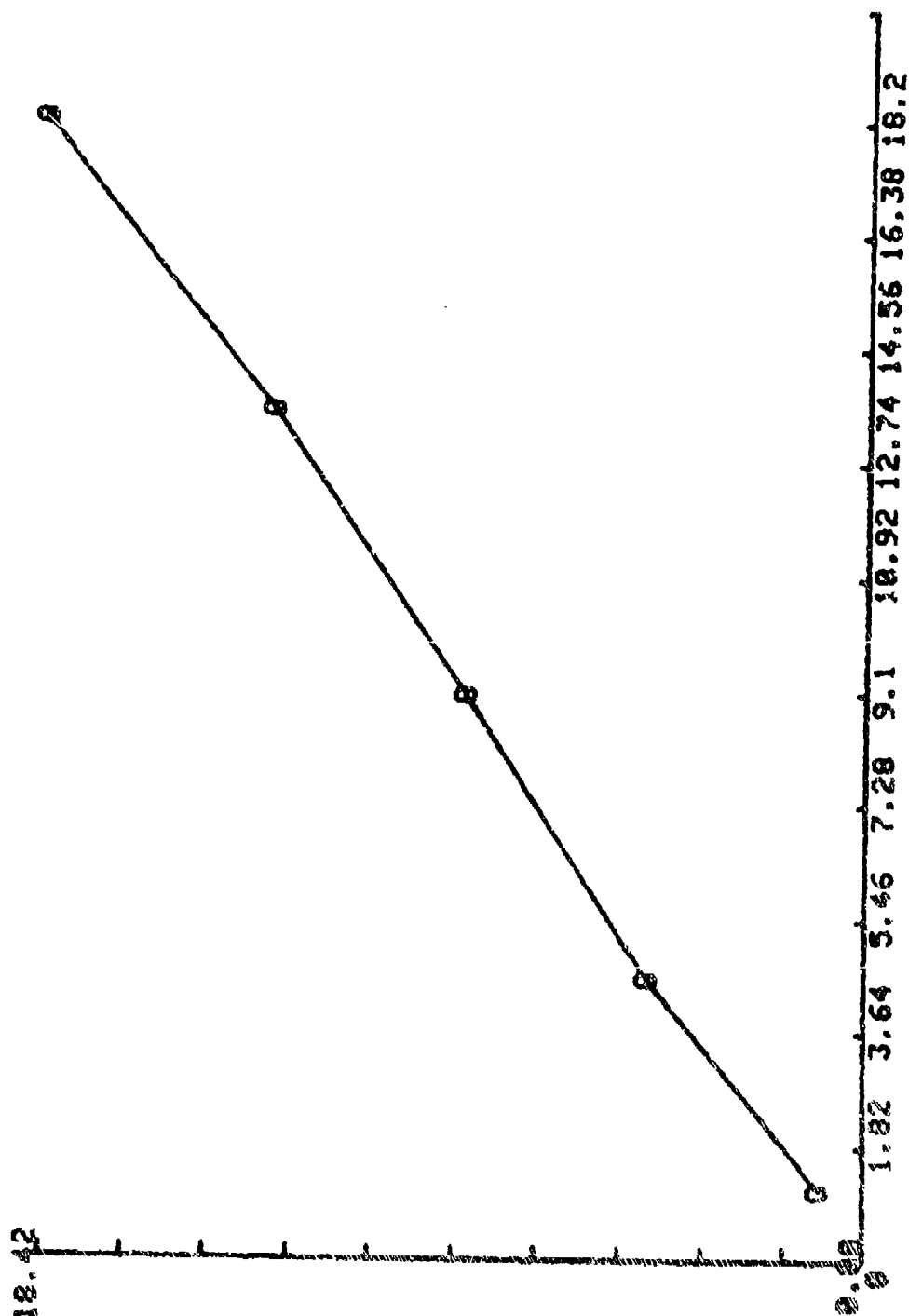
INTERCEPT= 7.484301867E-13

SLOPE= 1

R= 0.999092870759

MEAN SQR DEV OF POINTS FROM REGRESSION= 0.113034041379

202NN P8A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 FOUND CONCENTRATION



VERTICAL AXIS TIC INTERVAL = 1.84245376155
 TARGET CONCENTRATION

2CBMNH P&A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.16	4.54	9.1	13.6
18.2			

MEAN= 9.32 SD= 6.8318986889

STANDARD DEVIATION

0.17766609113	0.184354118948	0.289736636418	0.434184686213
0.772818156565			

MEAN= 0.355758336255 SD= 0.256174583963

NO. OF PAIRS 5

NO. RUNS 4 TOTAL X-Y 48 NO. CONCENTR 5

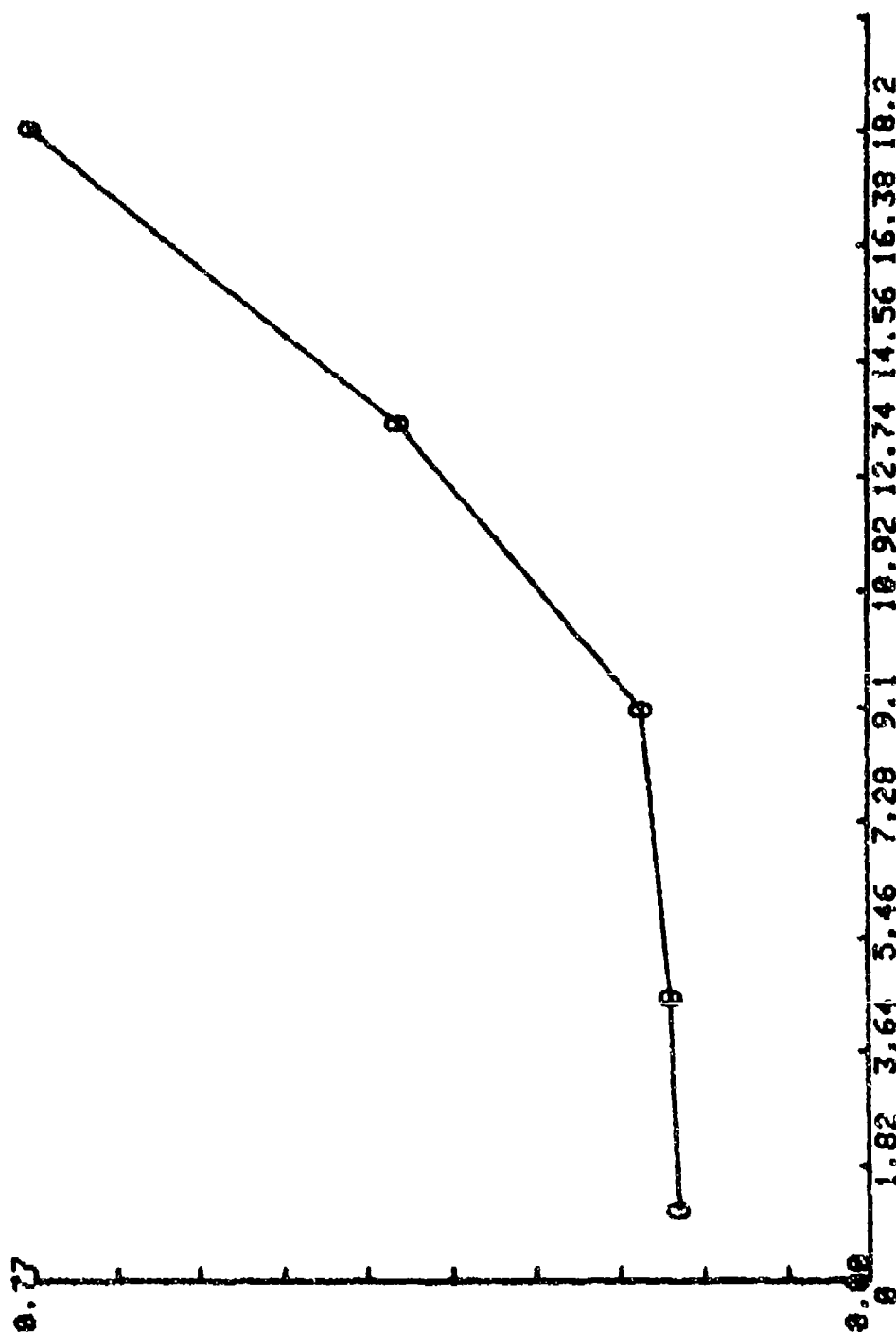
INTERCEPT= 0.8389962721701

SLOPE= 0.0339864875628

R= 0.986275898449

MEAN SQR DEV OF POINTS FROM REGRESSION= 0.015633189325

208MH P&A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 STANDARD DEVIATION



TARGET CONCENTRATION

VERTICAL AXIS TIC INTERVAL = 0.0772010156563

20BNN P&A PART 21 EVALUATION OF PPM SPIKE US PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.16 4.54 9.1 13.6
 18.2

MEAN= 9.32 SD= 6.0310906889

PERCENT INACCURACY

-12.4521334194 8.36919504451 -1.49617848624 -2.38163294503
 1.23372316222

MEAN= -1.34540532094 SD= 7.50001693665

NO. OF PAIRS 5

NO. RUNS 4 TOTAL X-Y 40 NO. CONCENTR 5

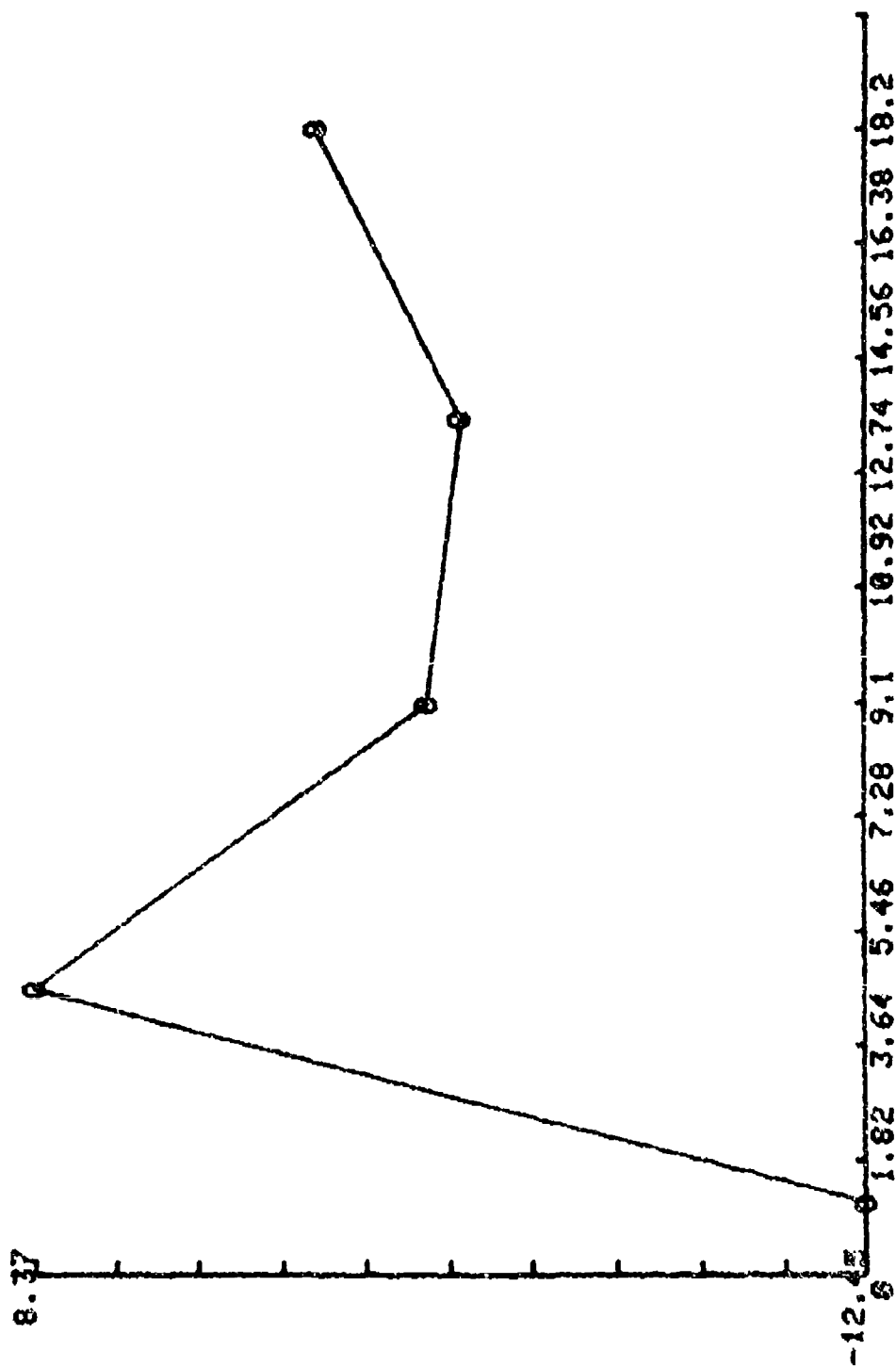
INTERCEPT= -4.4759137703

SLOPE= 0.335891463665

R= 0.303607335371

MEAN SQR DEV OF POINTS FROM REGRESSION= 60.1407531958

208MM P2A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 PERCENT INACCURACY



TARGET CONCENTRATION

VERTICAL AXIS TIC INTERVAL = 2.08213284639

20000 PPM PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.16 4.54 9.1 13.6
 18.2

MEAN= 9.32 SD= 6.8310906889

PERCENT IMPRECISION

17.4944780910 3.74786413117 2.33988587451 3.27842395175
 4.19446160700

MEAN= 6.20924673127 SD= 6.34681057728

NO. OF PAIRS 5
 NO. RUNS 4 TOTAL X-Y 40 NO. CONCENTR 5

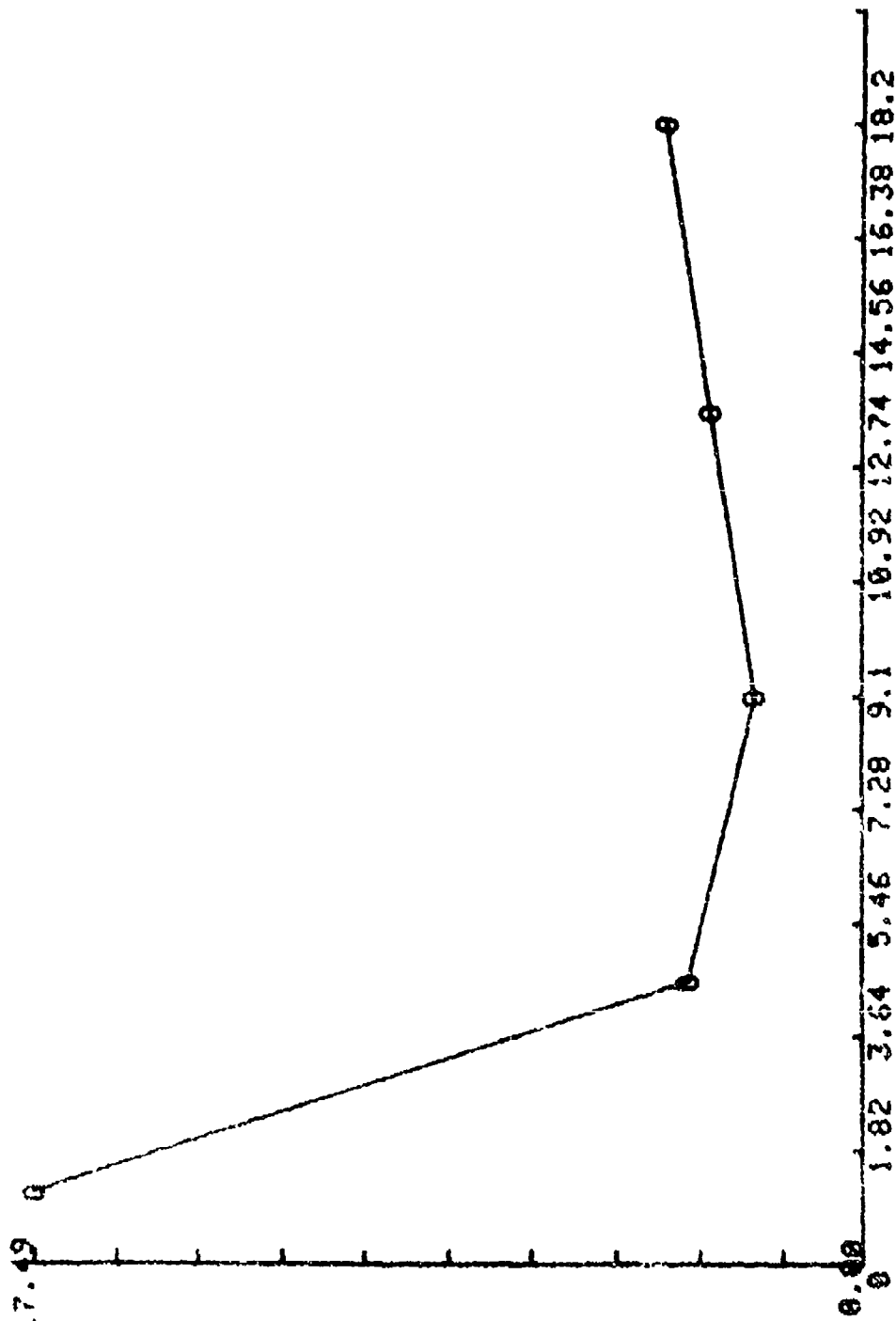
INTERCEPT= 11.6985529035

SLOPE= -0.588981348949

R= -0.634002253817

MEAN SQR DEV OF POINTS FROM REGRESSION= 32.1122977578

200MH P&R PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 PERCENT IMPRECISION



TARGET CONCENTRATION

VERTICAL AXIS TIC INTERVAL= 1.74944780918

2088N 1A PART 2: EVALUATION OF PPM SPIKE VS PPM RECOVERED
 COMBINED DATA ALL RUNS
 TARGET CONCENTR

1.16 4.54 9.1 13.6
 10.2

MEAN= 5.32 SD= 6.8310906809

PERCENT RECOVERY

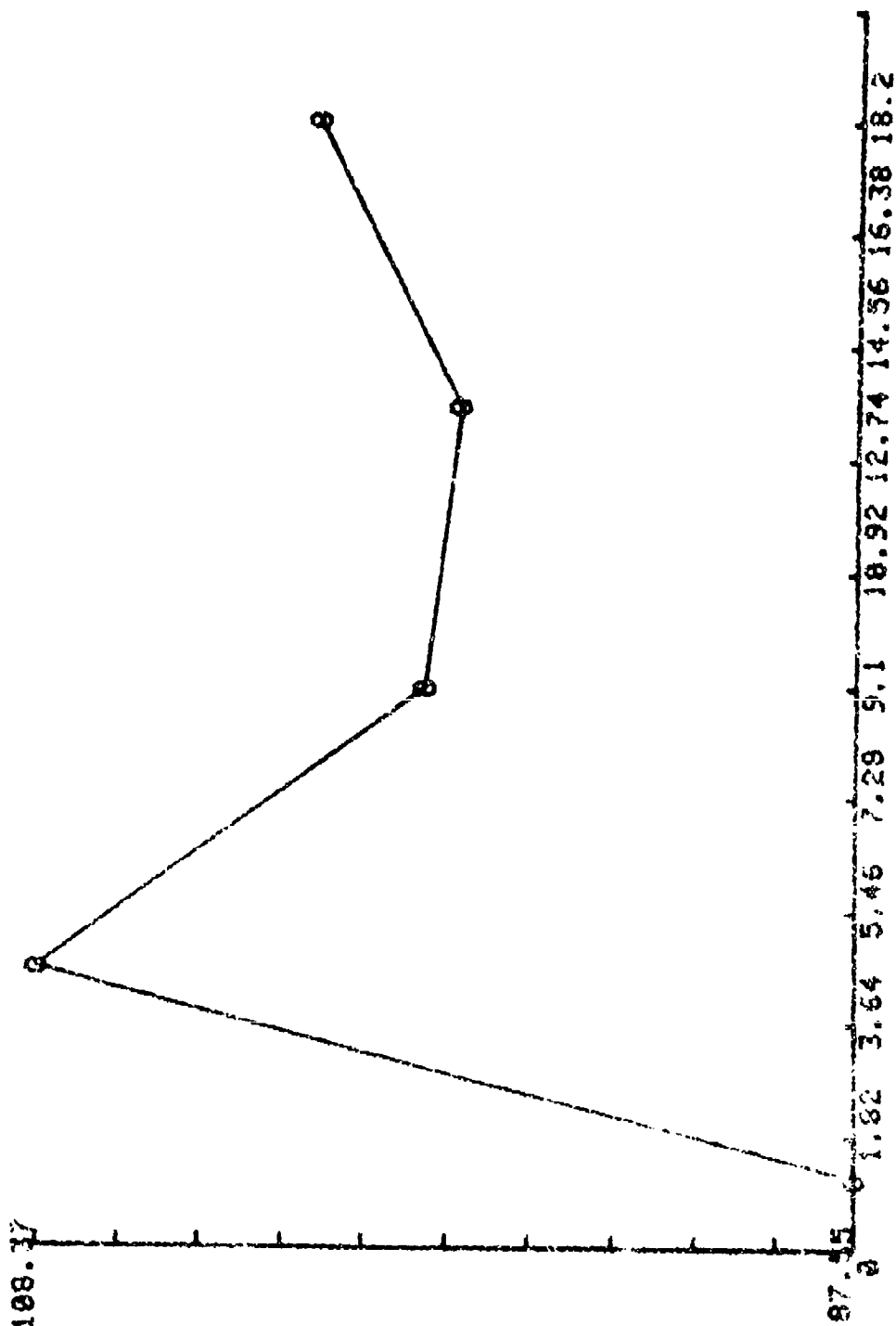
87.5479665806 108.369195045 98.5030215130 97.6103670542
 101.233723162

MEAN= 98.6545946711 SD= 7.50801693665

NO. OF PAIRS 5
 NO. RUNS 4 TOTAL X-Y 40 NO. CONCENTR 5

INTERCEPT= 95.5240862297
 SLOPE= 0.335891463665
 R= 0.30560733537
 MEAN SQR DEV OF POINTS FROM REGRESSION= 68.1407531950

208MM F&A PART 2: EVALUATION OF PPM SPIKE US PPM RECOVERED
 COMBINED DATA ALL RUNS
 PERCENT RECOVERY



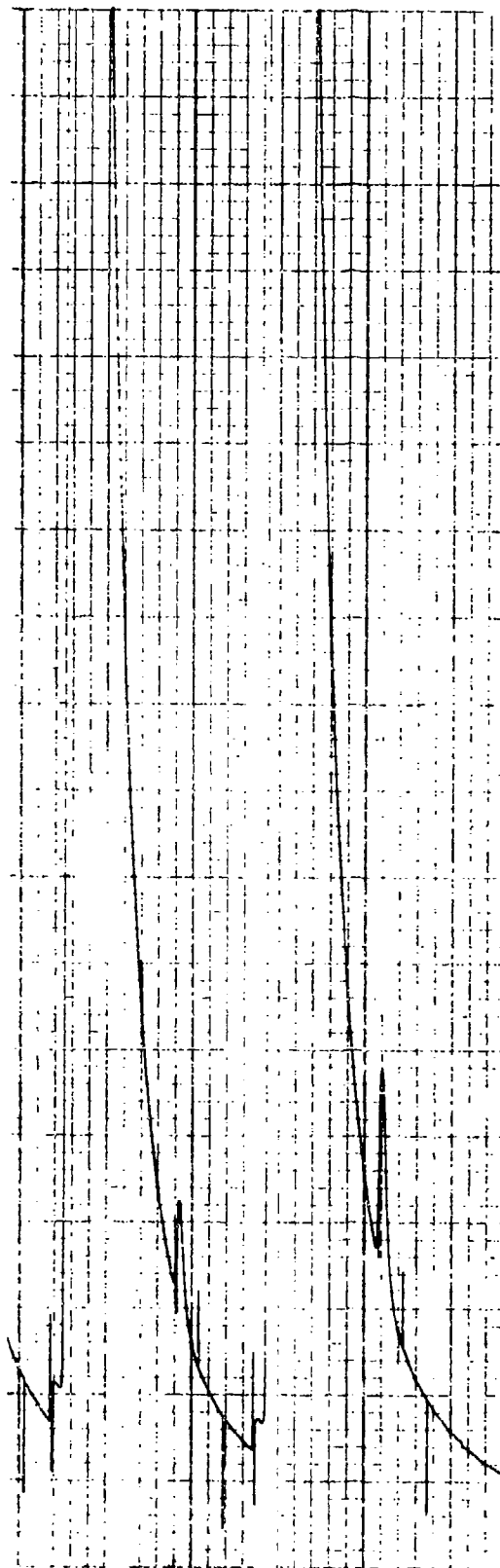
TARGET CONCENTRATION

VERTICAL AXIS TIC INTERVAL= 2.88213284639

APPENDIX C

GC/FID Chromatograms

Precision and Accuracy Data Set



GC/FID Chromatogram of
10 and 20 ppm CEA
Calibration Standard.

GC/FID CHROMATOGRAMS

CSS-23

CSS-22

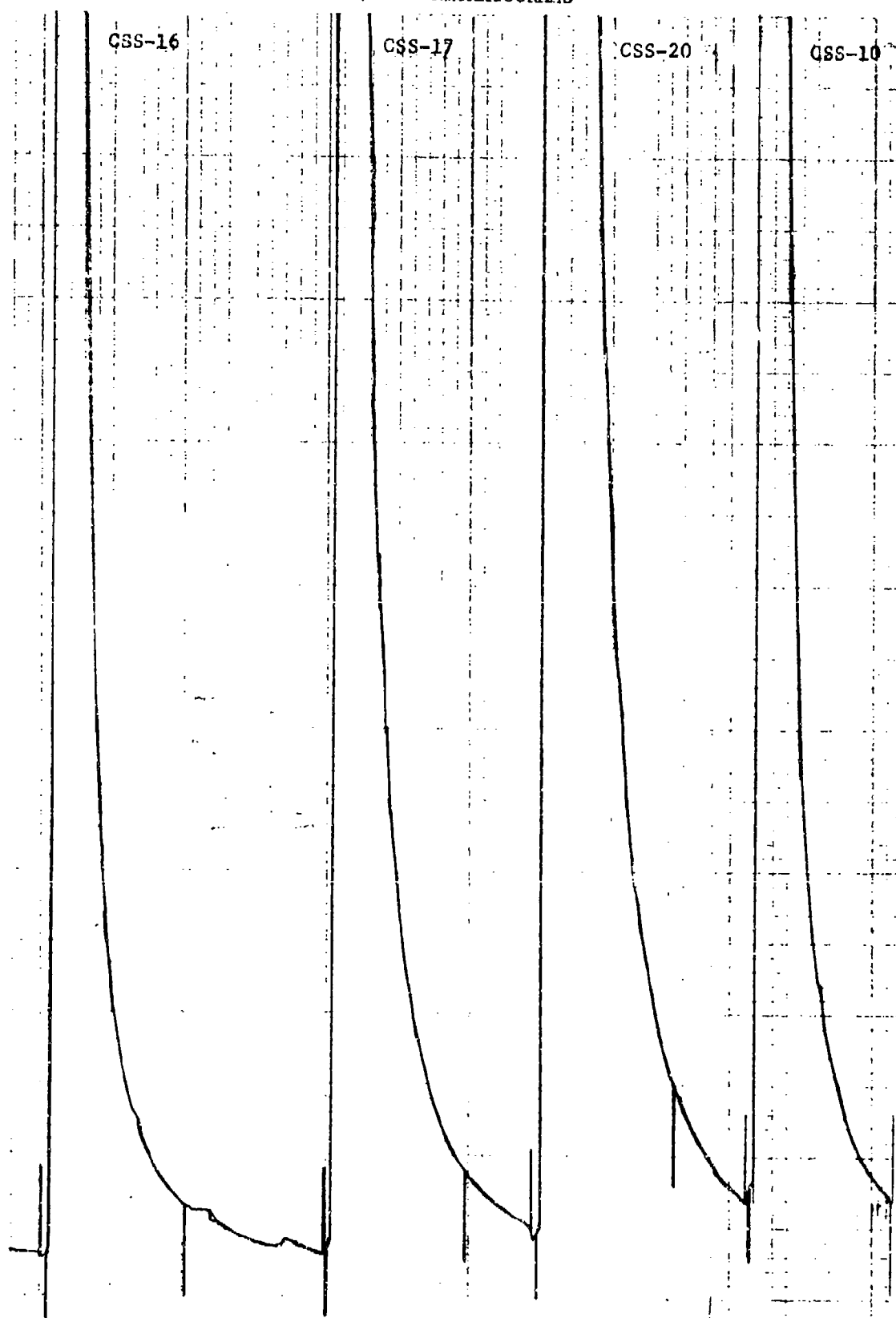
at 15 ppm

Spike Level

CSS-22

Blank

GC/FID CHROMATOGRAMS



ARMY SPIKE AND RECOVERY DATA

CEA

FUHD CONC

RUN 1

(1) 8 7.84 (2) 8 9.32

(3) 12 14.33 (4) 12 17.4

(5) 16 14.23 (6) 20 29.1

(7) 28 22.1

ARMY SPIKE AND RECOVERY DATA
CEA
ANALYSIS OF 7 TARGET CONC-FOUND CONC POINTS

TARGET CONC
MEAN= 13.7142857143 SD= 5.08957208224

FOUND CONC
MEAN= 16.3314285714 SD= 7.30408168962

NO. RUNS 1 TOTAL X-Y ALL RUNS 7 NO. CONCENTR 7
MEASURES (Y'S) EACH TARGET CONC 1

INTERCEPT= -1.48352341175

SLOPE= 1.29989735294

USE FOR ACCURACY

R= 0.895384688075

MEAN SQR DEV OF POINTS FROM REGRESSION= 12.9735179412

ST ERROR EST= 3.60187788251

USE FOR PRECISION

T FOR CONFIDENCE BAND

D.F.= 5

TWO TAIL P LEVEL IS .1

t= 2.01504863722

X(0) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U U

REPLICATES= 1

y(c)= 9.64962473693

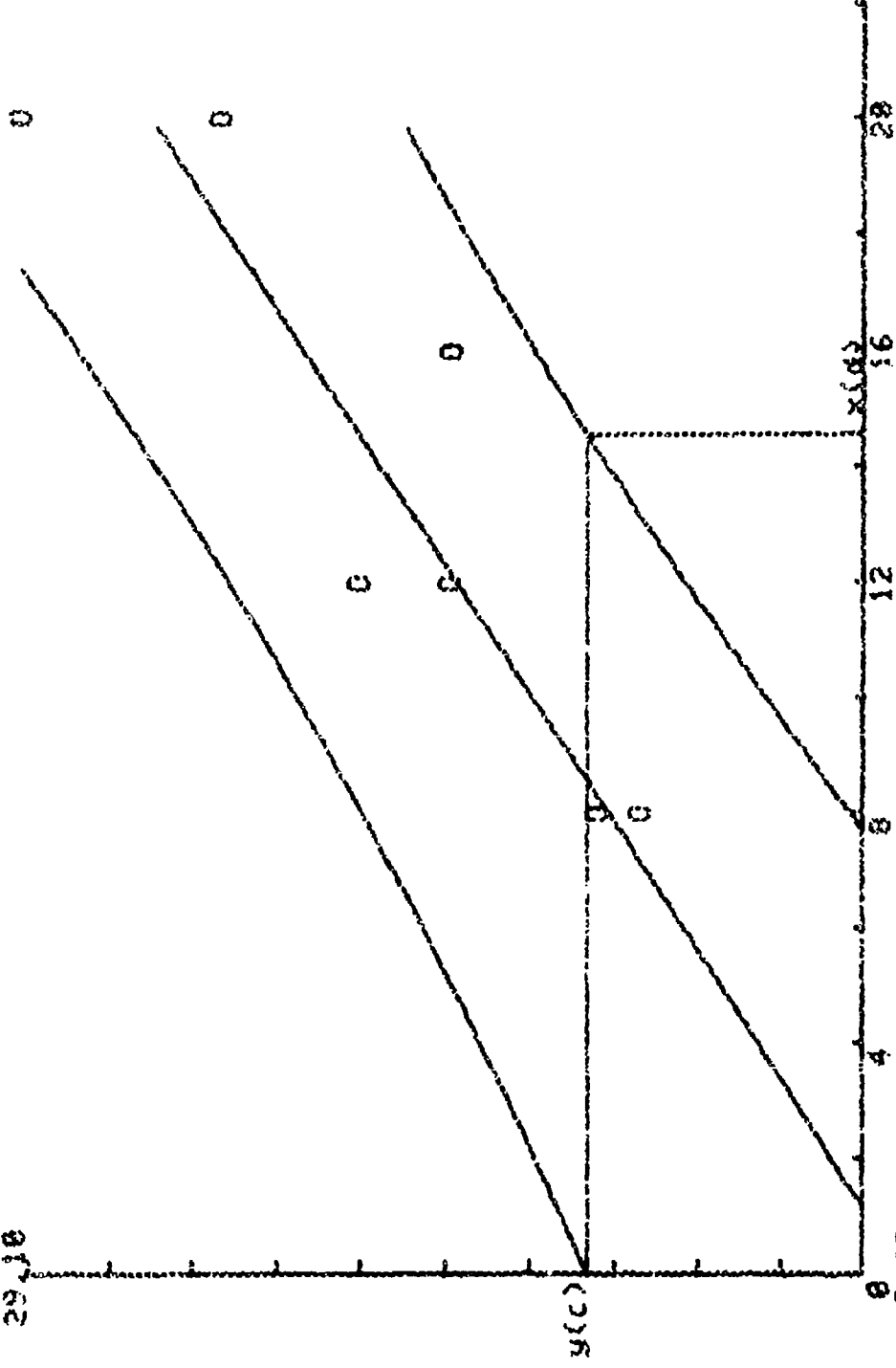
x(d)= 14.5558851858

ARMY SPIKE AND RECOVERY DATA

CEA

FOUND CONC

29.10



TARGET CONC

VERTICAL AXIS TIC INTERVAL = 2.91

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