**CHEMICAL
RESEARCH,
DEVELOPMENT &
ENGINEERING
CENTER**

ADB144715L

CRDEC-TR-132

# SUPERCRITICAL FLUID APPLICATION FOR THE ANALYSIS OF LEWISITE (L) AND 3-QUINUCLIDINYL BENZILATE (BZ)

Michael W. Ellzy
Foy E. Ferguson
Paul C. Bossle

RESEARCH DIRECTORATE

February 1990

U.S. ARMY
ARMAMENT
MUNITIONS
CHEMICAL COMMAND

Aberdeen Proving Ground, Maryland 21010-5423

## Disclaimer

## Destruction Notice

## Distribution Statement

Distribution authorized to U.S. Government agencies only because of test and evaluation; February 1990. Other requests for this document shall be referred to Commander, U.S. Army Chemical Research, Development and Engineering Center, ATTN: SMCCR-SPS-T, Aberdeen Proving Ground, Maryland 21010-5423.

CRDEC-TR-132

*ADB 144715 001*

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION: UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT: Distribution authorized to U.S. Government agencies only because of test and (continued on reverse)

4. PERFORMING ORGANIZATION REPORT NUMBER(S): CRDEC-TR-132

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION: CRDEC

6b. OFFICE SYMBOL (If applicable): SMCCR-RSL

7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS (City, State, and ZIP Code): Aberdeen Proving Ground, MD 21010-5423

7b. ADDRESS (City, State, and ZIP Code)

8a. NAME OF FUNDING/SPONSORING ORGANIZATION: CRDEC

8b. OFFICE SYMBOL (If applicable): SMCCR-RSL

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS (City, State, and ZIP Code): Aberdeen Proving Ground, MD 21010-5423

10. SOURCE OF FUNDING NUMBERS

| PROGRAM ELEMENT NO. | PROJECT NO. | TASK NO. | WORK UNIT ACCESSION NO. |
|---|---|---|---|
|  | 10LF01005 | F9C8 |  |

11. TITLE (Include Security Classification): Supercritical Fluid Application for the Analysis of Lewisite (L) and 3-Quinuclidinyl Benzilate (BZ)

12. PERSONAL AUTHOR(S): Ellzy, Michael W., Ferguson, Foy E., and Bossle, Paul C.

13a. TYPE OF REPORT: Technical

13b. TIME COVERED: FROM 88 Apr TO 88 Nov

14. DATE OF REPORT (Year, Month, Day): 1990 February

15. PAGE COUNT: 19

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

| FIELD | GROUP | SUB-GROUP |
|---|---|---|
| 20 | 13 |  |

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

Supercritical fluid application

Lewisite

BZ

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The main thrust of the research was the study of supercritical fluids as applied to chromatographing of L and BZ. The most important results obtained were (1) parts per billion/parts per million detection limits for BZ and L using flame ionization and ultraviolet detectors; and (2) compound separation on reverse phase 1-mm packed columns or delta bonded, 1-mm packed columns. The most important finding was that the extraction of BZ from soil using this approach appears to be feasible and easily accomplished.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☒ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION: UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL: SANDRA J. JOHNSON

22b. TELEPHONE (Include Area Code): (301) 671-2914

22c. OFFICE SYMBOL: SMCCR-SPS-T

DD Form 1473, JUN 86

Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

3. Distribution/Availability of Report (Continued)

evaluation; February 1990. Other requests for this document shall be referred to Commander, U.S. Army Chemical Research, Development and Engineering Center, ATTN: SMCCR-SPS-T, Aberdeen Proving Ground, Maryland 21010-5423.

# PREFACE

The work described in this report was authorized under Project No. FOLF0100SF978. This work was started in April 1988 and completed in November 1988.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

Reproduction of this document in whole or in part is prohibited except with permission of the Commander, U.S. Army Chemical Research, Development and Engineering Center, ATTN: SMCCR-SPS-T, Aberdeen Proving Ground, Maryland 21010-5423. However, the Defense Technical Information Center is authorized to reproduce the document for U.S. Government purposes.

This report has not been approved for release to the public.

CONTENTS

# LIST OF FIGURES

# SUPERCRITICAL FLUID APPLICATION FOR THE ANALYSIS OF LEWISITE (L) AND 3-QUINUCLIDINYL BENZILATE (BZ)

## 1. INTRODUCTION

The analysis of lewisite [dichloro (2-chlorovinyl) arsine] (L) and 3-quinuclidinyl benzilate (BZ) has been investigated by several researchers.[1,2] What is new, and until now has not been investigated, is the use of supercritical carbon dioxide ($CO_2$) to extract and chromatograph these two compounds.

Currently, these two compounds cannot be chromatographed by gas chromatography (GC) even with the advent of new fused silica column technology.[3,4] Our method provides a means of extracting these compounds from complex matrices (i.e., soils) and chromatographing them by a supercritical fluid chromatograph (SFC).

## 2. EXPERIMENTATION

With a SUPREX Corporation (Pittsburgh, PA) SFC/200A fluid chromatograph equipped with a flame ionization detector (FID), a 1-µL injection loop, an extractor unit able to hold a gram of soil, and a KRATOS Division (Newark, New Jersey) Spectroflow 757 UV detector, BZ was chromatographed using the instrument parameters outlined in Figure 1. Lewisite was chromatographed using the pressure program outlined in Figure 2. The fused silica restrictor attached to the end or exit line of the absorbance detector provided a $CO_2$ flow measured at the restrictor of 30 mL/min. All separations were performed on a Keystone Scientific (State College, PA) 1-mm by 10-cm packed C18 column. Data was collected on a Hewlett Packard (Rockville, MD) 3390 integrator. Standards were prepared between 1 µg/mL and 1000 µg/mL using ultraviolet (UV) grade methanol or hexane obtained from Fisher Scientific (Springfield, NJ). Ethyl ethylcarbonate (EEC) and ethyl n-ethylcarbanilate (ENEC) were obtained from Aldrich Chemical Company, Incorporated (Milwaukee, WI). The BZ and L were obtained from the U.S. Army Chemical Research, Development and Engineering Center (CRDEC) Chemical Transfer Facility. The UHP $CO_2$ and bone dry $CO_2$ were purchased from the Matheson Gas Products Company (East Rutherford, NJ).

## 3. RESULTS

Initial SFC results obtained with the UV detector resulted in a minimum detection level of 10 µg/mL when monitoring at the 225-nm wavelength using a 1-µL injection loop. The minimum detection limit was established as 250 µg/mL when FID was employed. The identity of the peak (Figure 1, bottom) for BZ was established using mass spectrographic analysis of the standard solutions running a calibration curve and analyzing the BZ with the use of two internal standards. Figure 3 shows a 3-component mixture of EEC, ENEC, and BZ. The lower portion of Figure 3 shows a chromatogram of the 2-component mixture and an attenuated 3-component mixture of the top chromatogram. Methyl benzilate was chromatographed and coeluted with the BZ component under our chromatographic conditions.

Page is Blank

DETECTOR 410 DEGREES C

PRESSURE PROGRAM

ISOTHERMAL OVEN TEMPERATURE 70 DEGREES C

| STAGE | PRESSURE ATM | TIME MIN | RATE ATM/MIN | TOTAL MIN |
|---|---|---|---|---|
| 1 | 50 | | | |
| 2 | 50 | 8.00 | 0.0 | 8.00 |
| 3 | 150 | 15.00 | 2.5 | 23.00 |
| 4 | 200 | 10.00 | 5.0 | 43.00 |
| 5 | 200 | 2.00 | 0.0 | 45.00 |

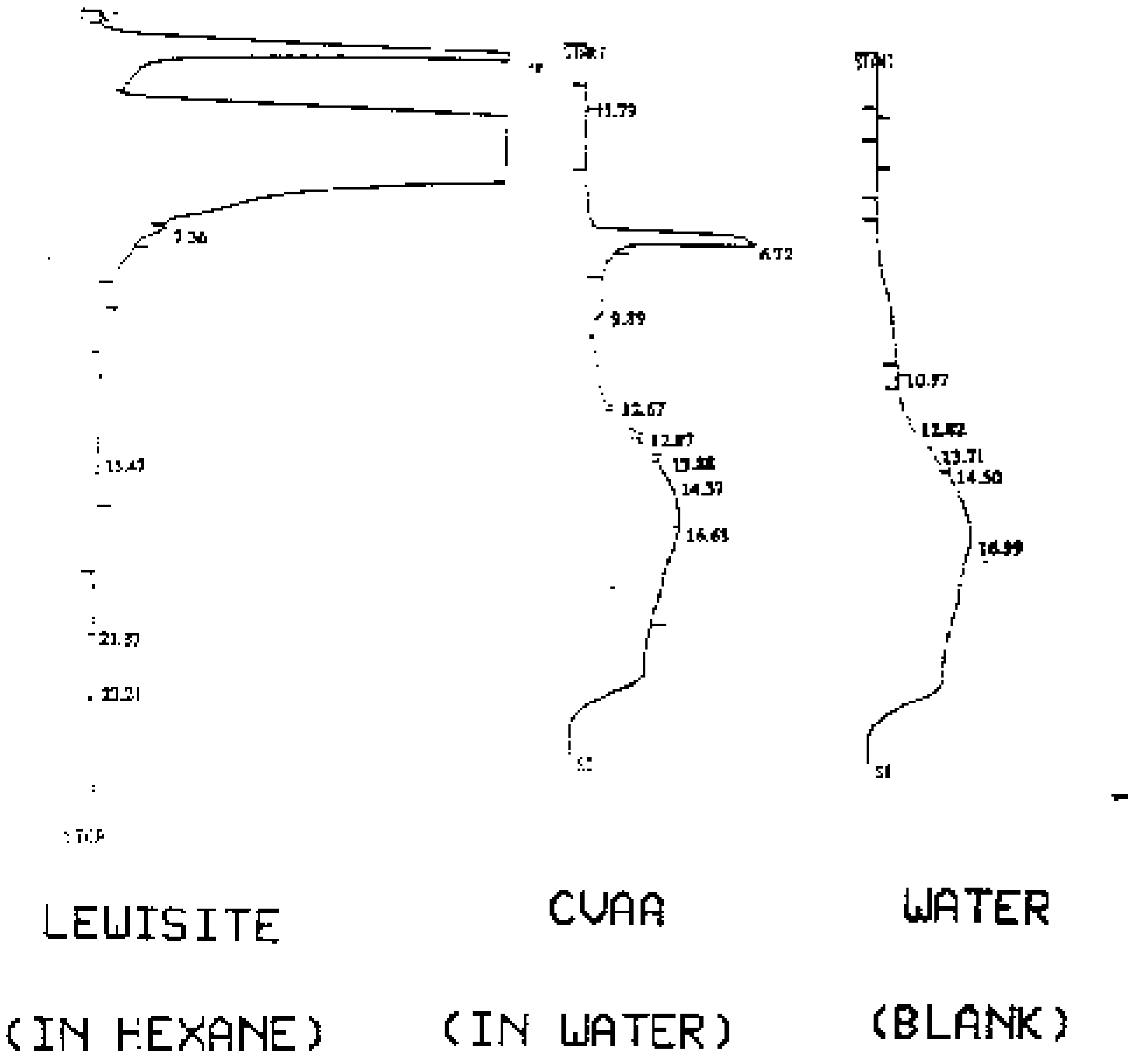


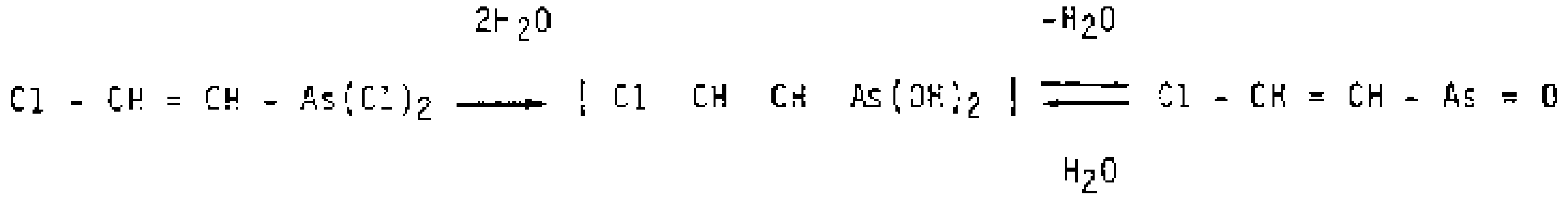
Figure 2. Pressure Program for Lewisite

Page

Blank

Typical chromatography resulting from L analysis is presented in the lower portion of Figure 2. The L peak in hexane is detected first using the FI and UV detectors. Identification of the L was accomplished by UV detector at 225 nm. It was necessary to disconnect the UV due to the pressure limitation (350 atm) of that detector. Lewisite oxide requires a pressure of 400 atm before it begins to elute from the column.

Lewisite is hydrolyzed rapidly and quantitatively in moisture to stable, water-soluble, and highly toxic, 2-chlorovinylarsenious acid (CVAA)[1] as shown below. The CVAA is the hydrated form of 2-chlorovinylarsenious oxide (lewisite oxide) and can exist only in aqueous solution. During our attempts to chromatograph L, the 0.01% moisture content of the $CO_2$ resulted in the formation of L oxide. To prevent this formation we switched to bone dry $CO_2$.



$$Cl - CH = CH - As(Cl)_2 \xrightarrow{2H_2O} [\,Cl \quad CH \quad CH \quad As(OH)_2\,] \underset{H_2O}{\overset{-H_2O}{\rightleftharpoons}} Cl - CH = CH - As = O$$

LEWISITE CVAA LEWISITE OXIDE

In our identification technique, we converted the L to chlorovinylarsenious acid and made water injections directly into the SFC (Figure 2, bottom). The hydrolyzed L was also analyzed using the high-performance liquid chromatography (HPLC) method developed in August 1988.[4] This process allowed us to compare overall concentration responses for the L and CVAA. If we hydrolyzed L (CVAA), the chromatogram would look similar to that of chromatograph labeled CVAA in water (Figure 2).

In addition, the overall molar response for L would not equate to the molar response obtained when analyzing for a standard that has been converted to CVAA.

We have established a minimum detection limit of 0.3 mg/mL using an FID. The UV detection for L has been established as 0.03 mg/mL. The CVAA or its solid analog, L oxide, is more likely to be encountered in the natural environment than L itself. Consequently, the amount of pre-existing L that was present in an aqueous matrix can be determined by analyzing for CVAA. The CVAA and L oxide are also potent blistering agents;[2] therefore it is necessary to include the two as part of any detection protocol for L. Lewisite treated with water results in conversion of both L and L oxide to CVAA. The molar response of CVAA allows one to determine the amount of L present in the standard solution. From this, we have established a minimum detection limit of 0.3 mg/mL using an FID. The UV detection for L has been established as 0.03 mg/mL.

A 1-g soil sample was extracted before spiking with BZ, EEC, and ENEC to identify any components in the soil. Out of five spike trials per concentration recovery, 3 components did not deviate more than ± 0.05% of the expected concentration value. This value showed good agreement based on the

Page missing from my copy

cok

# LITERATURE CITED

1. Bounder, N.M., *Lewisite (M-1), 1940 Summary of Data*, EATR-214, Edgewood Arsenal, Edgewood, MD, 21 August 1940, UNCLASSIFIED report.

2. Deiner, A., Shaw, F., Vigus, E., and Keller, J., *Automated 3-Quinuclidinyl Benzilate (BZ) Analysis and Feasibility Studies to Develop an Alarm*, CRDC-TR-84075, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, March 1985, UNCLASSIFIED report.

3. RESTEK Corporation, *HALFMIL Capillary Columns*, 2nd ed., February 1989.

4. Ellzy, M., Ferguson, F., and Janes, G., *Using the 608 Megabore Open Tubular Column for Trace Analysis GB and VX in Brine and Soil Samples*, CRDEC-TR-88168, U.S. Army Chemical Research and Development Center, Aberdeen Proving Ground, MD, September 1988, UNCLASSIFIED report.

Page Blank

DISTRIBUTION LIST 2

| Names | Copies |
|---|---|
| Commander | |
| U.S. Army Chemical Research, Development and Engineering Center | |
| SMCCR-DDR | 1 |
| SMCCR-DDW | 1 |
| SMCCR-DDP | 1 |
| SMCCR-HV | 1 |
| SMCCR-MSI | 2 |
| SMCCR-MU | 1 |
| SMCCR-MUM (A. Van de Wall) | 1 |
| SMCCR-NB | 1 |
| SMCCR-OPI (B. Eckstein) | 1 |
| SMCCR-OPF | 1 |
| SMCCR-OPP | 1 |
| SMCCR-OPR | 1 |
| SMCCR-PPC | 1 |
| SMCCR-PPI | 1 |
| SMCCR-PPP | 1 |
| SMCCR-RS | 1 |
| SMCCR-RSC | 1 |
| SMCCR-RSL | 1 |
| SMCCR-RSP | 1 |
| SMCCR-RSP-A (M. Miller) | 1 |
| SMCCR-RSP-B | 1 |
| SMCCR-RSP-P | 1 |
| SMCCR-RST | 1 |
| SMCCR-SF | 1 |
| SMCCR-ST | 1 |
| SMCCR-SPS-T | 2 |
| SMCCR-TDT (S. Lawhorne) | 1 |
| SMCCR-RSL (M. Ellzy) | 8 |
| Aberdeen Proving Ground, MD 21010-5423 | |
| | |
| Commandant | |
| U.S. Army Ordnance Missile and Munitions Center and School | |
| ATTN: ATSK-CMM (CPT Stiene) | 1 |
| ATSK-XO | 1 |
| Redstone Arsenal, AL 35897-6801 | |
| | |
| Commander | |
| U.S. Army Missile Command | |
| Redstone Scientific Information Center | |
| ATTN: AMSMI-RD-CS-R/ILL Documents | 2 |
| Redstone Arsenal, AL 35898-5241 | |
| | |
| Commander | |
| Anniston Army Depot | |
| ATTN: SDSAN-CS | 1 |
| Anniston, AL 36201-5009 | |

| Names | Copies |
|---|---|
| Commandant | |
| U.S. Army Chemical School | |
| ATTN: ATZN-CM-CC | 1 |
| ATZN-CM-CS (Deputy MLSD) | 1 |
| ATZN-CM-CT (Mr. Jennings) | 1 |
| ATZN-CM-MLB | 1 |
| ATZN-CM-NC | 1 |
| Fort McClellan, AL 36205-5020 | |
| | |
| Commander | |
| U.S. Army Aviation Center | |
| ATTN: ATZQ-CAT-CA-M (CPT R. Bridges) | 1 |
| Fort Rucker, AL 36362-5000 | |
| | |
| Commander | |
| Pine Bluff Arsenal | |
| ATTN: SMCPB-MM (Mr. Dunemn) | 1 |
| Pine Bluff, AR 71602-9500 | |
| | |
| Commander | |
| U.S. Army Electronic Proving Ground | |
| ATTN: STEEP-RM-O | 2 |
| Fort Huachuca, AZ 85613-7110 | |
| | |
| Commander | |
| U.S. Army Chemical Activity | |
| ATTN: APCA-SPO | 1 |
| APO San Francisco 96305-0008 | |
| | |
| Commander | |
| U.S. Army Science and Technology Center Far East Office | |
| ATTN: Chemical Officer/Munitions | 1 |
| APO San Francisco 96328-5000 | |
| | |
| AFDPRC/PR | 1 |
| Lowry AFB, CO 80230-5000 | |
| | |
| Director | |
| Environmental and Life Sciences | |
| Office of Under Secretary of Defense (Acquisition) | |
| Research and Advanced Technology | |
| ATTN: Dr. Joseph V. Osterman | 1 |
| The Pentagon, Room 3D129 | |
| Washington, DC 20301-3080 | |

HQDA, ODCSOPS
ATTN: DAMC-SWC 1
Pentagon, Room 3C549
WASH, DC 20310-0430

HQDA (SARD-ZCS)
ATTN: LTC Wilinoite 1
WASH, DC 20310-0634

Director
Defense Intelligence Agency
ATTN: DT-5A2 (Dr. C. Clark) 1
Washington, DC 20340-6053

Commander
Naval Sea Systems Command
ATTN: Code 55X25 1
Washington, DC 20362-5101

Commander
Naval Sea Systems Command
ATTN: Navsea 05R24 (Dr. Gloria Patton) 1
Washington, DC 20362-5101

Chief
Bureau of Medicine and Surgery
ATTN: BUMED-02C 1
Washington, DC 20372-5120

Commander
Naval Research Laboratory
ATTN: Code 6182 (Dr. Little) 1
4555 Overlook Avenue, SW
Washington, DC 20375-5000

HQ MSD/YCO 1
Eglin AFB, FL 32542-6008

USAFTAWC/TCC 1
Eglin AFB, FL 32542-6008

Officer In Charge
Naval School Explosive
Ordnance Disposal Detachment
Code N16 (CWO Timothy Garretson) 1
Eglin AFB, FL 32542-6009

Commander
U.S. Army Forces Command
Science and Technology Office
ATTN: FCSJ-SA (Dr. D. Snider) 1
Fort McPherson, GA 30330-6000

Chief, Special Programs Group
Center for Environmental Health
and Injury Control
ATTN: Log-In Control Officer 1
1600 Clifton Rd. N.E.
Bldg 1, Rm B413
Atlanta, GA 30333

Commandant
U.S. Army Infantry School
ATTN: ATSH-CD-CS-CS 1
Fort Benning, GA 31905-5400

Commander
U.S. Army Infantry Center
ATTN: ATZB-DPT-T-NBC (Building 2294) 1
Fort Benning, GA 31905-5823

Commander
U.S. Army Armament, Munitions and Chemical
Command
ATTN: AMSMC-ASN 1
AMSMC-IMF-L (Technical Library) 1
AMSMC-IRD 1
AMSMC-SFS 1
Rock Island, IL 61299-6000

Director
U.S. Army Material Command Field
Safety Activity
ATTN: AMXOS-C (Mr. K. Messerich) 1
AMXOS-C (Mr. L. Morgan) 1
Charlestown, IN 47111-9669

Commander
U.S. Army Armor Center and Fort Knox
ATTN: ATSB-CD-ML 1
Fort Knox, KY 40121-5215

Commander
U.S. Army Natick Research, Development
and Engineering Center
ATTN: STRNC-AC 1
Kansas Street
Natick, MA 01760-5015

Commander
U.S. Army Natick Research, Development
and Engineering Center
ATTN: STRNC-WTS 1
Kansas Street
Natick, MA 01760-5018

Commander
U.S. Army Natick Research, Development
and Engineering Center
ATTN: STRNC-IC (Mr. C. Williams) 1
STRNC-IP (Mr. Harbs) 1
STRNC-ITF (Mr. T. Tassinari) 1
STRNC-ITP (Dr. E. Wilusz) 1
Kansas Street
Natick, MA 01760-5019

Commander
U.S. Army Natick Research, Development
and Engineering Center
ATTN: STRNC-YBH 1
STRNC-YM (Dr. D. Rowley) 1
STRNC-YMT (Mr. J. A. Akkara) 1
STRNC-YMT (Mr. D. L. Kaplan) 1
STRNC-YSC (Dr. D. H. Robertson) 1
Kansas Street
Natick, MA 01760-5020

HQ AFSC/XTHO
ATTN: MAJ Sarvaideo 1
Andrews AFB, MD 20334-5000

Commanding Officer
Naval School Explosive Ordnance Disposal
ATTN: B1 3
Indian Head, MD 20640-5040

Commander
Detachment S, USACG
ATTN: IAGPC-S (III) 1
Fort Meade, MD 20755-5985

Commander
U.S. Army Laboratory Command
ATTN: AMCLD-PB (J. Gaul) 1
Adelphi, MD 20783-1145

Director
U.S. Army Survivability Management Office
ATTN: SLCSM-SE (Mrs. Liu) 1
2800 Powder Mill Road
Adelphi, MD 20783-1145

Director
U.S. Army Concepts Analysis Agency
ATTN: CSCA-RQN 1
8120 Woodmont Avenue
Bethesda, MD 20814-2797

Commander
U.S. Army Laboratory Command
Human Engineering Laboratory
ATTN: SLCHE-CC-LHD (Mr. Harrah) 1
Aberdeen Proving Ground, MD 21005-5001

Director
Vulnerability/Lethality Assessment
Management Office
ATTN: AMSLC-VL-NBC (Mr. M. Miller) 1
Aberdeen Proving Ground, MD 21005-5001

Director
U.S. Army Materiel Systems Analysis Activity
ATTN: AMXSY-CR (Mrs. C. Horley) 1
AMXSY-MP (Mr. H. Cohen) 1
Aberdeen Proving Ground, MD 21005-5071

Commander
U.S. Army Environmental Hygiene Agency
ATTN: HSHB-MO-A (MAJ Aiken) 1
HSHB-MO-O (Mr. D. B. Kiechner) 1
HSHB-MO-T (Mr. M. Weeks) 1
Aberdeen Proving Ground, MD 21010-5422

Commander
U.S. Army Armament, Munitions and Chemical
Command
ATTN: AMSMC-HOA (A) (Mr. J. K. Smart) 1
AMSMC-QAC (A) 1
AMSMC-QAE (A) 1
AMSMC-QAO-C (A) (Dr. P. Patel) 1
Aberdeen Proving Ground, MD 21010-5423

Commander
U.S. Army Medical Research Institute
of Chemical Defense
ATTN: SGRD-UV-AI-W 1
Aberdeen Proving Ground, MD 21010-5425

Director
Armed Forces Medical Intelligence Center
ATTN: AFMIC-IS 1
Building 1607
Fort Detrick, Frederick, MD 21701-5004

Commander
U.S. Army Medical Bioengineering Research
and Development Laboratory
ATTN: SGRB-UBG (Mr. Eaton) 1
SGRB-UBG-AL, Building 568 1
Fort Detrick, Frederick, MD 21701-5010

Commander
U.S. Army Aviation System Command
ATTN: AMSAV-ESC 1
AMSAV-NS (Mr. R. Breitenbach) 1
AMCPM-AAH 1
AMCPM-CH47M 1
AMCPEO-LHX-TV 1
Federal Center, 4300 Goodfellow Boulevard
St. Louis, MO 63120-1798

Director
U.S. Army Research Office
ATTN: AMXRO-CB (Dr. R. Ghirardelli) 1
PO Box 12211
Research Triangle Park, NC 27709-2211

Commander
U.S. Army Cold Regions Research and Engineering Laboratory
ATTN: CECRL-RG (Mr. D. Leggett) 1
72 Lyme Road
Hanover, NH 03755-1290

Commander
U.S. Army Armament Research, Development and Engineering Center
ATTN: SMCAR-IMI-I, B59 1
Picatinny Arsenal, NJ 07806-5000

Commander/Director
U.S. Army Atmospheric Sciences Laboratory
ATTN: SLCAS-AE (Dr. F. Niles) 1
SLCAS-AR-P (Dr. C. Bruce) 1
White Sands Missile Range, NM 88002-5501

Chief, USAS
ATTN: Eng Advisor 1
USMTM
APO New York 09038-5363

Commander
U.S. Army Science and Technical Center-Europe
ATTN: AMXMI-E 1
APO New York 09079-4734

Headquarters
112th Medical Brigade
ATTN: AGOH-MB-OT/NBC 1
2815 West Granville Road
Columbus, OH 43235-2712

HSD/YAGD 1
Wright-Patterson AFB, OH 45433-6503

FTD/TQTR 1
Wright-Patterson AFB, OH 45433-6508

WRDC/FIVE 1
Wright-Patterson AFB, OH 45433-6553

WRDC/FIVS/SURVIAC 1
Wright-Patterson AFB, OH 45433-6553

AAMRL/HET 1
Wright-Patterson AFB, OH 45433-6573

Commander
U.S. Army Depot Systems Command
ATTN: AMSDS-SF (Mr. T. Krietz) 1
Chambersburg, PA 17201-4170

Commander
Naval Air Development Center
ATTN: Code 60241 (D. Herbert) 1
Warminster, PA 18974-5000

Commandant
U.S. Army Academy of Health Sciences
ATTN: HSHA-CDF 1
HSHA-IPM 1
Fort Sam Houston, TX 78234-6100

Commander
U.S. Army Dugway Proving Ground
ATTN: STEDP-SD-TA-F (Technical Library) 2
Dugway, UT 84022-5000

HQDA (SGPS-PSP) 1
5109 Leesburg Pike
Falls Church, VA 22041-3258

Commander
U.S. Army Nuclear and Chemical Agency
ATTN: MONA-CM 1
7500 Backlick Road, Building 2073
Springfield, VA 22150-3198

Director
Office of Naval Research
Biological Sciences
ATTN: Code 1141 1
800 N. Quincy Street
Arlington, VA 22217-5000

Administrator
Defense Technical Information Center
ATTN: FDAC 2
Cameron Station, Building 5
Alexandria, VA 22304-6145

Commander
U.S. Army Materiel Command
ATTN: AMCCN 1
5001 Eisenhower Avenue
Alexandria, VA 22333-0001

Commander
Naval Surface Warfare Center
ATTN: Code H305 (Brumfield) 1
Code H33 (B. Furchak) 1
Dahlgren, VA 22448-5000

HQ TAC/DRPS 1
Langley AFB, VA 23665-5575

Commander
U.S. Army Foreign Science and Technology
Center
ATTN: AIFRIB 1
220 7th Street, NE
Charlottesville, VA 22901-5396

Commander
CINCLANT FLT
ATTN: Code N91C 1
Norfolk, VA 23511-6001

Director
Aviation Applied Technology Directorate
ATTN: SAVRT-TY-ASV (John Maglieri) 1
Fort Eustis, VA 23604-5577

Commander
U.S. Army Training and Doctrine Command
ATTN: ATCD-N 1
Fort Monroe, VA 23651-5000

# SUPERCRITICAL FLUID APPLICATION FOR THE ANALYSIS OF LEWISITE (L) AND 3-QUINUCLIDINYL BENZILATE (BZ)

M.W. ELLZY, F.E. FERGUSON, AND P.C. BOSSLE

## Abstract:

The main thrust of the research was the study of supercritical fluids as applied to chromatographing of L and BZ. The most important results obtained were: (1) Parts-per-billion/parts-per-million detection limits for BZ and L using flame ionization and ultraviolet detectors; (2) Compound separation on reverse phase 1 mm packed columns or delta bonded 1 mm packed columns. Most importantly the extraction of BZ from soil using this approach appears to be feasible and easily accomplished.

## Introduction:

The analysis of lewisite [dichloro (2-chlorovinyl) arsine] (L) and 3-quinuclidinyl benzilate (BZ) has been investigated by several researchers[1-2]. What is new and until now has not been investigated is the use of supercritical carbon dioxide to extract and chromatograph these two compounds.

Currently, these two compounds cannot be chromatographed by gas chromatography even with the advent of new fused silica column technology[3-4]. Our method provides a means of extracting these compounds from complex matrices (i.e., soils) and chromatographing them by a supercritical fluid chromatograph (SFC).

## Experimental:

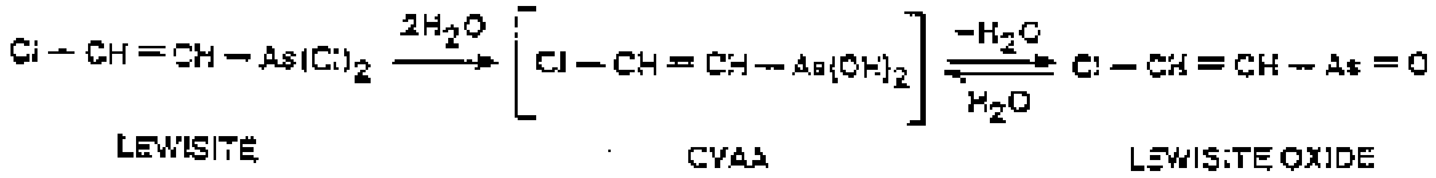
Using a SUPREX SFC/200A fluid chromatograph equipped with a flame ionization detector (FID), 1 ul injection loop, extractor unit able to hold a gram of soil, and a KRATOS Division Spectroflow 757 UV detector, BZ was chromatographed using the instrument parameters outined in figure 1. Lewisite was chromatographed using the pressure program outlined in figure 2. The fused silica restrictor attached to the end or exit line of the absorbance detector provided a $CO_2$ flow measured at the restrictor of 30 ml/min. All separations were performed on a Keystone Scientific 1 mm x 10cm packed C18 column. Data was collected on a Hewlett Packard 3390 integrator. Standards were prepared between 1 ug/ml and 1000 ug/ml using UV grade methanol or hexane obtained from Fischer Scientific. Ethyl ethylcarbanate (EEC) and ethyl n-ethylcarbanilate (ENEC) were obtained from Aldrich. BZ and L was obtained from CRDEC Chemical Transfer Facility. UHP $CO_2$ and bone dry $CO_2$ was purchased from Matheson Company.

Results:

Initial SFC results obtained with the UV detector resulted in a minimum detection level of 10 ug/ml, when monitoring at the 225 nanometer wavelength using a 1 ul injection loop. Minimum detection limit was established as 250 ug/ml. The identity of the peak (figure 1, bottom) for BZ was established using mass spectrographic analysis of the standard solutions running a calibration curve and analyzing the BZ with the use of two internal standards. Figure 3 shows a 3 component mixture of EEC ENEC and BZ. The lower portion of figure 3 shows a chromatogram of the 2 component mixture and an attenuated 3 component mixture of the top chromatogram. methyl bensilate was chromatographed and found to coelute with the BZ component under our chromatographic conditions.

Typical chromatography resulting from Lewisite analysis is presented in the lower portion of figure 2. The Lewisite peak in hexane is detected first using the FI and UV detectors. Identification of the Lewisite was accomplished by UV detector at 225 nanometers. It was necessary to disconnect the UV due to the pressure limitation (50 atm) of that detector. Lewisite oxide requires a pressure of 400 atm. before it begins to elute from the column.

Lewisite is hydrolyzed rapidly and quantitatively in moisture to stable, water-soluble, and highly toxic, 2-chlorovinylarsenious acid[1] as shown below. CVAA is the hydrated form of 2-chlorovinylarsenious oxide (lewisite oxide) and can exist only in aqueous solution. During our attempts to chromatograph Lewisite the one hundredth of a percent moisture content of the $CO_2$ resulted in the formation of Lewisite oxide. To prevent this formation we switched to bone dry $CO_2$.



$$Cl-CH=CH-As(Cl)_2 \xrightarrow{2H_2O} \left[Cl-CH=CH-As(OH)_2\right] \underset{H_2O}{\overset{-H_2O}{\rightleftharpoons}} Cl-CH=CH-As=O$$

As our identification technique we converted the Lewisite to chlorovinylarsenious acid and made water injections directly into the SFC (figure 2, bottom). This hydrolysized Lewisite was also analyzed using HPLC method developed in August 1988[4]. This process allowed use to compare overall concentration responses for both the Lewisite and CVAA. If we hydrolyzed Lewisite (CVAA) the chromatogram would look similar to that of chromatograph label CVAA in water (figure 2). Furthermore the overall molar response for Lewisite would not equate to the molar response obtained when analyzing for a standard which has been converted to CVAA.

We have established a minimum detection limit of 0.3 mg/ml using an FID. UV detection for Lewisite has been established as 0.03 mg/ml. CVAA or its solid analog, Lewisite oxide, are more likely to be encountered in the natural environment than Lewisite itself. Consequently, the amount of pre-existing Lewisite that was present in an aqueous matrix can be determined by analyzing for CVAA. CVAA and Lewisite oxide are also potent blistering agents[2] and should of necessity be part of any detection protocol for Lewisite. Lewisite treated with water results in conversion of both Lewisite and Lewisite oxide to CVAA. The molar response of CVAA allows one to determine the amount of Lewisite present in the standard solution. From this we have estrablished a minimum detection limit of 0.3 mg/ml using an FID. UV detection for Lewisite has been established as .03 mg/ml.

A one gram soil sample was extracted before spiking with BZ, EEC, and ENEC to identify any components in the soil. Using 5 trials per concentration recovery of all 3 components did not deviate more than + or - 0.05%. This value based on the expected when the spike concentration was injected directly in the SFC unit. This data was generated using the FID and a concentration range of 3 mg/ml to 0.5 mg/ml. Standard deviations were computed using area count deviations.

Conclusions:

Lewisite and BZ have been chromatographed using Supercritical Fluid Carbon Dioxide. Bone dry carbon dioxide was required to chromatograph Lewisite. The hydrolysis rate of Lewisite is so rapid that the hexane solvent used to prepare standard solutions had to be dried for 30 days before linear dilution could be accomplished. Following the parameter provided in figures 2 and 3 BZ and Lewisite have respective retention times of 17.08 and 0.9 with actual retention deviation being effected by manual injection. All separations were accomplished using a 1 mm x 10 cm packed C18 column.

Minimum detections have been established as 0.025 mg/ml and 0.3 mg/ml using FI detection for BZ and Lewisite respectively. While it was possible to extract Lewisite from soil the soil had to be moisture free and extraction efficiency was at best 75%. BZ on the other hand was in most cases quantititave recovered from soil with the worst recovery of 87% based on amount used to spike. This study indicates the feasibility of reproducible recovering BZ from soil and chromatographing the extracted compound. Chromatographing Lewisite can be successful using this method, although due to the rapid elution of Lewisite we believe a slower flow rate should be employed to increase separation. One must remember at 50 atms and 70 degrees C Lewisite is chromatographed in the sub-supercritical $CO_2$ range. Decreasing the flowrate by decreasing restrictor inner diameter will result in frequent plugging if SFC system to include standards are not extremely water free. Finally, though it is not advisable to inject water into the SFC unit, CVAA in water does chromatograph using the pressure program outlined in figure 2.

References:

1. Bouder, N. M., "Lewisite (M-1), 1940 Summary of Data", EATR 214, Copy No. 1, 21 August 1940.

2. Deiner, A., Shaw, F., Vigus, E., Keller, J., "Automated 3-Quinuclidinyl Benzilate (BZ) Analysis and Feasibility Studies to Develop an Alarm, CRDC-TR-84075, March 1985.

3. RESTEK Corporation, HALFMIL Capillary Columns, Second Edition.

4. Ellzy, M., Ferguson, F., Janes, G., "Using the 608 Megabore Open Tubular Column for Trace Analysis of GB and VX in Brine and Soil Samples", CRDEC-TR-88168, September 1988.

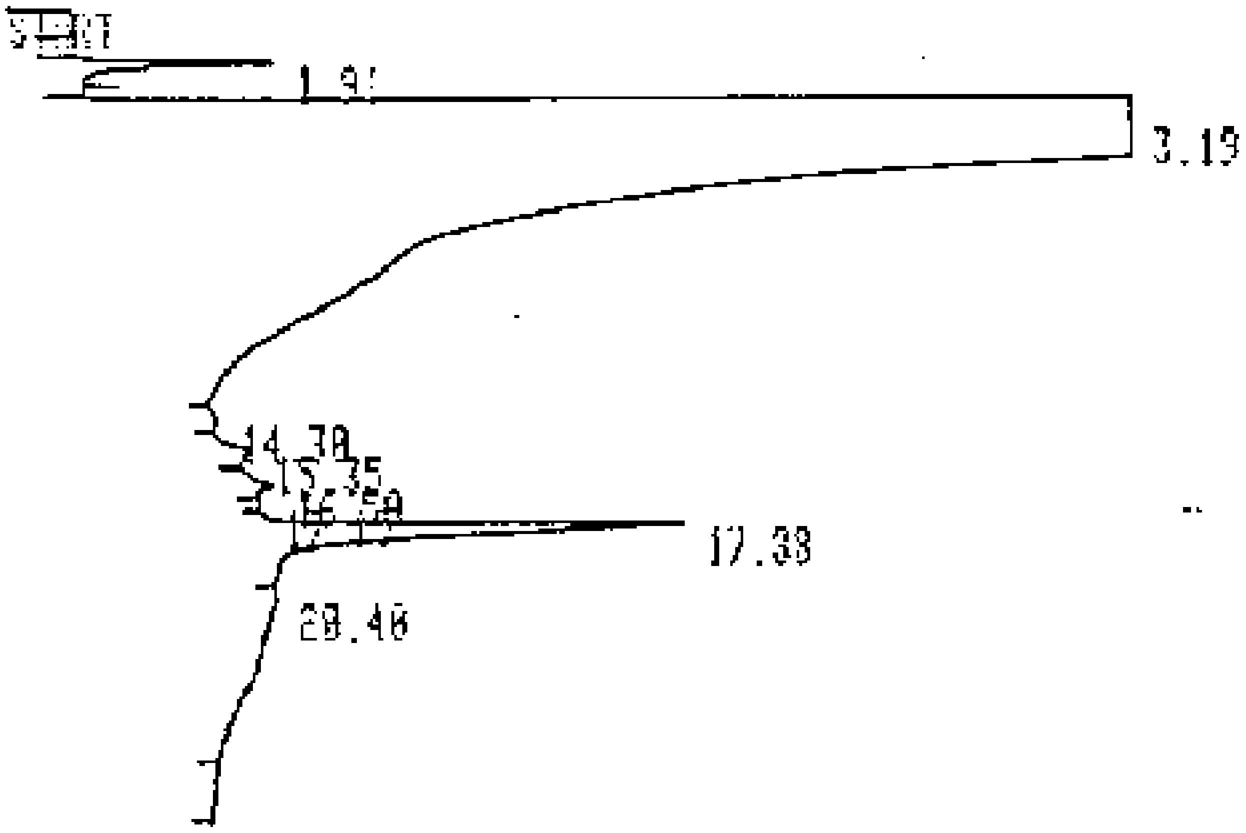
## 5 COMPONENT MIXTURE

DETECTOR 410 DEGREES C

PRESSURE PROGRAM

ISOTHERMAL OVEN TEMPERATURE 70 DEGREES C

| STAGE | PRESSURE ATM | TIME MIN | RATE ATM/MIN | TOTAL MIN |
|---|---|---|---|---|
| 1 | 100 | | | |
| 2 | 100 | 8.00 | 0.0 | 8.00 |
| 3 | 150 | 5.00 | 10.0 | 13.00 |
| 4 | 200 | 10.00 | 5.0 | 23.00 |
| 5 | 200 | 2.00 | 0.0 | 25.00 |
| 6 | 300 | 5.00 | 10.0 | 30.00 |



BZ in Methanol [5mg/ml]

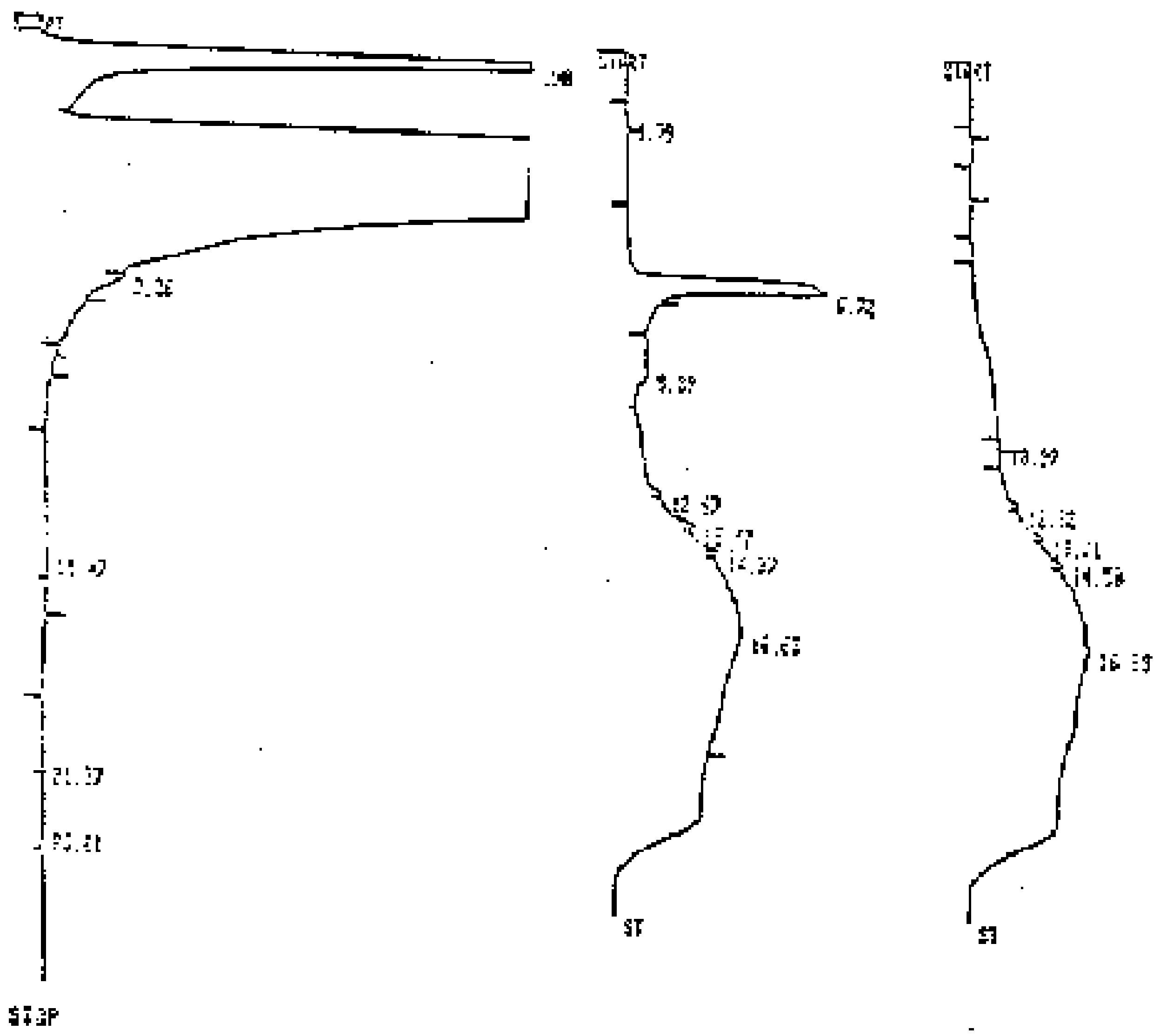
FIGURE 1

DETECTOR 410 DEGREES C

PRESSURE PROGRAM

ISOTHERMAL OVEN TEMPERATURE 70 DEGREES C

| STAGE | PRESSURE ATM | TIME MIN | RATE ATM/MIN | TOTAL MIN |
|---|---|---|---|---|
| 1 | 50 | | | |
| 2 | 50 | 8.00 | 0.0 | 8.00 |
| 3 | 150 | 15.00 | 2.5 | 23.00 |
| 4 | 200 | 10.00 | 5.0 | 43.00 |
| 5 | 200 | 2.00 | 0.0 | 45.00 |



LEWISITE

(IN HEXANE)

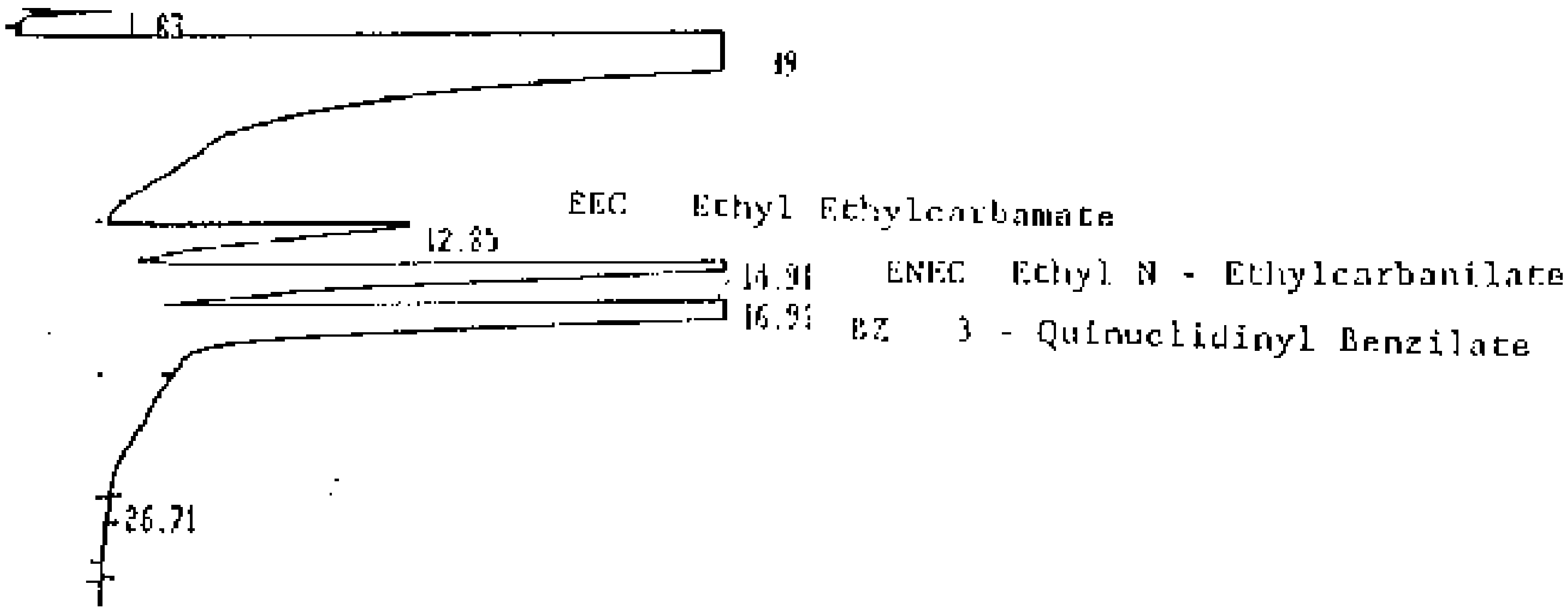
CVAA

(IN WATER)

WATER

(BLANK)

Figure 2

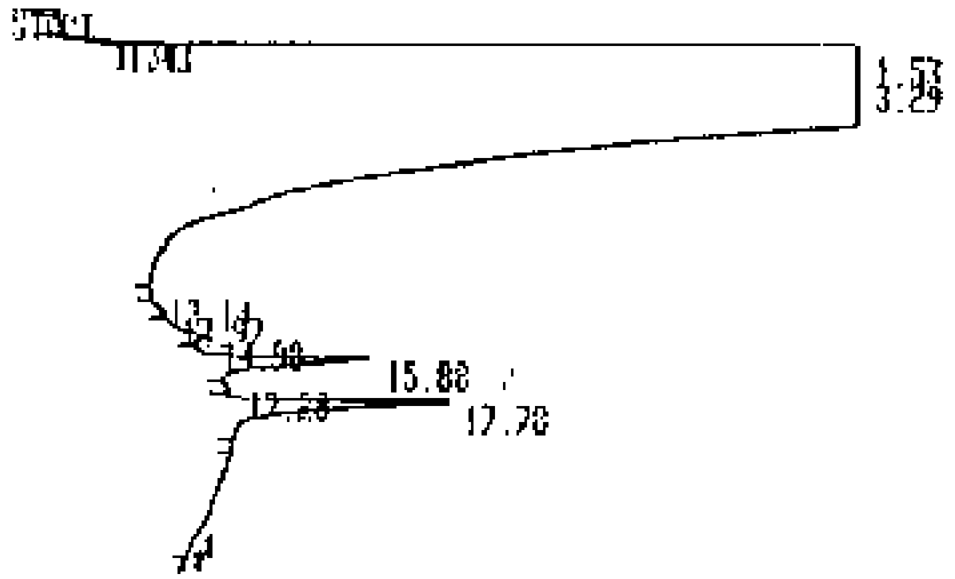


EEC Ethyl Ethylcarbamate

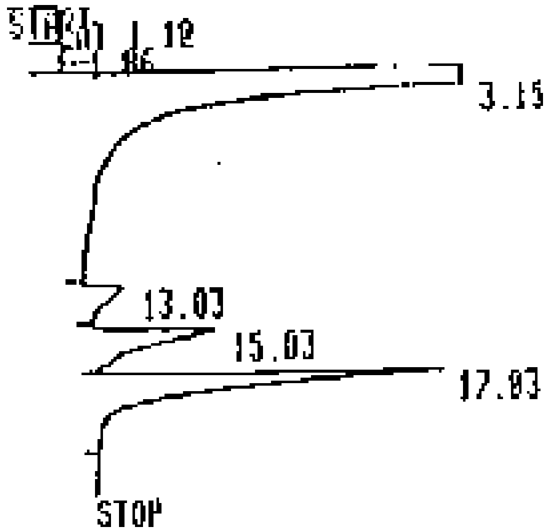
ENEC Ethyl N - Ethylcarbanilate

BZ 3 - Quinuclidinyl Benzilate

3 Componet Mixture Attenuation 8



Mixture of EEC [2.72mg/ml] and ENEC [3.26mg/ml]



3 Componet Mixture Attenuation 12
Concentration 10,20 and 30mg/ml respectively

FIGURE 3