

APPENDIX I.
APPLICATION WORK ORDER

PESTICIDE USE RECOMMENDATION

Phone: (805) 399-2951

WILBUR-ELLIS COMPANY
P.O. BOX 637
SHAFTER CA 93263

Doc #: 20000505

Fld #: 200137

Operator ID: 15951500178

Crop/Var: CARROTS

Grower: KERN RIDGE GROWERS

Site#: HC1

Invoice: KERN RIDGE GROWERS

Ranch: HAY CORP 1995

Applicator: WECO-KERN

Loctn: WHEELER RIDGE

Row S: 40

Application: GROUND

Lot: HC1

Band: 22

Posted: YES

Cty: 15

-----Surrounding Crops-----

Scheduled: 08/24/95

Sec: 26

North: ALMONDS N East:

Planted Ac: 80.0

Twn: 11N

East: ALMONDS N West:

Treated Ac: 80.0

Rng: 19W

South: GRAPES (WINE) S East:

Volumn/Ac: 100 GAL

B/M: SB

West: OPEN GROUND S West:

| Product..... | EPA Reg No..... | Rate/Unit..... | Pest/Reason..... | Total Qty Unit |
|------------------------|-----------------|-------------------------|------------------|----------------|
| SOIL PREP | 14488-52935- - | 50.000 gal/treated acre | NUTGRASS | 2200.00 GA |
| 10-34-0 LIQUID | N/A - - - | 50.000 gal/treated acre | FERTILIZER | 4000.00 LB |
| TILL-IT ZINC [CHELATE] | WECO N/A - - - | 0.500 gal/treated acre | FERTILIZER | 40.00 GA |

PRECAUTIONS/RESTRICTIONS.....

*Restricted: YES

Days to Harvest: N/A

Avoid Drift: YES

Notice of Intent Required: YES

Avoid Water Contamination: YES

Chemical Category: I DANGER

Toxic to Bees: NO

Closed Mixing System Required: YES

Toxic to Fish: YES

Posting Required: YES

Toxic to Birds: NO

Re-entry Interval: 48.00 HOURS

Feed/Graze Treated Area/Crop: NO

ENVIRONMENTAL CHANGES/COMMENTS.....

SOIL PREP: DON'T SEED EARLIER THAN 21 DAYS AFTER APP. WHEN TARPING METHOD IS USED

I certify that I have considered alternatives and mitigation measures that would substantially lessen any significant impact on the crop or environment and have adopted those found feasible.

[] Pest is present [] Pest is known to occur [] Other Proper timing is needed
Expires: [/ /] PCA Name: [TIMOTHY GERMAN] Date: 8/22/95

PCA signature: Timothy German PCA #: 2963

PLANTBACK RESTRICTIONS or LIMITATIONS

Page : 1

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SOIL PREP : THIS PRODUCT IS TOXIC TO FISH. DO NOT APPLY DIRECTLY TO WATER, OR TO AREAS WHERE SURFACE WATER IS PRESENT, OR TO INTERTIDAL AREAS BELOW THE MEAN HIGH WATER MARK. DO NOT APPLY WITHIN 3 FEET OF DRIP LINE OF DESIRABLE PLANTS, SHRUBS OR TREES. DO NOT USE IN CONFINED AREAS WITHOUT ADEQUATE VENTILATION OR WHERE FUMES MAY ENTER NEARBY HOUSES CONTAINING GROWING PLANTS. DO NOT USE IN GREENHOUSES WHERE DESIRABLE PLANTS ARE PRESENT. CULTIVATE SOIL THOROUGHLY BEFORE TREATMENT, BREAKING UP ALL LARGE CLODS. IF SOIL CRUSTS FOLLOWING PRETREATMENT IRRIGATION, LIGHTLY CULTIVATE IT AGAIN BEFORE TREATMENT. FOR APPLICATION OVER COVER CROPS, NO CULTIVATION OF SOIL IS REQUIRED PRIOR TO TREATMENT. AT TIME OF TREATMENT, SOIL TEMPERATURE SHOULD BE 40-90 deg. F AT A DEPTH OF 3". TO PREVENT RAPID EVAPORATION OF PRODUCT FROM SOIL, AVOID TREATING SOIL DURING TIMES OF DAY WHEN SOIL TEMPERATURES EXCEED 90 deg. F. INSTEAD, MAKE APPLICATION DURING EARLY MORNING HOURS WHEN SOIL TEMPERATURE IS COOLEST. APPLICATION SHOULD BE MADE UNDER "GOOD SEED BED MOISTURE CONDITIONS", THAT IS, SOIL MOISTURE SHOULD BE ABOUT 50-80% OF FIELD CAPACITY. WHEN NECESSARY, 1-2 WEEKS PRIOR TO TREATMENT SPRINKLE OR FLOOD IRRIGATE SOIL TO INCREASE MOISTURE CONTENT. SOIL MUST BE MOISTENED TO AT LEAST DESIRED TREATMENT DEPTH. TO BE MOST EFFECTIVE, SOIL PREP SHOULD BE SEALED IN SOIL. SEALING METHODS INCLUDE APPLYING IRRIGATION WATER OR PLASTIC TARPULINS AND PACKING SOIL WITH A ROLLER OR DRAG. TARPULINS SHOULD BE SPREAD LOOSELY OVER TREATED AREA AND SECURED TO PREVENT REMOVAL BY WIND. THEY SHOULD REMAIN IN PLACE FOR AT LEAST 48 HOURS. SEVEN DAYS AFTER TREATMENT, SEALED AREA SHOULD BE CULTIVATED TO A DEPTH OF 2" TO AERATE SOIL. WHEN TARPULINS ARE USED TO SEAL SOIL, WAIT AT LEAST 21 DAYS BEFORE PLANTING. IF RAINFALL OCCURS LESS THAN 24 HOURS AFTER TREATMENT, LACK OF CONTROL AT OR NEAR SOIL SURFACE MAY RESULT. ON WELL DRAINED SOILS WHICH HAVE A LIGHT TO MEDIUM TEXTURE AND WHICH ARE NOT EXCESSIVELY WET OR COLD FOLLOWING APPLICATION, PLANTING CAN BEGIN 14-21 DAYS AFTER TREATMENT. IF SOILS ARE HEAVY OR ESPECIALLY HIGH IN ORGANIC MATTER, OR IF THEY REMAIN WET AND/OR COLD (BELOW 60 deg. F) FOLLOWING APPLICATION, A MINIMUM INTERVAL OF 30 DAYS SHOULD BE OBSERVED. WHERE DOSAGE IS GREATER THAN 75 GALLONS PER ACRE, WAIT AT LEAST 60 DAYS. AFTER WAITING PERIOD HAS PASSED, IF THERE IS ANY QUESTION ABOUT COMPLETE ESCAPE OF SOIL PREP FROM SOIL, TRANSPLANT SEEDLING INTO TREATED SOIL. IF PLANT DEVELOPS NORMALLY WITHOUT ANY SIGNS OF CHEMICAL INJURY, CROP PLANTING CAN BEGIN. **** SOIL PREP MAY BE INJECTED INTO SOIL OR APPLIED TO SOIL SURFACE AND INCORPORATED WITH A DISC, ROTARY TILLER, POWER MULCHER OR BED-SHAPING EQUIPMENT. SEAL IMMEDIATELY WITH IRRIGATION WATER, TARPULIN OR BY PACKING SOIL WITH ROLLER OR DRAG. IN CALIFORNIA, READ AND FOLLOW THE TECHNICAL INFORMATION BULLETIN TO MINIMIZE OFF-SITE MOVEMENT OF ODORS WHEN APPLYING METAM SODIUM. THE MINIMIZATION OF OFF-SITE MOVEMENT IS THE RESPONSIBILITY OF THE APPLICATOR. ALL MIXING AND LOADING OF METAM SODIUM MUST BE THROUGH A CLOSED SYSTEM. A NOTICE OF INTENT MUST BE FILED AT LEAST 24 HOURS PRIOR TO APPLICATION TO ANY FIELD THAT IS IN A SENSITIVE AREA AS DEFINED ON THE TECHNICAL BULLETIN.

APPENDIX II
SAMPLING PROTOCOL

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

PESTICIDE MONITORING PROTOCOL

**Methyl Isocyanate (MIC) and Methyl Isothiocyanate (MITC) Monitoring
After an Application of Metam Sodium During the Summer 1995**

Engineering and Laboratory Branch
Monitoring and Laboratory Division

Project No. C94-046A

Date: July 31, 1995

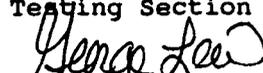
APPROVED:



Don Fitzell, Project Engineer



Peter K. Ouchida, Manager,
Testing Section



George Lew, Chief,
Engineering and Laboratory Branch

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Methyl Isocyanate (MIC) and Methyl Isothiocyanate (MITC) Monitoring
After an Application of Metam Sodium During the Summer 1995

I. Introduction

At the request of the Office of Environmental Health Hazard Assessment (OEHHA), the Air Resources Board (ARB) will conduct ambient air monitoring for methyl isocyanate (MIC) and methyl isothiocyanate (MITC), near a soil injection application of the soil fumigant, metam sodium. MITC is responsible for the pesticidal activity of metam sodium. MITC and hydrogen sulfide are breakdown products of metam sodium and have been the subject of earlier studies by the ARB and the Department of Pesticide Regulation (DPR). Recent research has indicated that MIC may be a breakdown product of MITC. This monitoring is being done as a follow-up to the prior studies in an attempt to determine whether MITC breaks down into MIC in ambient air in order to identify potential related health risks.

The monitoring is scheduled for the summer of 1995 and will be conducted prior to, during, and for a period of up to 72 hours following an application. Monitoring will be coordinated with the DPR, the County Agricultural Commissioner's Office, and an applicator.

II. Sampling

It is anticipated that a field in Kern County will be chosen for this application monitoring. Prior to application, background samples will be taken to establish if any MIC, or MITC are detectable. Air samples of 12 hours in duration will be collected for a period of 72 hours following the initiation of the application. Charcoal tubes will be used to trap MITC and specially treated XAD-7 resin tubes will be used for MIC. The sampling tubes will be changed at approximately 7:00 a.m. and 7:00 p.m. Air will be pulled through the sampling tubes using battery powered pumps. The MIC samples will be collected at a rate of approximately 75 milliliters per minute (ml/min.); the MITC samples will be collected at a rate of approximately 2 liters per minute (lpm). Samples will be collected using the sampling train shown in ATTACHMENT I.

Four sampling locations for each compound will be used: one on each side (assuming a rectangular field) of the field at a distance of approximately 15 yards. These distances are approximate and dependent on the physical obstacles surrounding the field.

Calibrated rotameters will be used to set and measure sample flow rates. Samplers will be leak checked prior to and after each sampling period with the sampling tubes installed. Any change in the flow rates will be recorded in the field log book. The field log book will also be used to record start and stop times, sample identifications and any other significant data, including field

size, application rate, formulation, method of application, and length of application.

A meteorological station will be set up to determine wind speed and direction. This station will continue to operate throughout the sampling period. Weather data will also be obtained from the nearest California Irrigation Management Information System (CIMIS) station. These data will be included in the final report.

If time and personnel permit, Tedlar bag grab samples will be taken. These will be used by the analytical laboratory for research and development of a possible method of analysis for methyl isocyanide (MICN), another possible breakdown product of metam sodium.

III. Analysis

The analysis will be conducted by staff of the Environmental Health Laboratory Branch of the Department of Health Services in Berkeley. All samples will be stored in an ice chest containing dry ice or a freezer until analysis. Analysis of MITC samples will be by gas chromatography/nitrogen-phosphorus detector (GC/NPD) after extraction of the tubes with carbon disulfide. The MIC samples will be analyzed by high performance liquid chromatography/fluorescence detector after extraction of the XAD-7 tubes with 4 ml of acetonitrile. The Standard Operating Procedure (S.O.P.) for the analysis of both compounds will be included in the final report.

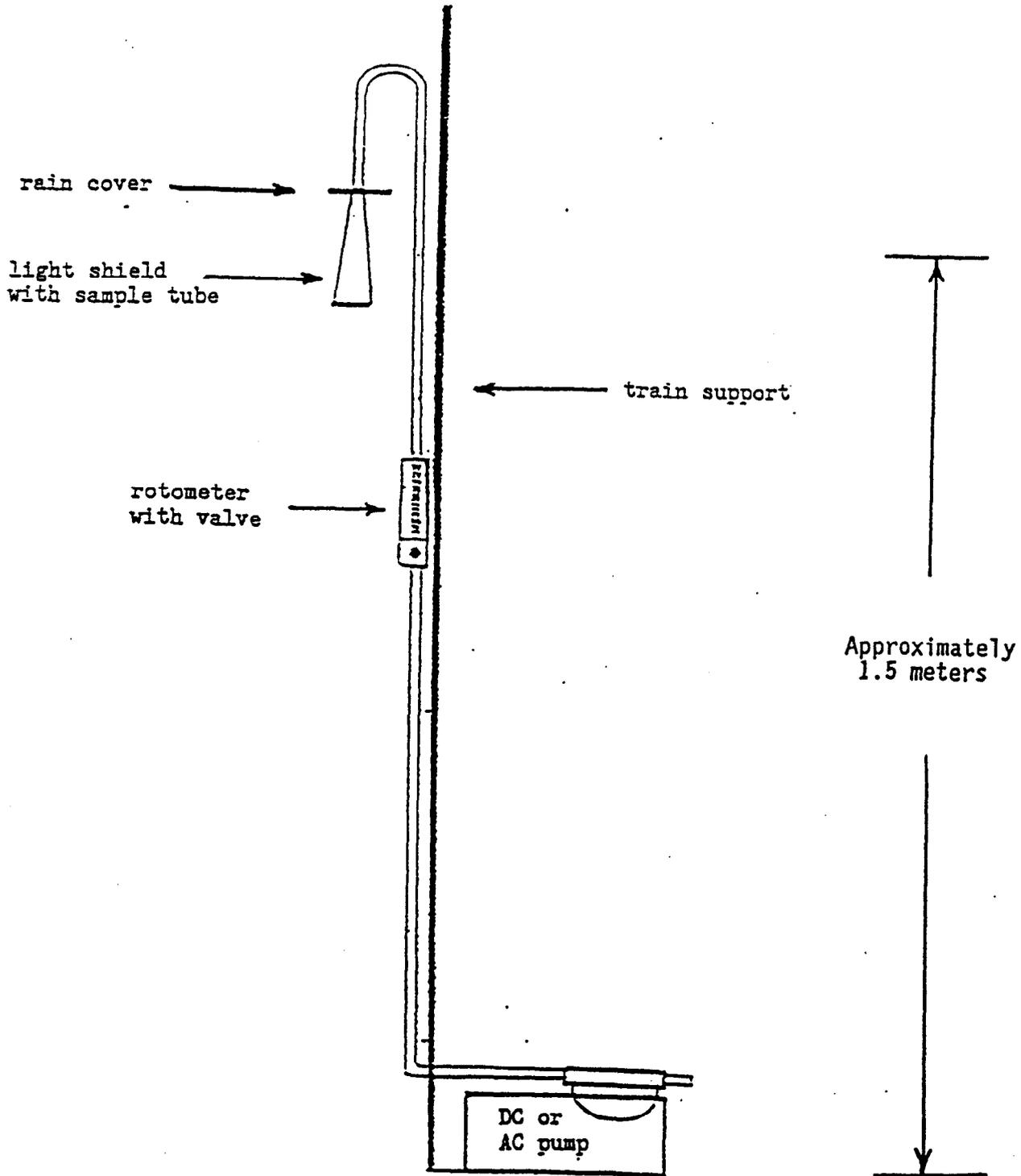
IV. Quality Assurance

Procedures will follow ARB's "Quality Assurance Plan for Pesticide Monitoring" (ATTACHMENT II). The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. A chain of custody sheet will accompany all samples. Sampler flow rates will be calibrated prior to and after sampling in the field.

V. Personnel

ARB personnel will consist of Don Fitzell (Project Engineer) and two Instrument Technicians.

ATTACHMENT I
PESTICIDE MONITORING APPARATUS



ATTACHMENT II

QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

State of California
California Environmental Protection Agency
Air Resources Board

QUALITY ASSURANCE PLAN
FOR PESTICIDE MONITORING

Prepared by the
Monitoring and Laboratory Division
and
Stationary Source Division

Revised: February 4, 1994

APPROVED:


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This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) an application has occurred. These are referred to as **ambient** and **application** monitoring, respectively. To help clarify the differences between these two monitoring programs, **ambient** and **application** are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

A. Quality Assurance Policy Statement

It is the policy of the ARB to provide DPR with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

II. Siting

Probe siting criteria for ambient pesticide monitoring are listed in TABLE 1. Normally four sites will be chosen. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. One of these sites is usually designated to be an urban area "background" site and is located away from any expected applications; however, because application sites are not known prior to the start of monitoring, a "zero level" background may not occur. Detectable levels of some pesticides may also be found at an urban area background site if they are marketed for residential as well as commercial use.

Probe siting criteria for placement of samplers near a pesticide application for collection of samples are the same as ambient monitoring (TABLE 1). In addition, the placement of the application samplers should be to obtain upwind and downwind concentrations of the pesticide. Since winds are variable and do not always conform to expected patterns, the goal is to surround the

application field with one sampler on each side (assuming the normal rectangular shape) at a distance of about 20 yards from the perimeter of the field. However, conditions at the site will dictate the actual placement of monitoring stations. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed.

III. Sampling

All sampling will be coordinated through the County Agricultural Commissioner's Office and the local Air Quality Management District (AQMD) or Air Pollution Control District (APCD). Monitoring sites will be arranged through the cooperation of applicators, growers or owners for application monitoring. For selection of ambient sites, ARB staff will work through authorized representatives of private companies or government agencies.

A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for ambient monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site.

B. Schedule

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Field application monitoring will follow the schedule guidelines outlined in TABLE 2.

C. Blanks and Spikes

Field blanks should be included with each batch of samples submitted for analysis. This will usually require one blank for an application monitoring and one blank per week for an ambient monitoring program. Whenever possible, trip spikes should be provided for both ambient and application monitoring. The spiked samples should be stored in the same manner as the samples and returned to the laboratory for analysis.

D. Meteorological Station

Data on wind speed and direction will be collected during application monitoring by use of an on-site meteorological station. If appropriate

equipment is available, temperature and humidity data should also be collected and all meteorological data recorded on a data logger. Meteorological data are not collected for ambient monitoring.

E. Collocation

For both ambient and application monitoring, precision will be demonstrated by collecting samples from a collocated sampling site. An additional ambient sampler will be collocated with one of the samplers and will be rotated among the sampling sites so that duplicate samples are collected at at least three different sites. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. The duplicate sampler for application monitoring should be downwind at the sampling site where the highest concentrations are expected. When feasible, duplicate application samples should be collected at every site.

F. Calibration

Field flow calibrators (rotometers, flow meters or critical orifices) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard should be verified, certified or calibrated with respect to a primary standard at least once a year with the method clearly documented. Sampling flow rates should be checked in the field and noted before and after each sampling period. Before flow rates are checked, the sampling system should be leak checked.

G. Flow Audit

A flow audit of the field air samplers should be conducted by an independent agency prior to monitoring. If results of this audit indicate actual flow rates differ from the calibrated values by more than 10%, the field calibrators should be rechecked until they meet this objective.

H. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results.

I. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the U.S. EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

| <u>Height Above Ground (Meters)</u> | <u>Minimum Distance From Supporting Structure (Meters)</u> | | <u>Other Spacing Criteria</u> |
|-------------------------------------|--|-------------------|---|
| | <u>Vertical</u> | <u>Horizontal</u> | |
| 2-15 | 1 | 1 | <ol style="list-style-type: none"> 1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute. |

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

All samplers should be sited approximately 20 yards from the edge of the field; four samplers to surround the field whenever possible. At least one site should have a collocated (duplicate) sampler.

The approximate sampling schedule for each station is listed below; however, these are only approximate guidelines since starting time and length of application will dictate variances.

- Background sample (minimum 1-hour sample: within 24 hours prior to application).
- Application + 1 hour after application combined sample.
- 2-hour sample from 1 to 3 hours after the application.
- 4-hour sample from 3 to 7 hours after the application.
- 8-hour sample from 7 to 15 hours after the application.
- 9-hour sample from 15 to 24 hours after the application.
- 1st 24-hour sample starting at the end of the 9-hour sample.
- 2nd 24-hour sample starting 24 hours after the end of the 9-hour sample.

IV. Protocol

Prior to conducting any pesticide monitoring, a protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.
2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).
3. Specification of sampling periods and flow rates.
4. Description of the analytical method.
5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

V. Analysis

Analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, an analytical audit and systems audit should be performed by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis. After a history of competence is demonstrated, an audit prior to each analysis is not necessary. However, during each analysis spiked samples should be provided to the laboratory to demonstrate accuracy.

A. Standard Operating Procedures

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. includes: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures. The limit of quantitation must be defined if different than the limit of detection. The method of calculating these values should also be clearly explained in the S.O.P.

1. Instrument and Operating Parameters

A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

The S.O.P. plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Control

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection (and quantitation if different from the limit of detection). Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three

replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as $\mu\text{g}/\text{m}^3$ (microgram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume; however, the minimum and maximum concentrations possible for that sample should also be presented.

The final report should indicate the dates of sampling as well as the dates of analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring are sent to the Department of Pesticide Regulation, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering Evaluation Branch.

A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building). A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum quantitation limit), total number of samples and number of samples above the minimum quantitation limit. For this purpose, collocated samples are averaged and treated as a single sample.

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as

much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

CALIFORNIA AIR RESOURCES BOARD
 MONITORING & LABORATORY DIVISION
 P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: _____ Date: ____/____/____
 Sample/Run #: _____ Time: _____
 Job name: _____
 Sample Location: _____
 Type of Sample: _____
 Log #'s: _____

| ACTION | DATE | TIME | INITIALS | | METHOD OF STORAGE freezer, ice or dry ice |
|------------------|------|------|----------|----------|--|
| | | | GIVEN BY | TAKEN BY | |
| Sample Collected | | | | | |
| Transfer | | | | | |

| LOG # | ID # | DESCRIPTION |
|-------|------|-------------|
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |

RETURN THIS FORM TO: _____

APPLICATION CHECKLIST

1. Field size.
2. Field location (Section, Range and Township).
3. Application rate.
4. Formulation.
5. Method of application (ground, air, irrigation, injection, tarping after application, etc.)
6. Length of application.
7. Any unusual weather conditions during application or monitoring period (rain, fog, wind).
8. Any visible drift from the field?
9. Pattern of application (e.g., east to west).

APPENDIX III
MIC ANALYTICAL S.O.P.

DETERMINATION OF METHYL ISOCYANATE (MIC)

| | |
|--|--|
| Method No.: EHLB 104 - Modified OSHA Method No.54 (Ref. 6.1) | |
| <p>Analyte: Methyl Isocyanate</p> <p>Synonyms: MIC, isocyanatomethane, isocyanic acid methyl ester, methyl-carbylamine</p> <p>CAS No. 624-83-9</p> <p>Structure: $H_3C-N=C=O$</p> | <p>Physical Properties:</p> <p>MW: 57.05 bp: 39.1°C at 760 mm Hg mp: -17°C sp gr: 0.9599 @ 20°C vp: 348 mm Hg @ 20°C color: clear, colorless odor: sharp flash pt: < -18°C (open cup)</p> |
| <p>Matrix: Air Target Concentration: 47 µg/m³ or 20 ppbv (ACGIH TWA)</p> | <p>Precision: 2.89% Accuracy: 93.5%</p> |
| <p>Recommended Air Volume and Sampling Rate: 108L @ 0.075 LPM</p> | <p>Limit of Detection: 0.032 ppbv Limit of Quantitation: 0.25 ppbv</p> |
| <p>Procedure: Samples are collected by drawing a known volume of air through XAD-7 tubes coated with 1-(2-pyridyl)piperazine (1-2PP). Samples are desorbed with acetonitrile (ACN) and analyzed by high performance liquid chromatography (HPLC) using a fluorescence detector.</p> | |
| <p>Special requirements: The coated XAD-7 tubes should be stored under refrigeration before sampling.</p> | |

1. General Discussion

- 1.1 Environmental Health Laboratory Branch (EHLB) evaluated OSHA Method No. 54 for the sampling and analysis of methyl isocyanate (MIC), a possible degradation product of the agricultural soil fumigants metam sodium and methyl isothiocyanate (MITC). Samples are collected by drawing a known volume of air through XAD-7 tubes coated with 1-(2-pyridyl)piperazine. Samples are desorbed with acetonitrile and analyzed by high performance liquid chromatography (HPLC) using a fluorescence detector. The OSHA method recommends an air volume and sampling rate of 15 L and 0.050 L/min, respectively, resulting in a limited sampling period of only 5 hours. However, for health risk assessment purposes it is desirable to employ ambient air samplers capable of sampling air continuously over a 24-hr. period.

Prepared by Miles Imada, Mario Fracchia, SuzAnne Twiss and Diamon Pon, Outdoor Air Quality Section, Environmental Health Laboratory Branch, Division of Environmental and Occupational Disease Control, California Department of Health Services, Berkeley, CA.

This 24-hr. sampling requirement necessitated the modification of OSHA Method No. 54 with the use of a sequential pair of higher capacity XAD-7 sampling tubes containing 175 mg each of the coated resin, as compared to the original sampling tube containing 80 mg (front segment) and 40 mg (breakthrough segment). The following text contains pertinent sections from the original OSHA Method No. 54 combined with the EHLB modified sampling and analysis procedures.

- 1.2 Toxic effects. Inhalation of MIC vapors may cause irritation of the eyes, nose, throat, and lungs. Cough, shortness of breath, increased phlegm and chest pains may be present. The liquid splashed in the eyes may cause permanent damage. The liquid splashed on the skin may cause irritation. Exposure to MIC may cause a person to become allergic to it so that extremely low levels of exposure may cause an asthmatic attack. (Refs. 6.2 and 6.3)
- 1.3 Advantages. The analytical procedure is specific and sensitive for MIC.
- 1.4 Disadvantages. XAD-7 tubes coated with 1-2PP are not commercially available.

Due to differences between individual columns, the mobile phase for the HPLC has to have the pH adjusted for every bottle of solvent that is made. The pH affects the retention time of the 1-2PP and the response of the fluorescence detector.

2. Limit defining parameters. (The analyte air concentrations listed throughout this method are based on an air volume of 108 L collected at a flowrate of 75 mL/min over a 24-hr. sampling period. Solvent desorption volume is 4 mL. Amounts are expressed as the equivalent weight of MIC, even though the MIC derivative was analyzed (Refer to Section 4.3.2). Limit defining parameters were determined using a fluorescence detector.)

- 2.1 Limit of detection (LOD) of the analytical procedure (Refs. 6.4 and 6.5).

The detection limit of the analytical procedure is based on the lowest MIC standard concentration of the calibration curve, i.e., 0.0156 $\mu\text{g/mL}$. Seven replicate analyses of this concentration yielded a standard deviation of 0.0006 $\mu\text{g/mL}$. The LOD is determined as the product of the standard deviation and the student's single-sided t test value for 99% confidence, i.e., 3.143. These measurements assure the analyst that the LOD is the minimum concentration of substance that can be reported with 99% confidence that the analyte concentration is greater than zero.

The detection limit of the analytical procedure is thus calculated to be 0.002 $\mu\text{g/mL}$ or 0.02 ng per 10 μL injection of MIC with the fluorescence detector. This results in an analytical LOD at 8 ng MIC per sample.

- 2.2 Detection limit of the overall procedure.

The limit of detection in terms of airborne concentrations is 74 ng/m^3 or 0.032 ppbv.

- 2.3 Limit of quantitation (LOQ) (Ref. 6.5).

LOQs are usually recommended to be set at a value equal to 10 times the standard deviation of the seven replicate analysis stated in Section 2.1. However, EHLB has conservatively selected the

lowest MIC calibration standard as the LOQ, i.e., 0.015625 $\mu\text{g}/\text{mL}$. The LOQ is thus 0.062 μg per sample or in terms of airborne concentrations 0.58 $\mu\text{g}/\text{m}^3$ or 0.25 ppbv.

2.4 Storage Test

OSHA found that the recovery of MIC spiked samples (0.789 μg MIC/tube) used in an 18-day storage test averaged 98.3% when the samples were stored at 21°C. An average recovery of 100.6% were found for identically spiked samples that were stored in the refrigerator at 4°C.

2.5 Precision (analytical method procedure)

The separate coefficient of variations obtained from seven replicate determinations of analytical standards at concentrations of 0.125, 0.065, 0.03125 and 0.015625 $\mu\text{g}/\text{mL}$ are 1.5%, 1.45%, 2.48% and 2.87% respectively. The overall coefficient of variation is 2.1%.

2.6 Precision (procedure based on spiked samples containing 0.8 μg MIC)

OSHA found the precision at the 95% confidence level for an 18-day storage test to be $\pm 15.6\%$. This includes an additional $\pm 5\%$ for sampling error. OSHA recommends that precision for the overall procedure at the target concentration is $\pm 25\%$ or better at the 95% confidence level.

2.7 Overall Accuracy and Precision

A 20 ppbv test atmosphere was prepared in a Tedlar bag from which a duplicate set of air samples were collected over a 24-hr period at a sampling rate of 0.075 L/min. (See Section 5.) Estimation of the accuracy and precision values were derived from the duplicate set of samples. The accuracy of the air sampling and analytical method taken into consideration the desorption efficiency correction averaged 93.5%. For these same air samples, the precision is 2.89%. This corresponds well with the overall 2.1% coefficient of variation found from replicate analyses of MIC standards (Section 2.5).

3. Sampling Procedure

3.1 Apparatus. Samples are collected by use of sampling pumps that are calibrated to within $\pm 5\%$ of the recommended flow rate with the sampling device in-line.

3.1.1 Preparation of 1-2PP coated XAD-7 tubes.

XAD-7 tubes from SKC (SKC 226-97, 8 x 110 mm tube containing 175 mg XAD-7 resin) are coated with 0.5 mg of 1-(2-pyridyl)piperazine (1-2PP) in the following manner. Dissolve the 1-2PP in methylene chloride and place in a separatory funnel. Add 0.05 M sulfuric acid and shake carefully. The 1-2PP is now in the aqueous layer. Separate the layers and discard the organic layer. Make the aqueous layer basic with potassium hydroxide. Extract with methylene chloride and separate the layers. Remove the methylene chloride from the clean 1-2PP using a stream of nitrogen gas. This procedure reduces the contaminant in the 1-2PP that interferes with the HPLC analysis. Make a solution of 1.0 mg/mL of clean 1-2PP in methylene chloride. Open both ends of the XAD-7 tube and with a syringe inject 450 to 600 μL of the 1-2PP solution onto the

beads. A flow limited by a 0.075 L/min critical orifice (30 G hypodermic needle) at > 20 in Hg vacuum is used to draw the solution completely through the XAD-7 resin. Dry the wet tubes in an unheated vacuum oven for 1 hour.

3.1.2 Place plastic caps on the open ends of the tubes, wrap in aluminum foil, place in a capped jar and store them in freezer as a precaution to prevent decomposition of the 1-2PP. Exposure to strong sunlight should be avoided.

3.2 Reagents

No sampling reagents are required.

3.3 Sampling technique

3.3.1 Attach the coated XAD-7 tube to the sampling pump with flexible, plastic tubing such that the front section of the sampling tube is exposed vertically directly to the atmosphere. Do not place any tubing in front of the sampling tube.

3.3.2 The recommended flow rate is 0.075 L/min with a recommended total air volume of 108 L.

3.3.3 After sampling for 24 hours, remove the sampling device and install the two plastic caps on the open ends of the tube.

3.3.4 Wrap each sample end-to-end with a seal.

3.3.5 With each set of samples, submit at least one blank. The blank should be handled the same as the other samples except that no air is drawn through it. Similarly a sufficient number of MIC spiked tubes should be submitted with each batch of samples to monitor effects of field and storage conditions.

3.4 Desorption efficiency

The average desorption efficiency of MIC derivative is 89.6% for loadings ranging from 1.2 to 5.0 µg MIC.

3.5 Recommended air volume and sampling rate

3.5.1 The recommended air volume is 108 L.

3.5.2 The recommended air sampling rate is 0.075 L/min.

3.6 Interferences (sampling)

Any compound that could react with 1-2PP, or compete with it in the reaction to derivatize MIC, should be considered as an interference. Potential interferences include anhydrides, amines, alcohols and carboxylic acid.

4. Analytical Procedure

4.1 Apparatus

- 4.1.1 High performance liquid chromatograph equipped with an ultraviolet (UV) or fluorescence detector, manual or automatic injector, and chart recorder.
- 4.1.2 HPLC column capable of separating MIC from any interferences. The column employed in this study was a (25-cm x 4.6-mm i.d.) DuPont Zorbax CN (6 μ m) column.
- 4.1.3 An electronic integrator, or some other suitable method of measuring detector response.
- 4.1.4 Vials, 2 dram (7.4 mL) with Teflon-lined caps.
- 4.1.5 Volumetric flasks, pipets, and syringes for preparing standards, making dilutions, and making injections.
- 4.1.6 Suitable glassware for preparation of MIC urea derivative.
- 4.1.7 pH meter for adjusting the mobile phase.
- 4.1.8 Mechanical shaker.

4.2 Reagents

- 4.2.1 Methylene chloride, hexane and acetonitrile, HPLC grade.
- 4.2.2 Water, distilled, deionized and filtered (0.22 micron). Our laboratory employs a commercially available water filtration system for the preparation of HPLC grade water.
- 4.2.3 1-(2-Pyridyl)piperazine, Aldrich.
- 4.2.4 Methyl isocyanate, K&K.
- 4.2.5 Ammonium acetate, HPLC grade.
- 4.2.6 Glacial acetic acid.

4.3 Standard preparation

4.3.1 Preparation of purified derivative

A solution containing 0.1 g of MIC in 25 mL of methylene chloride is slowly added to a solution of 0.3 g of 1-2-PP in 50 mL of methylene chloride while stirring. The resulting solution is stirred for 1 hour. Reduce the volume of methylene chloride to less than 10 mL by evaporation with a stream of dry nitrogen. The solution is added dropwise to 800 mL of hexane while stirring and the resulting precipitate is collected. The precipitate is redissolved in a minimal volume of methylene chloride and reprecipitated in hexane. The precipitate is collected and washed with hexane. The approximate yield is 0.35 g of the derivative after being dried under vacuum. This preparation is a modification of the procedure reported by Goldberg et al. (Ref. 6.6)

4.3.2 Preparation of standards

A stock standard solution is prepared by dissolving the MIC derivative into ACN. The derivative is expressed as free MIC by multiplying the amount of MIC urea weighed by the conversion factor 0.2590.

$$(\text{MW MIC})/(\text{MW MIC Urea}) = 57.05/220.27 = 0.2590$$

Working standards are prepared by diluting the stock standard solutions with ACN.

4.4 Sample preparation

4.4.1 The XAD-7 tube is opened and the entire contents including the glass wool plugs and the 175 mg coated resin are placed into a 2 dram vial.

4.4.2 Four milliliters of ACN are added to each vial.

4.4.3 A PTFE-lined cap is placed on each vial.

4.4.4 The vials are shaken for 60 min.

4.5 Analysis

4.5.1 Reverse phase HPLC conditions.

The mobile phase used in this analysis has to be adjusted to optimize the separation on each individual DuPont Zorbax CN column. The concentration of ACN is varied first to separate the MIC derivative from the interference. Then the pH is adjusted to move the 1-2PP to an acceptable retention time. The increase or decrease of the pH do not substantially affect the separation of the MIC derivative and the interference. The amount of response from the fluorescence detector is decreased as the pH is lowered.

| | |
|------------------------|--|
| column: | 25-cm x 4.6-mm i.d. stainless steel column packed with 6 μ m DuPont Zorbax CN |
| mobile phase: | 0.005-0.02 M ammonium acetate (0.8 g/L) in 15% ACN / 85% water (v/v) adjusted to pH 6.1 with acetic acid |
| flow rate: | 1.0 mL/min |
| fluorescence detector: | 240 nm excitation 370 nm emission |
| UV detector: | 254 nm |
| injection size: | 10 μ L |
| retention time: | 8-12 min. |
| chromatogram: | Figure 3.5.1 |

4.5.2 An external standard procedure is used to prepare a calibration curve using a stock solution from which working standards are made. The calibration curve is prepared daily. The samples are bracketed with analytical standards.

4.6 Interferences (analytical)

4.6.1 Any compound having the same retention time as the MIC derivative is an interference. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

4.6.2 Retention time on a single column is not proof of chemical identity. Analysis by an alternate HPLC column, absorbance response ratioing, and mass spectrometry are additional means of identification.

4.7 Calculations

The concentration in μ g/mL of MIC present in a sample is determined from the detector response of the analyte. Comparison of sample response with a least squares curve fit for standards allows the analyst to determine the concentration of MIC in μ g/mL for the sample (Figure 1). Since the sample volume is 4 mL, the results in μ g/m³ of air are expressed by the following equation:

$$\mu\text{g}/\text{m}^3 = (\mu\text{g}/\text{mL})(4 \text{ mL})/(\text{air volume, m}^3)(\text{desorption efficiency})$$

4.8 Safety precautions

4.8.1 Avoid exposure to the MIC standards.

4.8.2 Avoid skin contact with all solvents.

4.8.3 Wear safety glasses at all times.

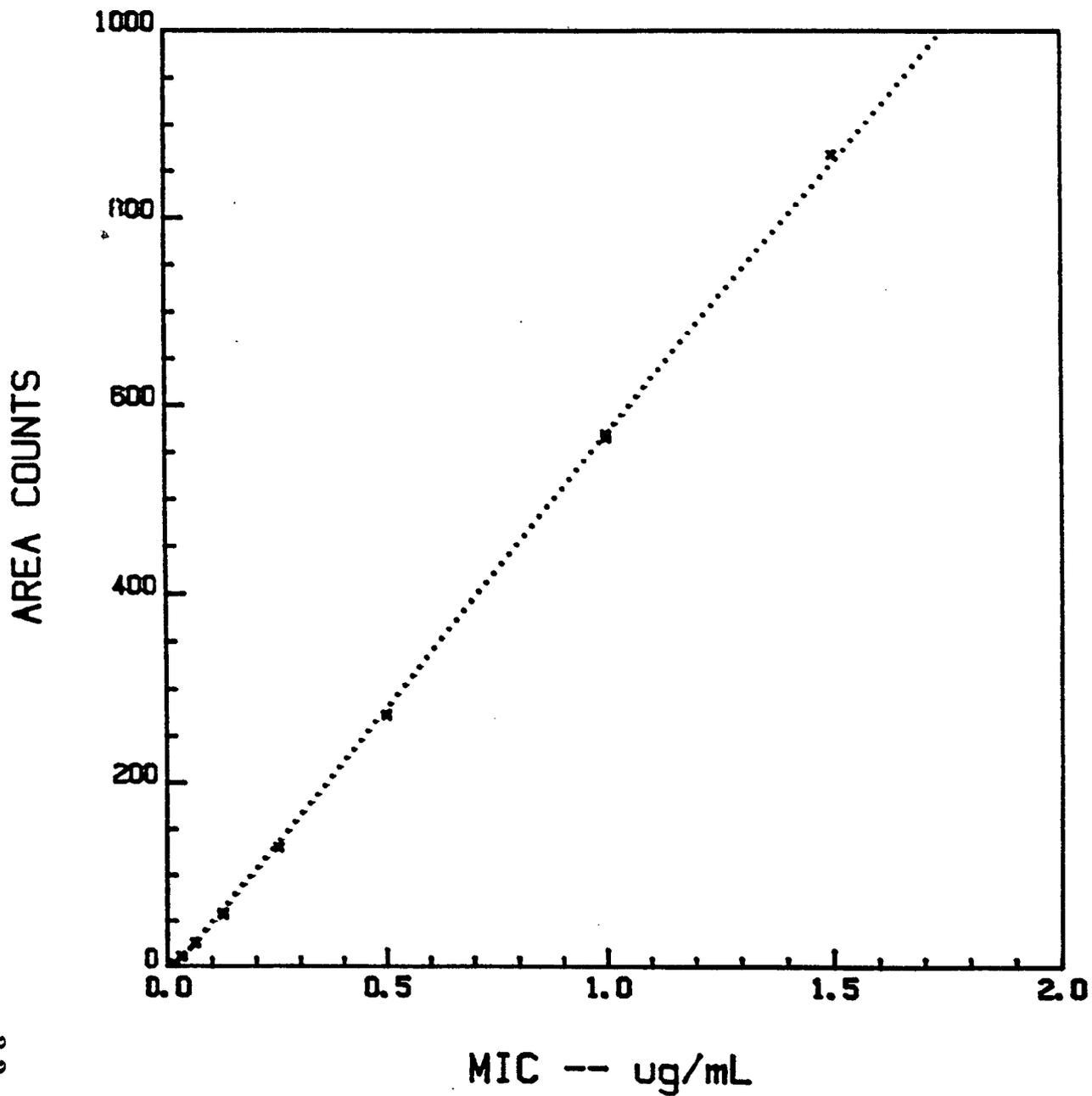
5. Gas sampling bag study to determine accuracy and precision (Figure 2)

A Tedlar gas sampling bag (42" x 38.5") was filled with 212.7 L of dry air. During the filling process, 9.9 μL of an MIC standard solution (1.0 μg MIC/ μL of methylene chloride) were injected through a septum resulting in a final concentration of 19.9 ppbv (46 $\mu\text{g}/\text{m}^3$). This test atmosphere was then sampled for 1413 min (23.58 hr) at 77.3 and 72.9 mL/min respectively, using 2 sets of XAD-7 sampling tubes coated with 1-2PP. A set consists of 2 tubes connected in series, the second tube serves as a breakthrough trap. Taken into consideration the MIC desorption efficiency (89.6%), the airborne concentrations found in the sampled tubes were 18.8 ppbv (94% recovery) and 18.6 ppbv (93% recovery) respectively. Therefore, the accuracy at the 20 ppbv level averaged 93.5%. Precision in terms of the coefficient of variation of the duplicate samples was 2.89%.

6. References

- 6.1 OSHA Analytical Method No. 54, "Methyl Isocyanate (MIC)"; OSHA Analytical Laboratory, Salt Lake City, Utah, April 1985.
- 6.2 "Occupational Health Guidelines for Chemical Hazards" NIOSH/OSHA, January 1981, DHHS (NIOSH) Publication No. 81-123.
- 6.3 Material Safety Data Sheet from Sigma-Aldrich Corporation, Milwaukee, WI; Valid 5/93-7/93.
- 6.4 Federal Register, Vol. 49, No. 209, October 1984. Appendix B to Part 136 "Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11".
- 6.5 Keith, L.H.; Crummett, W.; Deegan, J. Jr.; Libby, R.A.; Taylor, J.K.; and Wentler, G. "Principles of Environmental Analysis", Anal. Chem. 55:2210 (1983).
- 6.6 Goldberg, P.A.; Walker, R.F.; Ellwood, P.A.; Hardy, H.L. J. Chromatogr. 1981, 212, 93.

FIGURE 1. MIC CALIBRATION CURVE



WITH 1-(2-PYRIDYL)PIPERAZINE

SYMBOL = *

LINETYPE =

$y = a + b \cdot x$

$n = 17$

$a = -9.7002$

$b = 578.9811$

$s_{y,x} = 6.2248$

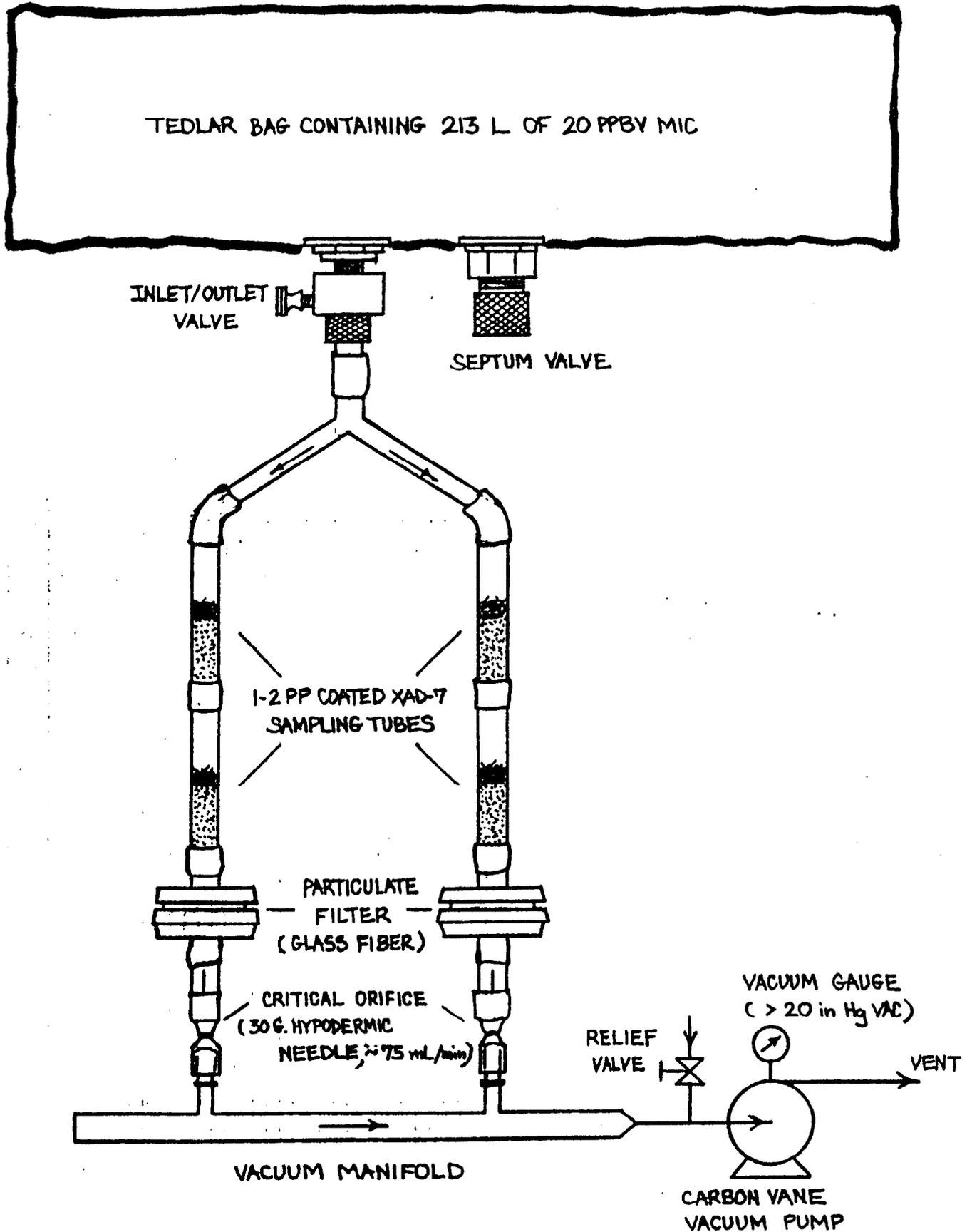
$s_e = 1.8840$

$s_y = 3.5032$

$r = 0.9997$

| DATA LISTING | |
|------------------|------------------|
| $\mu\text{g/mL}$ | Area Counts |
| 0.000 | 0.00 0.00 |
| 0.0156 | 3.01 3.36 |
| 0.0313 | 11.35 10.69 |
| 0.0625 | 25.22 25.66 |
| 0.1256 | 56.47 58.25 |
| 0.250 | 129.09 129.41 |
| 0.500 | 271.88 273.89 |
| 1.000 | 568.80 565.12 |
| 1.500 | 869.12 |

FIGURE 2. SETUP OF SAMPLING KNOWN MIC TEST ATMOSPHERES
(NOT DRAWN TO SCALE)



APPENDIX III
MITC ANALYTICAL S.O.P.

ICI Procedure for the Analysis Of MITC

METHYL ISOTHIOCYANATE FROM METHAM-SODIUM
DETERMINATION IN AIR

Written by: S. C. Leung

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de Guigne Technical Center
August 26, 1982
Method No. RRC-82-35

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Method No. RRC-82-35 Date 8/26/82
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TITLE:
 METHYL ISOTHIOCYANATE FROM METHAM-SODIUM
 DETERMINATION IN AIR

I. SCOPE

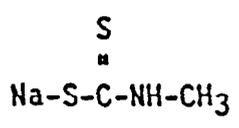
This method is designed to measure methyl isothiocyanate (MITC) in air. The method is applicable for methyl isothiocyanate concentrations between 0.01 and 6 mg per cubic meter in a 40-liter air sample. Methyl isothiocyanate is the active fumigant to which VAPAM® is converted upon application to soil.

II. SUMMARY OF METHOD

A known volume of air is drawn through a charcoal tube via a battery-operated sampling pump. The methyl isothiocyanate present in the air is quantitatively adsorbed on the charcoal. The charcoal is then desorbed with carbon disulfide; the extract is analyzed for methyl isothiocyanate by gas chromatography with nitrogen-phosphorus alkali flame ionization detection.

III. INTRODUCTION

VAPAM® soil fumigant, common name Metham-sodium, is sodium N-methyldithiocarbamate:



VAPAM® is generally formulated as an aqueous solution containing 32.7% anhydrous sodium salt and is nonvolatile. Its activity is due to decomposition to methyl isothiocyanate (CH₃NCS).

IV. APPARATUS AND REAGENTS

A. Apparatus

1. Gas Chromatograph. Hewlett-Packard Model 5710A or equivalent, equipped with a nitrogen-phosphorus alkali flame ionization detector (NP-AFID).



2. Recorder. Sensitivity of 1 millivolt full scale, 1 second response.
3. Quantitation Aid. Electronic digital integrator, on-line data acquisition system or other device for measuring peak areas.
4. Gas Purification Traps. For purifying helium, air and hydrogen required for gas chromatograph. Model 236 (Guild Corp., P. O. Box 217, Bethel Park, PA 15102) or equivalent.
5. Gas Chromatograph Column. Pyrex tubing (1.8 m x 2 mm i.d.), washed with KOH solution, silanized and dried. Pack the tubing with 10% SP 2250 on 100/120 mesh Supelcoport or equivalent. See Appendix A for details of column preparation and conditioning.
6. Syringe. 10-microliter capacity with fixed needle, Hamilton 701N or equivalent.
7. Personal Air Sampling Pump. DuPont P-200 or equivalent; capable of drawing 100 mL/minute of air through the charcoal tube for 8 hours.
8. Glass Vials. 2-dram, equipped with polyseal-lined caps.
9. Charcoal Tubes. Glass tube with both ends flame sealed, 7 cm long with a 6-mm o.d. and a 4-mm i.d., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. Such charcoal tubes are commercially available from SKC, Inc., Eighty four, PA 15330, Cat. No. 226-01.
10. Charcoal Tube Holder. Nylon sample tube holder equipped with collar clip and tygon connecting tube for supporting the charcoal tube in a vertical position in the employee's breathing zone. SKC Cat. No. 222-3-1, or equivalent.
11. Silica Gel Tubes. For use as moisture pre-trap in the presence of high (>80%) relative humidity. These are glass tubes with both ends flame sealed, 7 cm long with a 6-mm O.D., containing 2 sections of 75/150 mg of silica gel. SKC Cat. No. 226-10, or equivalent.



B. Reagents

1. Carbon Disulfide. Mallinckrodt AR grade, Cat. No. 4352 or equivalent.
2. Gases. Supplied to gas chromatograph via lines equipped with gas purification traps and suitable line regulators.
 - a. Helium. High purity cylinder helium.
 - b. Hydrogen. High purity cylinder hydrogen.
 - c. Air. Dry air, free from organic contaminants, from cylinder or compressor.
3. Methyl Isothiocyanate. Analytical Reagent grade. Aldrich Cat. No. 11777-1.

IV. PROCEDURE

A. Air Sampling

Break both ends of the charcoal tube to provide openings for air to pass through. The smaller section of charcoal is used as a backup section and therefore is placed nearest the sampling pump. Use tubing from the sample tube holder to connect the back of the tube to the pump. Turn on the pump and set the flow rate to 100 mL/min. Calibrate the trap-pump assembly via RRC method 76-46; record the calibration data.

To take an air sample, support the charcoal tube in a vertical position with the sample tube holder and clip the trap to the employee's clothing so that the trap is located as close as possible to his or her breathing zone. Attach the pump to the employee via a convenient pocket. Turn on the pump, and take a 6-8 hour sample. At the end of the sampling period record the time. Remove the trap-pump assembly from the employee; recalibrate the assembly and record the recalibration data.

For sampling at relative humidity greater than 80%, connect a silica gel tube in front of the charcoal tube by means of a short tygon tubing during the entire sampling period. The silica gel is used as a drying agent preceding the charcoal to eliminate the effect of moisture (see Section VI.B.).



B. Gas Chromatographic Conditions

Set the temperature of oven, injection port, and detector on the gas chromatograph. Establish suitable flow rates for the various gases; optimizing the detector response according to the manufacturer's directions.

The following conditions are given for a Hewlett-Packard Model 5710A chromatograph with a N-P AFID detector and a 1.8 m x 2 mm i.d., 10% SP2250 column.

| | |
|-----------------------------|---|
| Column temperature: | 95°C, isothermal |
| Injection port temperature: | 250°C |
| Detector temperature: | 300°C |
| Helium carrier gas flow: | 30 mL/min |
| Hydrogen flow: | 3 mL/min |
| Air flow: | 60 mL/min |
| Quantitation: | digital integrator or data system; set attenuation to obtain a measurable peak from 0.5 ng of MITC. |

Under the above conditions, MITC elutes in approximately 2.4 minutes.

C. Calibration

Prepare five calibration standards containing 0.1, 1.0, 5.0, 10.0 and 20.0 micrograms of methyl isothiocyanate per mL of carbon disulfide to cover the desired range of calibration. Prepare standard solutions fresh weekly, and refrigerate standard solutions when not in use. Inject 5.0 microliters of each solution into the chromatograph at least twice and record the peak areas. Plot the average peak area against the corresponding MITC concentration (micrograms/mL), and draw the best-fitted straight line through the points. Check calibration periodically by occasionally alternating injections of standards with those of samples.

D. Sample Analysis

Score each charcoal tube with a file in front of the glass wool plug and break the tube open. Remove the glass wool plug and place it in a 2-dram vial that contains 1.0 mL of carbon disulfide. Pour the charcoal in the front section into the vial, tapping the side of the tube to dislodge any charcoal that adheres to the walls. Immediately cap the vial with a polyseal-lined cap. Remove the separating foam plug



and transfer the backup section into another 2-dram vial containing 1.0 mL of carbon disulfide; immediately cap the vial. Desorb the MITC for 30 minutes, agitating the sample occasionally to facilitate desorption.

Inject 5.0 microliters of the carbon disulfide extract from each section of the charcoal tube into the gas chromatograph. Dilute the extract if necessary to keep the response(s) within the range. Analyze the sample extracts immediately after calibration has been completed. If analysis of the extract cannot be completed on the same day, refrigerate the extract at 0°C. However, do not store the extract for more than 2 days due to the high volatility of carbon disulfide.

V. CALCULATIONS

A. Mean Flow Rate

Calculate the mean flow rate for the pump-trap assembly by the following equation:

$$F = \text{mean flow rate (L/min)} = \frac{A + B}{2}$$

where A = average initial flow rate, L/min

B = average final flow rate, L/min

B. MITC Concentration in Air

Use the calibration curve and the MITC peak area obtained from the sample extract to determine the amount of MITC in each section of the trap. Calculate the concentration of MITC in air by the following equation:

$$\text{MITC concentration (mg/M}^3\text{)} = \frac{(W1 + W2)}{F \times T}$$

where W1 = weight of MITC found in front section of charcoal tube, micrograms

W2 = weight of MITC found in backup section of charcoal tube, micrograms

F = mean flow rate, L/min

T = sampling time, minutes



VI. DISCUSSION

A. Precision and Accuracy

Desorption Efficiency (DE) for MITC was determined by introduction of known amounts of MITC directly into charcoal tubes at levels of 0.5, 5, 25, and 50 micrograms of MITC. Six replicates were prepared at each of the above levels. All samples were analyzed; the D.E. of MITC is shown in Table 1 (see Reference B for statistical procedure used).

The collection efficiency of this method was tested by generating MITC vapors with the use of the dynamic U-tube system adapted from the literature (References C & D). An average MITC recovery of 94% was obtained for 26 test trials with a relative standard deviation of 10%. Recovery data for MITC in air are shown in Table 2.

The present method was applied also to aqueous solutions of metham-sodium. In this recovery test, a known amount of metham-sodium in aqueous solution was injected onto moistened vermiculite placed at one end of the U-tube while air was pulled through the U-tube at 0.1 L/min and carried the MITC vapors into a charcoal tube at the other end of the U-tube. The presence of water and vermiculite is known to speed up the rate of decomposition of metham-sodium to MITC (Reference E). At the end of each sampling test, both sections of each charcoal tube were removed for desorption and analysis to obtain recovery of MITC. Under these conditions, at least 75% of metham-sodium (up to 190 ug) was converted to MITC in 5 hours. Longer time (16 hours) was required for the conversion of 380 ug of metham-sodium. A summary of the recovery data of MITC from metham-sodium in air is shown in Table 4.

B. Other Comments

The effect of humidity on the recoveries of MITC from air was also studied. A summary of recovery data from air of various relative humidities (R.H.) is shown in Table 5. No significant losses occurred when MITC was sampled at R.H. between 50% and 70%. However, at lower concentrations (less than 0.01 mg/M³) and R.H. greater than 80%, humidity has a more serious effect (see Table 5). To avoid losses of MITC due to effects of moisture, the use of a silica gel tube preceding the charcoal tube is recommended for sampling at R.H. greater than 80%. Recoveries of MITC at high R.H. (>81%) with the use of the silica gel pre-trap showed no significant differences from recoveries at lower R.H. (see Table 6).

Experimentally no breakthrough was observed when 230 micrograms of MITC was adsorbed in the charcoal tube from air with 70 liters of air pulled through the tube at a sampling flow rate of 200 mL/min. This was determined by analysis of both the front and the backup section of the charcoal tube. In general, if more than 25% of the total sample is in the backup section, significant breakthrough may have occurred and the sample is not valid.

Storage stability tests indicated that recoveries of samples stored for 14 days under refrigeration at 4°C agreed within +15% relative to those of initial samples (see Table 2).

VII. SAFETY PRECAUTIONS

A. Methyl Isothiocyanate

Methyl isothiocyanate is toxic, skin irritant and lachrymator.

Avoid contact with skin and eye.

Avoid inhalation of mist, sprays or vapors.

Use only with adequate ventilation and wear gloves.

B. Carbon Disulfide

Carbon disulfide is flammable and vapor harmful.

Keep away from heat and open flame.

Keep container closed.

Use only with adequate ventilation.

Avoid prolonged breathing of vapor.

Avoid prolonged or repeated contact with skin.

VIII. REFERENCES

- A. WRC Notebook: 7397-34 to 50
7411-9 to 36
7550-25 to 44
7893-7 to 10



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- C. L. W. Severs, R. G. Melcher and M. J. Kocsis, Am. Ind. Hyg. Assoc. J., 39, 321 (1978).
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Method No. _____

Page 9

Appendix A

A. Column Preparation and Conditioning

Wash inside of Pyrex column with 1% aqueous KOH and let stand filled with KOH solution 15 minutes. Rinse well with four successive methanol and two successive toluene washes. Fill column with a solution of 5% dimethyldichlorosilane in toluene and let stand 15 minutes. Drain and rinse with toluene. Finally, rinse with methanol and dry with a stream of nitrogen.

Pack the gas chromatographic column with the 10% SP 2250 packing under moderate vacuum with light tapping. Do not use a vibrator. The packing should not extend into the end areas of the column that are heated by the injection port and detector. Install the packed column in the chromatograph with the exit end free. Turn on the carrier gas to 20-40 mL/min, set the initial temperature to 80°C and hold it there for about 30 minutes. This will purge the column of oxygen and water vapor. Increase the column temperature at a rate of 2°C/min. The final conditioning temperature should be 240°C. Condition the column eight hours or more with 20-40 mL/min of carrier gas flowing. After conditioning, cool the oven and complete the installation of the column.

Table 1. Desorption Efficiency (D.E.) of Methyl Isothiocyanate

| Test 1 | | | Test 2 | | | Test 3 | | | Test 4 | | |
|------------------------|------------------------|------|------------------------|------------------------|------|------------------------|------------------------|------|------------------------|------------------------|------|
| μg Taken | μg Found | D.E. |
| 0.50 | 0.42 | 0.84 | 5.14 | 4.71 | 0.92 | 21.4 | 19.8 | 0.93 | 51.5 | 52.3 | 1.02 |
| 0.50 | 0.43 | 0.86 | 5.14 | 4.93 | 0.96 | 21.4 | 20.1 | 0.94 | 51.5 | 53.0 | 1.03 |
| 0.50 | 0.43 | 0.86 | 5.14 | 4.86 | 0.95 | 21.4 | 19.8 | 0.93 | 51.5 | 51.4 | 0.99 |
| 0.50 | 0.43 | 0.86 | 5.00 | 4.60 | 0.92 | 21.4 | 20.4 | 0.95 | 51.5 | 50.6 | 0.98 |

| | | | | | | | | |
|-----------------|---|-------|--|-------|--|--------|--|-------|
| n | = | 4 | | 4 | | 4 | | n |
| Mean D.E. | = | 0.86 | | 0.94 | | 0.94 | | 1.01 |
| St. dev. | = | 0.010 | | 0.021 | | 0.0096 | | 0.024 |
| CV ₁ | = | 0.012 | | 0.022 | | 0.010 | | 0.024 |

$$\overline{CV}_1 = 0.018$$

NOTES: CV₁ = coefficient of variation

\overline{CV}_1 = Pooled coefficient of variation.

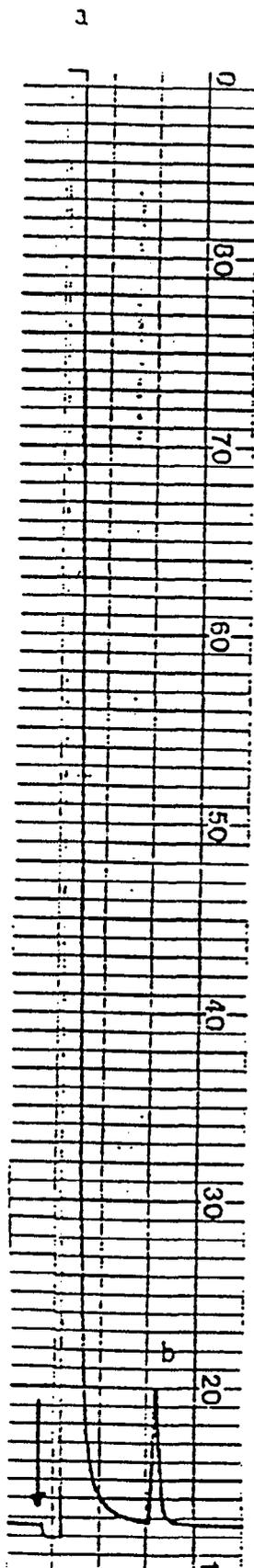
Table 2. Storage Stability of Methyl Isothiocyanate

| Test 1 | | | Test 2 | | | Test 3 | | | Test 4 | | |
|----------|-------------------|------------|----------|-------------------|------------|----------|-------------------|------------|----------|-------------------|------------|
| µg Taken | µg Found | % Recovery | µg Taken | µg Found | % Recovery | µg Taken | µg Found | % Recovery | µg Taken | µg Found | % Recovery |
| 0.50 | 0.42 ^a | 84 | 5.14 | 4.71 ^a | 92 | 21.44 | 19.8 ^a | 92 | 51.45 | 52.3 ^a | 102 |
| 0.50 | 0.43 ^a | 86 | 5.14 | 4.93 ^a | 96 | 21.44 | 20.1 ^a | 94 | 51.45 | 53.0 ^a | 103 |
| 0.50 | 0.43 ^a | 86 | 5.14 | 4.86 ^a | 95 | 21.44 | 19.8 ^a | 92 | 51.45 | 51.1 ^a | 99 |
| 0.50 | 0.43 ^a | 86 | 5.00 | 4.60 ^a | 92 | 21.44 | 20.4 ^a | 95 | 51.45 | 50.6 ^a | 98 |
| 0.50 | 0.39 ^b | 78 | 5.15 | 5.16 ^b | 100 | 25.47 | 24.6 ^b | 97 | 51.45 | 50.1 ^b | 97 |
| 0.50 | 0.39 ^b | 78 | 5.15 | 5.19 ^b | 101 | 25.47 | 24.3 ^b | 95 | 51.45 | 45.3 ^b | 88 |
| 0.50 | 0.38 ^c | 76 | 5.15 | 4.59 ^c | 89 | 25.47 | 23.2 ^c | 91 | 51.45 | 46.8 ^c | 91 |
| 0.50 | 0.37 ^c | 74 | 5.15 | 4.71 ^c | 92 | 25.47 | 22.6 ^c | 89 | 51.45 | 55.6 ^c | 108 |
| 0.50 | 0.38 ^c | 76 | 5.14 | 4.11 ^c | 80 | 21.44 | 15.9 ^c | 74 | 51.45 | 44.9 ^c | 87 |
| 0.50 | 0.39 ^c | 78 | 5.14 | 4.01 ^c | 78 | 21.44 | 16.7 ^c | 78 | 51.45 | 45.7 ^c | 89 |

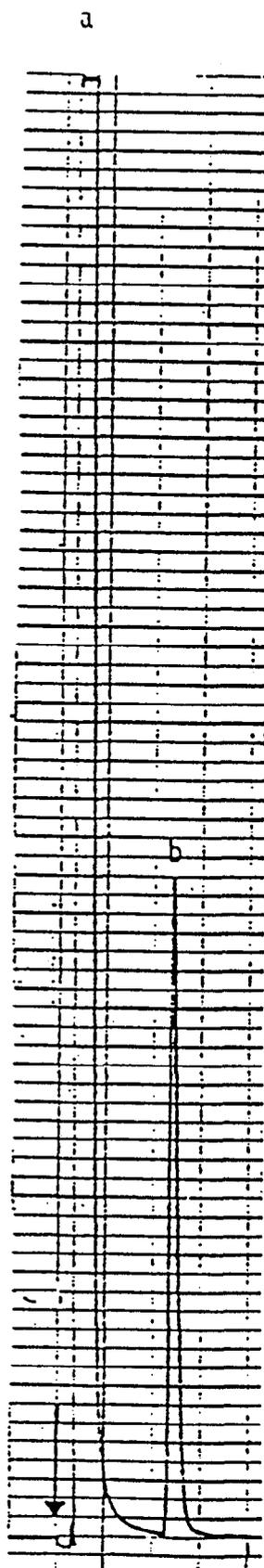
NOTES: a = Samples analyzed after being stored for 1 day under refrigeration
 b = Samples analyzed after being stored for 7 days under refrigeration
 c = Samples analyzed after being stored for 14 days under refrigeration
 % Recovery not corrected for desorption efficiency (D.E.)

FIGURE 1. Typical Chromatogram for MITC Analysis

Standard, 1 ug/mL



Sample 7397-49-8, at 5.1 ug MITC



a = Solvent

b = MITC, 2.3 min.

Table 3. Recovery Data for MITC in Air

Temperature = 65-68°F; R.H. = 58-70%

| L/min Flow Rate | Minutes Sampling Time | Liters Air Volume | ug MITC Taken | ug MITC Found | % Recovery |
|-----------------|-----------------------|-------------------|---------------|---------------|------------|
| 0.1 | 430 | 48 | 0.5 | 0.44 | 88 |
| 0.1 | 430 | 40 | 0.5 | 0.44 | 88 |
| 0.1 | 430 | 45 | 0.5 | 0.44 | 88 |
| 0.1 | 510 | 47 | 0.5 | 0.36 | 72 |
| 0.1 | 510 | 52 | 0.5 | 0.37 | 74 |
| 0.1 | 510 | 53 | 0.5 | 0.39 | 78 |
| 0.1 | 410 | 40 | 5.15 | 4.20 | 82 |
| 0.1 | 410 | 40 | 5.15 | 4.49 | 87 |
| 0.1 | 410 | 43 | 5.15 | 4.72 | 92 |
| 0.1 | 380 | 36 | 5.15 | 4.71 | 92 |
| 0.1 | 420 | 39 | 5.15 | 5.34 | 104 |
| 0.1 | 430 | 44 | 5.15 | 5.05 | 98 |
| 0.1 | 420 | 40 | 10.29 | 10.9 | 106 |
| 0.1 | 460 | 43 | 25.47 | 27.3 | 107 |
| 0.1 | 460 | 47 | 25.47 | 25.7 | 101 |
| 0.1 | 460 | 45 | 25.47 | 26.0 | 102 |
| 0.1 | 450 | 50 | 25.47 | 25.3 | 99 |
| 0.1 | 450 | 42 | 25.47 | 25.2 | 99 |
| 0.1 | 450 | 48 | 25.47 | 24.2 | 95 |
| 0.1 | 360 | 38 | 51.45 | 46.9 | 91 |
| 0.1 | 370 | 37 | 51.45 | 48.6 | 94 |
| 0.1 | 450 | 45 | 51.45 | 48.5 | 94 |
| 0.1 | 450 | 46 | 51.45 | 53.4 | 104 |
| 0.1 | 460 | 46 | 51.45 | 49.5 | 96 |
| 0.1 | 390 | 38 | 51.45 | 50.6 | 98 |
| 0.1 | 450 | 47 | 227.4 | 207 | 91 |
| 0.2 | 370 | 71 | 227.4 | 195 | 86* |
| 0.2 | 370 | 71 | 225.6 | 180 | 80* |
| 0.2 | 370 | 66 | 225.6 | 179 | 79* |

Mean = 94
RSD = 10%
n = 26

NOTES: % Recovery not corrected for desorption efficiency (D.E.)

* = Samples collected at flow rates greater than 0.1 L/min;
not included in the calculation of mean % recovery

Table 4. Recovery Data for MITC from Metham-sodium in Air

| L/min Flow Rate | Minute Sampling Time | Liters Air Volume | ug Metham-Sodium Taken | Theoretical ug MITC Taken | ug MITC Found | % MITC Found based on Theoretical MITC Taken |
|-----------------|----------------------|-------------------|------------------------|---------------------------|---------------|--|
| 0.11 | 380 | 42 | 23.7 | 13.4 | 11.9 | 89 |
| 0.12 | 400 | 50 | 47.0 | 26.8 | 25.4 | 95 |
| 0.12 | 320 | 38 | 94.7 | 53.5 | 46.3 | 87 |
| 0.12 | 320 | 40 | 189.5 | 107.2 | 84.1 | 79 |
| 0.12 | 430 | 52 | 189.5 | 107.2 | 79.3 | 74 |
| 0.11 | 990 | 110 | 189.5 | 107.2 | 78.7 | 73 |
| 0.11 | 320 | 36 | 379.0 | 214.0 | 110 | 51* |
| 0.11 | 440 | 48 | 379.0 | 214.0 | 99 | 46* |
| 0.13 | 990 | 125 | 379.0 | 214.0 | 190 | 89 |

NOTES: * = low recoveries on these samples due to incomplete conversion of MITC from Metham-sodium.

Table 5. Effects of Relative Humidity (R.H.) on Recoveries of MITC from Air

Sampling Flow Rate = 0.1 L/min.

| % R.H. | No. of Samples | Hours Sampling Time | Liters Air Volume | ug MITC Taken | % Recovery |
|--------|----------------|---------------------|-------------------|---------------|-----------------|
| 58 | 3 | 7 | 40 - 48 | 0.5 | 88* (87 - 88)** |
| 70 | 3 | 7 | 47 - 53 | 0.5 | 74 (71 - 79) |
| 81 | 4 | 7 | 38 - 44 | 0.5 | 43 (32 - 57) |
| 81 | 2 | 4 | 25 | 0.5 | 66 (59 - 72) |
| 92 | 3 | 7 | 41 - 42 | 0.5 | 53 (41 - 63) |
| 92 | 2 | 4 | 22 - 25 | 0.5 | 72 (70 - 75) |
| 58 | 3 | 7 | 36 - 44 | 5 | 98 (92 - 104) |
| 70 | 3 | 7 | 40 - 43 | 5 | 87 (82 - 92) |
| 81 | 5 | 7 | 34 - 57 | 5 | 50 (44 - 58) |
| 81 | 2 | 4 | 21 - 24 | 5 | 69 (66 - 72) |
| 92 | 3 | 7 | 37 - 42 | 5 | 55 (48 - 62) |
| 92 | 3 | 4 | 20 - 26 | 5 | 83 (78 - 89) |
| 58 | 3 | 7 | 43 - 47 | 25.5 | 103 (101 - 107) |
| 70 | 3 | 7 | 42 - 49 | 25.5 | 98 (91 - 99) |
| 81 | 1 | 6 | 35 | 25.5 | 78 |
| 92 | 3 | 7 | 39 - 41 | 25.5 | 77 (73 - 82) |
| 92 | 1 | 4 | 26 | 25.5 | 76 |
| 58 | 2 | 6 | 37 - 38 | 51.5 | 93 (91 - 94) |
| 70 | 4 | 7 | 38 - 46 | 51.5 | 98 (94 - 104) |
| 81 | 1 | 6 | 36 | 51.5 | 97 |
| 81 | 1 | 6 | 39 | 227.4 | 80 |
| 92 | 1 | 6 | 36 | 51.5 | 100 |
| 92 | 1 | 7 | 42 | 102.9 | 100 |
| 92 | 1 | 7 | 41 | 227.4 | 83 |

NOTES: * = Mean
 ** = Range
 % Recovery not corrected for desorption efficiency (D.E.)

Table 6. Recovery Data for MITC in Air at High (>81%) Relative Humidity with the Use of Silica Gel as a Pre-trap for Moisture

Sampling Flow Rate = 0.1 L/min.

| % R.H. | Hours Sampling Time | Liters Air Volume | ug MITC Taken | ug MITC Found | % Recovery |
|--------|---------------------|-------------------|---------------|---------------|------------|
| 81 | 6 | 36 | 0.5 | 0.40 | 79 |
| 81 | 7 | 42 | 0.5 | 0.37 | 74 |
| 81 | 7 | 41 | 5 | 4.43 | 89 |
| 81 | 7 | 46 | 5 | 4.35 | 87 |
| 92 | 6 | 38 | 0.5 | 0.38 | 75 |
| 92 | 7 | 45 | 0.5 | 0.36 | 71 |
| 92 | 7 | 44 | 5 | 4.39 | 88 |
| 92 | 7 | 44 | 5 | 4.21 | 84 |
| 92 | 7 | 46 | 25 | 22.9 | 92 |
| 92 | 7 | 45 | 25 | 22.7 | 91 |
| 92 | 7 | 46 | 59 | 55.9 | 95 |
| 92 | 7 | 40 | 59 | 51.9 | 88 |

NOTE: % Recovery not corrected for desorption efficiency (D.E.)

APPENDIX IV
CIMIS WEATHER DATA

Hourly Weather Data for Station #125 Arvin-Edison
in Region -SJV- San Joaquin Valley

CIMIS Project

| DATE | HOUR | ETo in. | PRECIP in. | RADIATION | | VAPOR PRESS mBars | AIR TEMP F | REL HUM % | DEW PNT F | WIND SPEED mph | WIND DIR 0-360 | RESULT WIND mph | SOIL TEMP F |
|---------|------|------------|---------------|---------------------|------|-------------------------|------------------|-----------------|-----------------|----------------------|----------------------|-----------------------|-------------------|
| | | | | SOLAR --Ly/day-- | NET | | | | | | | | |
| 8/23/95 | 1 | 0.00 | 0.0 | -2 | -81 | 21.49 | 78.4 | 65 | 66 | 2.3 | 125 | 1.5 | 84 |
| | 2 | 0.00 | 0.0 | -2 | -82 | 20.81 | 77.4 | 65 | 65 | 1.4 | 120 | 0.9 | 83 |
| | 3 | -0.00 | 0.0 | -2 | -80 | 21.05 | 74.5 | 72 | 65 | 2.1 | 29 | 2.0 | 83 |
| | 4 | 0.00 | 0.0 | -2 | -83 | 19.13 | 74.9 | 65 | 62 | 2.7 | 49 | 2.6 | 83 |
| | 5 | 0.00 | 0.0 | -2 | -84 | 18.40 | 73.9 | 64 | 61 | 1.8 | 35 | 1.7 | 82 |
| | 6 | 0.00 | 0.0 | 19 | -69 | 18.27 | 73.0 | 66 | 61 | 1.7 | 58 | 1.4 | 82 |
| | 7 | 0.00 | 0.0 | 316 | 159 | 21.00 | 74.1 | 73 | 65 | 2.7 | 174 | 2.6 | 82 |
| | 8 | 0.01 | 0.0 | 738 | 443 | 21.16 | 79.2 | 62 | 65 | 3.2 | 199 | 3.1 | 81 |
| | 9 | 0.02 | 0.0 | 1077 | 707 | 20.18 | 85.7 | 48 | 64 | 2.3 | 316 | 1.7 | 81 |
| | 10 | 0.02 | 0.0 | 1436 | 978 | 19.38 | 89.6 | 41 | 63 | 3.5 | 315 | 3.3 | 81 |
| | 11 | 0.03 | 0.0 | 1678 | 1170 | 19.39 | 91.7 | 38 | 63 | 4.3 | 272 | 3.6 | 82 |
| | 12 | 0.03 | 0.0 | 1785 | 1265 | 19.95 | 93.5 | 37 | 63 | 3.7 | 248 | 2.7 | 82 |
| | 13 | 0.03 | 0.0 | 1785 | 1268 | 19.66 | 95.4 | 35 | 63 | 3.6 | 235 | 2.2 | 83 |
| | 14 | 0.03 | 0.0 | 1669 | 1180 | 20.00 | 96.9 | 34 | 64 | 4.3 | 280 | 3.6 | 83F |
| | 15 | 0.03 | 0.0 | 1421 | 987 | 18.66 | 98.1 | 30 | 62 | 4.4 | 275 | 3.9 | 84F |
| | 16 | 0.02 | 0.0 | 1087 | 731 | 18.62 | 98.6 | 30 | 61 | 5.5 | 270 | 5.1 | 85 |
| | 17 | 0.02 | 0.0 | 687 | 438 | 19.05 | 97.7 | 31 | 62 | 7.7 | 258 | 7.6 | 85 |
| | 18 | 0.01 | 0.0 | 266 | 171 | 20.28 | 95.1 | 36 | 64 | 5.0 | 264 | 4.9 | 85 |
| | 19 | 0.00 | 0.0 | 23 | -35 | 19.98 | 90.8 | 40 | 63 | 2.7 | 196 | 1.8 | 86 |
| | 20 | 0.00 | 0.0 | -2 | -54 | 18.07 | 88.8 | 39 | 61 | 2.8 | 177 | 1.9 | 85 |
| | 21 | 0.00 | 0.0 | -2 | -59 | 13.76 | 87.6 | 31 | 53 | 3.3 | 146 | 1.0 | 85 |
| | 22 | 0.00 | 0.0 | -1 | -61 | 11.06 | 82.5 | 29 | 47 | 2.9 | 39 | 2.5 | 85 |
| | 23 | 0.00 | 0.0 | -2 | -61 | 10.34 | 77.9 | 32 | 45 | 3.1 | 35 | 3.0 | 85 |
| | 24 | 0.00 | 0.0 | -2 | -62 | 9.21 | 74.9 | 31 | 42 | 3.3 | 37 | 2.7 | 84 |
| 8/23/95 | | 0.28 | = TOTAL ETo | | | | | | | | | | |
| 8/24/95 | 1 | 0.00 | 0.0 | -2 | -137 | 9.29 | 76.9 | 29 | 43 | 2.0 | 65 | 1.3 | 84 |
| | 2 | 0.00 | 0.0 | -2 | -124 | 12.26 | 73.5 | 44 | 50 | 2.5 | 127 | 1.0 | 83 |
| | 3 | 0.00 | 0.0 | -2 | -119 | 12.57 | 67.8 | 54 | 51 | 3.1 | 57 | 2.7 | 83 |
| | 4 | 0.00 | 0.0 | -2 | -124 | 11.24 | 68.8 | 47 | 48 | 3.0 | 34 | 2.9 | 82 |
| | 5 | 0.00 | 0.0 | -2 | -120 | 12.04 | 67.2 | 53 | 49 | 2.4 | 97 | 1.4 | 82 |
| | 6 | -0.00 | 0.0 | 21 | -97 | 14.04 | 63.7 | 70 | 54 | 2.6 | 150 | 2.4 | 81 |
| | 7 | 0.00 | 0.0 | 354 | 153 | 14.25 | 68.1 | 61 | 54 | 2.3 | 31 | 2.0 | 81 |
| | 8 | 0.01 | 0.0 | 782 | 441 | 14.88 | 74.3 | 51 | 55 | 3.0 | 336 | 2.8 | 79 |
| | 9 | 0.02 | 0.0 | 1187 | 698 | 14.17 | 80.8 | 39 | 54 | 2.5 | 321 | 2.3 | 78 |
| | 10 | 0.02 | 0.0 | 1531 | 967 | 13.01 | 85.8 | 31 | 52 | 2.6 | 274 | 2.0 | 78 |
| | 11 | 0.03 | 0.0 | 1754 | 1149 | 12.76 | 88.1 | 28 | 51 | 3.3 | 275 | 2.6 | 78 |
| | 12 | 0.03 | 0.0 | 1862 | 1275 | 13.46 | 90.4 | 28 | 52 | 4.0 | 261 | 3.6 | 79 |
| | 13 | 0.03 | 0.0 | 1893 | 1253 | 11.56 | 93.1 | 22 | 48 | 3.7 | 217 | 2.9 | 79 |
| | 14 | 0.03 | 0.0 | 1746 | 1194 | 9.32 | 95.2 | 16 | 43 | 3.9 | 216 | 2.4 | 80 |
| | 15 | 0.03 | 0.0 | 1473 | 999 | 9.33 | 95.6 | 16 | 43 | 6.1 | 257 | 5.7 | 81 |
| | 16 | 0.02 | 0.0 | 1140 | 745 | 8.77 | 96.0 | 15 | 41 | 5.9 | 255 | 5.6 | 82 |
| | 17 | 0.02 | 0.0 | 734 | 451 | 8.78 | 95.8 | 15 | 41 | 5.3 | 262 | 5.2 | 82 |
| | 18 | 0.01 | 0.0 | 326 | 181 | 10.50 | 93.4 | 20 | 46 | 4.3 | 257 | 4.3 | 83 |
| | 19 | 0.00 | 0.0 | 28 | -55 | 11.05 | 87.7 | 25 | 47 | 3.2 | 173 | 2.4 | 83 |

Ly/day/2.065=W/sq.m in.*25.4=mm (F-32)*5/9=c mph*.447=m/s mBars*.1=kPa

QUALITY CONTROL FLAGS

A-hist. ave. C-not collected E-one sensor hist. ave. F-out of normal range
H-missing hourly I-ignore M-missing Q-related sensor miss. S-not in service

Hourly Weather Data for Station #125 Arvin-Edison in Region -SJV- San Joaquin Valley CIMIS Project

| DATE | HOUR | ETo in. | PRECIP in. | RADIATION SOLAR --Ly/day-- | NET | VAPOR PRESS mBars | AIR TEMP F | REL HUM % | DEW PNT F | WIND SPEED mph | WIND DIR 0-360 | RESULT WIND mph | SOIL TEMP F |
|---------|------|------------------|---------------|----------------------------------|------|-------------------------|------------------|-----------------|-----------------|----------------------|----------------------|-----------------------|-------------------|
| 8/24/95 | 20 | 0.00 | 0.0 | -2 | -80 | 8.06 | 83.6 | 20 | 39 | 3.7 | 105 | 3.5 | 83 |
| | 21 | 0.00 | 0.0 | -2 | -82 | 7.60 | 84.2 | 19 | 37 | 4.7 | 130 | 3.6 | 83 |
| | 22 | 0.00 | 0.0 | -2 | -68 | 12.43 | 78.3 | 38 | 50 | 5.3 | 185 | 4.9 | 82 |
| | 23 | 0.00 | 0.0 | -2 | -66 | 13.68 | 76.4 | 44 | 53 | 3.3 | 175 | 2.7 | 82 |
| | 24 | 0.00 | 0.0 | -2 | -71 | 9.96 | 72.9 | 36 | 44 | 3.5 | 124 | 3.2 | 82 |
| 8/24/95 | | 0.28 = TOTAL ETo | | | | | | | | | | | |
| 8/25/95 | 1 | 0.00 | 0.0 | -2 | -134 | 8.08 | 71.7 | 31 | 39 | 2.9 | 144 | 2.7 | 81 |
| | 2 | 0.00 | 0.0 | -2 | -122 | 10.37 | 68.1 | 44 | 46 | 3.2 | 44 | 2.4 | 81 |
| | 3 | 0.00 | 0.0 | -3 | -126 | 8.75 | 65.1 | 41 | 41 | 2.8 | 63 | 2.6 | 81 |
| | 4 | 0.00 | 0.0 | -3 | -122 | 9.20 | 62.3 | 48 | 42 | 2.0 | 67 | 1.5 | 80 |
| | 5 | 0.00 | 0.0 | -3 | -122 | 9.17 | 61.6 | 49 | 42 | 2.3 | 96 | 1.9 | 80 |
| | 6 | 0.00 | 0.0 | 17 | -107 | 9.31 | 59.7 | 53 | 43 | 2.7 | 81 | 2.4 | 79 |
| | 7 | 0.00 | 0.0 | 346 | 147 | 11.28 | 64.9 | 54 | 48 | 2.0 | 168 | 1.2 | 79 |
| | 8 | 0.01 | 0.0 | 768 | 434 | 11.96 | 72.2 | 44 | 49 | 1.6 | 306 | 0.8 | 79 |
| | 9 | 0.02 | 0.0 | 1179 | 688 | 12.44 | 76.9 | 39 | 50 | 2.3 | 241 | 1.9 | 78 |
| | 10 | 0.02 | 0.0 | 1523 | 961 | 11.95 | 80.3 | 34 | 49 | 3.4 | 234 | 2.8 | 78 |
| | 11 | 0.03 | 0.0 | 1750 | 1147 | 12.22 | 83.3 | 31 | 50 | 2.5 | 272 | 1.7 | 78 |
| | 12 | 0.03 | 0.0 | 1860 | 1271 | 12.64 | 86.2 | 30 | 51 | 3.5 | 275 | 2.6 | 79 |
| | 13 | 0.03 | 0.0 | 1884 | 1277 | 12.75 | 88.9 | 27 | 51 | 3.6 | 279 | 2.8 | 80 |
| | 14 | 0.03 | 0.0 | 1746 | 1211 | 14.24 | 89.5 | 30 | 54 | 4.3 | 239 | 3.8 | 80 |
| | 15 | 0.03 | 0.0 | 1479 | 1014 | 13.45 | 90.4 | 28 | 52 | 3.8 | 222 | 3.3 | 81 |
| | 16 | 0.02 | 0.0 | 1132 | 750 | 12.88 | 91.3 | 26 | 51 | 4.2 | 227 | 3.7 | 82 |
| | 17 | 0.02 | 0.0 | 732 | 453 | 10.64 | 92.7 | 20 | 46 | 5.2 | 246 | 5.0 | 82 |
| | 18 | 0.01 | 0.0 | 326 | 181 | 10.93 | 91.8 | 21 | 47 | 3.6 | 230 | 3.3 | 83 |
| | 19 | 0.00 | 0.0 | 24 | -56 | 11.34 | 84.5 | 28 | 48 | 3.9 | 132 | 3.7 | 83 |
| | 20 | 0.00 | 0.0 | -2 | -80 | 8.47 | 81.9 | 23 | 40 | 3.0 | 97 | 2.5 | 83 |
| | 21 | 0.00 | 0.0 | -2 | -83 | 7.54 | 82.9 | 20 | 37 | 5.7 | 102 | 5.5 | 82 |
| | 22 | 0.00 | 0.0 | -1 | -77 | 9.07 | 80.5 | 25 | 42 | 5.1 | 139 | 3.4 | 82 |
| | 23 | 0.00 | 0.0 | -2 | -67 | 11.92 | 70.9 | 46 | 49 | 2.6 | 96 | 1.4 | 82 |
| | 24 | 0.00 | 0.0 | -2 | -68 | 12.02 | 72.2 | 45 | 49 | 6.3 | 192 | 5.9 | 81 |
| 8/25/95 | | 0.27 = TOTAL ETo | | | | | | | | | | | |
| 8/26/95 | 1 | 0.00 | 0.0 | -2 | -109 | 12.57 | 72.6 | 46 | 51 | 8.0 | 193 | 7.9 | 81 |
| | 2 | 0.00 | 0.0 | -2 | -108 | 12.43 | 71.0 | 48 | 50 | 4.9 | 197 | 3.8 | 80 |
| | 3 | 0.00 | 0.0 | -2 | -111 | 11.18 | 68.9 | 46 | 47 | 2.5 | 168 | 1.7 | 80 |
| | 4 | 0.00 | 0.0 | -3 | -107 | 10.84 | 63.0 | 55 | 47 | 2.3 | 108 | 1.7 | 80 |
| | 5 | 0.00 | 0.0 | -3 | -106 | 10.57 | 59.6 | 61 | 46 | 3.6 | 74 | 3.5 | 79 |
| | 6 | 0.00 | 0.0 | 18 | -92 | 10.62 | 59.6 | 61 | 46 | 3.1 | 84 | 2.9 | 79 |
| | 7 | 0.00 | 0.0 | 330 | 146 | 11.75 | 66.8 | 52 | 49 | 1.7 | 78 | 1.1 | 79 |
| | 8 | 0.01 | 0.0 | 763 | 435 | 14.12 | 72.4 | 52 | 54 | 1.3 | 303 | 1.1 | 78 |
| | 9 | 0.02 | 0.0 | 1175 | 683 | 11.61 | 75.8 | 38 | 48 | 2.3 | 241 | 1.9 | 78 |
| | 10 | 0.02 | 0.0 | 1508 | 950 | 11.67 | 78.2 | 35 | 49 | 2.7 | 240 | 1.9 | 78 |
| | 11 | 0.03 | 0.0 | 1756 | 1156 | 12.56 | 80.3 | 36 | 51 | 3.4 | 253 | 2.7 | 78 |
| | 12 | 0.03 | 0.0 | 1860 | 1265 | 13.12 | 82.5 | 35 | 52 | 3.4 | 252 | 2.5 | 78 |
| | 13 | 0.03 | 0.0 | 1860 | 1290 | 13.29 | 85.1 | 32 | 52 | 3.2 | 287 | 2.2 | 79 |

Ly/day/2.065=W/sq.m in.*25.4=mm (F-32)*5/9=c mph*.447=m/s mBars*.1=kPa

QUALITY CONTROL FLAGS

A-hist. ave. C-not collected E-one sensor hist. ave. F-out of normal range
 H-missing hourly I-ignore M-missing Q-related sensor miss. S-not in service

Hourly Weather Data for Station #125 Arvin-Edison
in Region -SJV- San Joaquin Valley

CIMIS Project

| DATE | HOUR | ETo in. | PRECIP in. | RADIATION | | VAPOR | AIR | REL DEW | WIND | WIND | RESULT | SOIL | |
|---------|------|------------|---------------|------------|------|-------|------|---------|------|-------|--------|------|------|
| | | | | SOLAR | NET | PRESS | TEMP | HUM | PNT | SPEED | DIR | WIND | TEMP |
| | | | | --Ly/day-- | | mBars | F | % | F | mph | 0-360 | mph | F |
| 8/26/95 | 14 | 0.03 | 0.0 | 1717 | 1194 | 13.21 | 87.6 | 30 | 52 | 2.8 | 301 | 2.1 | 80 |
| | 15 | 0.03 | 0.0 | 1492 | 1019 | 13.27 | 88.8 | 29 | 52 | 3.7 | 272 | 3.2 | 80 |
| | 16 | 0.02 | 0.0 | 1143 | 754 | 11.98 | 90.1 | 25 | 49 | 3.8 | 244 | 3.3 | 81 |
| | 17 | 0.01 | 0.0 | 713 | 445 | 12.94 | 90.8 | 26 | 51 | 3.3 | 240 | 3.1 | 82 |
| | 18 | 0.01 | 0.0 | 296 | 169 | 15.11 | 88.3 | 33 | 56 | 4.1 | 204 | 4.0 | 82 |
| | 19 | 0.00 | 0.0 | 22 | -45 | 15.72 | 82.2 | 42 | 57 | 2.8 | 138 | 2.5 | 82 |
| | 20 | 0.00 | 0.0 | -2 | -65 | 12.30 | 79.3 | 36 | 50 | 4.1 | 105 | 4.0 | 82 |
| | 21 | 0.00 | 0.0 | -2 | -69 | 10.94 | 81.4 | 30 | 47 | 5.4 | 112 | 5.2 | 82 |
| | 22 | 0.00 | 0.0 | -1 | -68 | 10.89 | 80.3 | 31 | 47 | 4.9 | 133 | 4.1 | 82 |
| | 23 | 0.00 | 0.0 | -2 | -59 | 14.46 | 71.9 | 54 | 54 | 2.0 | 24 | 1.4 | 81 |
| | 24 | 0.00 | 0.0 | -2 | -58 | 14.24 | 67.7 | 62 | 54 | 1.8 | 26 | 1.4 | 81 |
| 8/26/95 | | 0.26 | = TOTAL ETO | | | | | | | | | | |
| 8/27/95 | 1 | -0.00 | 0.0 | -3 | -94 | 15.21 | 66.3 | 69 | 56 | 2.0 | 340 | 1.0 | 81 |
| | 2 | -0.00 | 0.0 | -3 | -95 | 14.00 | 63.8 | 69 | 54 | 2.6 | 103 | 1.3 | 80 |
| | 3 | -0.00 | 0.0 | -3 | -96 | 13.02 | 61.8 | 69 | 52 | 2.6 | 52 | 2.1 | 80 |
| | 4 | -0.00 | 0.0 | -3 | -98 | 11.95 | 61.5 | 64 | 49 | 2.7 | 53 | 2.6 | 79 |
| | 5 | -0.00 | 0.0 | -3 | -98 | 11.85 | 61.2 | 64 | 49 | 2.6 | 85 | 2.2 | 79 |
| | 6 | 0.00 | 0.0 | 17 | -86 | 11.50 | 60.7 | 63 | 48 | 3.2 | 80 | 2.9 | 79 |
| | 7 | 0.00 | 0.0 | 317 | 145 | 12.97 | 65.6 | 60 | 51 | 1.8 | 153 | 1.0 | 78 |
| | 8 | 0.01 | 0.0 | 743 | 430 | 13.81 | 71.6 | 52 | 53 | 3.0 | 221 | 2.8 | 78 |
| | 9 | 0.02 | 0.0 | 1141 | 724 | 14.58 | 74.9 | 49 | 55 | 4.3 | 218 | 4.1 | 78 |
| | 10 | 0.02 | 0.0 | 1481 | 978 | 13.96 | 77.9 | 43 | 53 | 4.1 | 219 | 3.7 | 78 |
| | 11 | 0.03 | 0.0 | 1723 | 1162 | 14.54 | 81.4 | 40 | 55 | 2.8 | 275 | 1.8 | 78 |
| | 12 | 0.03 | 0.0 | 1855 | 1266 | 14.79 | 83.5 | 38 | 55 | 3.2 | 255 | 2.1 | 78 |
| | 13 | 0.03 | 0.0 | 1738 | 1232 | 15.45 | 85.9 | 37 | 56 | 3.9 | 289 | 3.2 | 79 |
| | 14 | 0.03 | 0.0 | 1707 | 1191 | 14.79 | 88.0 | 33 | 55 | 3.5 | 260 | 2.4 | 80 |
| | 15 | 0.03 | 0.0 | 1450 | 997 | 14.75 | 89.7 | 31 | 55 | 3.9 | 240 | 2.7 | 80 |
| | 16 | 0.02 | 0.0 | 1087 | 723 | 14.36 | 90.9 | 29 | 54 | 3.4 | 232 | 2.9 | 81 |
| | 17 | 0.01 | 0.0 | 675 | 424 | 14.98 | 90.6 | 30 | 55 | 3.6 | 204 | 3.1 | 81 |
| | 18 | 0.01 | 0.0 | 279 | 159 | 15.83 | 88.6 | 34 | 57 | 4.9 | 192 | 4.8 | 82 |
| | 19 | 0.00 | 0.0 | 19 | -46 | 15.70 | 83.4 | 40 | 57 | 3.2 | 149 | 2.8 | 82 |
| | 20 | 0.00 | 0.0 | -2 | -62 | 12.82 | 79.1 | 38 | 51 | 3.8 | 98 | 3.7 | 82 |
| | 21 | 0.00 | 0.0 | -2 | -64 | 12.14 | 81.3 | 33 | 50 | 4.5 | 102 | 4.3 | 82 |
| | 22 | 0.00 | 0.0 | -2 | -61 | 13.56 | 78.8 | 40 | 53 | 3.3 | 103 | 1.4 | 82 |
| | 23 | 0.00 | 0.0 | -2 | -59 | 13.72 | 72.7 | 50 | 53 | 2.0 | 25 | 1.5 | 81 |
| | 24 | 0.00 | 0.0 | -2 | -57 | 14.31 | 69.3 | 59 | 54 | 2.7 | 126 | 0.5 | 81 |
| 8/27/95 | | 0.25 | = TOTAL ETO | | | | | | | | | | |

Ly/day/2.065=W/sq.m in.*25.4=mm (F-32)*5/9=c mph*.447=m/s mBars*.1=kPa

QUALITY CONTROL FLAGS

A-hist. ave. C-not collected E-one sensor hist. ave. F-out of normal range
H-missing hourly I-ignore M-missing Q-related sensor miss. S-not in service

APPENDIX V
EHLB LABORATORY REPORT

M e m o r a n d u m

Date : December 21, 1995

To : Don Fitzell
Engineering and Laboratory Branch
Monitoring and Laboratory Division
Air Resources Board

From : Miles Imada 
Supervising Air Pollution Specialist
Environmental Health Laboratory Branch
(510) 540-2640

Subject : **MIC/MITC Pesticide Analytical Data**

ARB Engineering and Laboratory Branch (ELB) completed sampling for methyl isocyanate (MIC) and methyl isothiocyanate (MITC) during August 21-25, 1995 in Kern County. A total of 45 MIC field samples (including blanks and spikes) plus 12 ARB MIC audit samples were submitted for HPLC/fluorescence analyses. Also a total of 50 MITC field samples (including blanks and spikes) plus 6 ARB MITC audit samples were submitted for GC/NPD analyses.

MIC

Analyses on collected MIC samples were performed using EHLB Method No. 104 (Modified OSHA Method 54). Reagent blanks and field blanks were run with the daily field samples analyses. A QC reference control solution representing 0.2 $\mu\text{g}/\text{mL}$ was analyzed with all batches of samples run. Environmental Health Laboratory Branch (EHLB) spiked archives and field spikes at 0.96 or 1.92 μg MIC loadings were also run. Analytical results are recorded in the attached pages 1-7.

After the samples were analyzed, ARB audit tubes were submitted. These tubes were apparently spiked at the LOD level and not at the LOQ level. MIC was essentially undetected. A second set of ARB audit tubes spiked at the same levels as the first set were submitted. No MIC was found. The ARB spiking solution (prepared by Chem Services) was submitted and analyzed. This solution was found to have a concentration 36% of its purported value.

Mr. Don Fitzell
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December 21, 1995

All quantitations in this study are based on the calibration standards made up of the MIC-urea derivative prepared in 1993. To confirm its stability and purity, a fresh batch of MIC-derivative was prepared using fresh MIC and 1,2-pyridylpiperazine (1,2-PP). In addition, an independent source of the MIC derivative was obtained from the federal OSHA laboratory in Salt Lake City, Utah. MIC-derivative standards were prepared from the OSHA laboratory (12 years old), EHLB (prepared in 1993), and fresh EHLB (prepared in 1995) derivatives. The standard curves from all three sources are in close agreement (see Fig. 1). This verifies the stability of the MIC-derivative from which the MIC standard curves are prepared.

EHLB Method number 104 recovery studies in 1993 gave values approaching 100%. Fresh MIC was obtained in 1995, and a subsequent assay of the 1993 and 1995 MIC showed the 1993 MIC to be 77% pure and the 1995 MIC 90% pure. Based on a 77% purity factor, the EHLB archive and field spike recovery is 99.0%.

MITC

Analyses were performed using Stauffer, Inc. Method RRC-82-35, modified by substituting larger capacity sorbent tubes for the smaller sampling tubes specified. QC solutions representing 1.0 and 0.2 $\mu\text{g}/\text{mL}$ MITC were analyzed with all batches of samples run. Reagent blanks (carbon disulfide) were run with the daily field samples analyses. Charcoal tube EHLB archive and field spikes at the same levels as solutions reference control solutions, 1.0 and 0.2 $\mu\text{g}/\text{mL}$, were also analyzed with all batches of samples run.

After the samples were analyzed, charcoal tubes prepared and submitted by ARB as audit samples were analyzed by EHLB. MITC was quantitated in four of the six audit tubes. Two of the tubes were analyzed as "MITC not present above the limit of detection." The ARB spiking solution was submitted to EHLB for confirmation. A working standard at 1.0 $\mu\text{g}/\text{mL}$ was prepared from ARB's spiking solution. EHLB working standards at 1.0 $\mu\text{g}/\text{mL}$ were also prepared from MITC stock made by two different EHLB chemists. Analyses were done on two different days using fresh working standards. On the second analytical day, a fresh stock was also prepared, made from a new lot of crystalline MITC from Aldrich, and a working 1.0 $\mu\text{g}/\text{mL}$ standard made from it. Blanks and QC solutions were also analyzed. The ARB solution gave an average concentration 2.5 times its nominal value.

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The EHLB archive and field spike charcoal tubes were prepared by EHLB using crystalline MITC of 97% purity. Recovery studies in 1992 gave values approaching 75%. EHLB archive and field spike recovery for this set, analyzing tubes spiked on two different days three weeks apart, gave an average recovery of 73%.

Mario Fracchia (ATSS 8-571-3025) and Diamon Pon performed the MIC analyses while Paul Larkin (ATSS 8-571-2144) worked on the MITC analyses.

Attachment

cc: Sue Twiss/EHLB
Mario Fracchia/EHLB
Paul Larkin/EHLB
Diamon Pon/EHLB
Steve Nunn ARB/MLD

Control No: C94-046A
Lab Number: 50405

DATA SHEET FOR PESTICIDES

COMPOUND: METHYL ISOCYANATE (MIC)

Date Samples Submitted: August 29, 1995 Submitted by: Don Fitzell

Dates Samples Analyzed: Aug. 31. to Oct. 3, 1995

Analysts: M. Fracchia and D. Pon

| <u>Sample ID</u> | <u>Front Tube</u> | <u>MIC µg</u> | <u>Back Tube</u> | <u>TOTAL MIC µg</u> | <u>TOTAL MIC* Blank corrected µg</u> |
|------------------|-------------------|-------------------|------------------|-----------------------------|--|
| <u>0WX</u> | 0.06 | | < 0.02 | 0.06 | 0.01 |
| <u>0SX-1</u> | 0.08 | | < 0.02 | 0.08 | 0.03 |
| <u>0SX-2</u> | 0.07 | | < 0.02 | 0.07 | 0.02 |
| <u>0EX</u> | 0.08 | | < 0.02 | 0.08 | 0.03 |
| <u>0NX</u> | 0.08 | | < 0.02 | 0.08 | 0.03 |
| <u>1WX</u> | 0.12 | | 0.02 | 0.14 | 0.07 |
| <u>1SX-1</u> | 0.07 | | < 0.02 | 0.07 | 0.02 |
| <u>1SX-2</u> | 0.12 | | < 0.02 | 0.12 | 0.07 |
| <u>1EX</u> | 0.12 | | < 0.02 | 0.12 | 0.07 |
| <u>1NX</u> | 0.11 | | < 0.02 | 0.11 | 0.06 |

COMMENTS: * Front and back tubes corrected for the mean EHLB archive and field XAD-7 blanks of $0.05 \pm 0.02 \mu\text{g}$ MIC/ tube.

Control No: C94-046A
Lab Number: 50405

DATA SHEET FOR PESTICIDES

COMPOUND: METHYL ISOCYANATE (MIC)

Date Samples Submitted: August 29, 1995 Submitted by: Don Fitzell

Dates Samples Analyzed: Aug. 31. to Oct. 3, 1995

Analysts: M. Fracchia and D. Pon

| CORRECTED Sample ID | MIC µg | | TOTAL MIC | TOTAL MIC** Blank corrected |
|------------------------|------------|-----------|--------------|--------------------------------|
| | Front Tube | Back Tube | µg | µg |
| <u>2WX</u> | 0.14 | < 0.02 | 0.14 | 0.09 |
| <u>2SX-1</u> | 0.17 | < 0.02 | 0.17 | 0.12 |
| <u>2SX-2</u> | 0.20 | 0.02 | 0.22 | 0.15 |
| <u>2EX</u> | 0.19 | < 0.02 | 0.19 | 0.14 |
| <u>2NX</u> | 0.22 | < 0.02 | 0.22 | 0.17 |
| <u>3WX</u> | 0.10 | 0.04 | 0.14 | 0.05 |
| <u>3SX-1</u> | 0.14 | 0.04 | 0.18 | 0.09 |
| <u>3SX-2</u> | 0.19 | 0.03 | 0.22 | 0.14 |
| <u>3EX</u> | 0.14 | 0.04 | 0.18 | 0.09 |
| <u>3NX*</u> | 0.14 | 0.03 | 0.17 | 0.09 |

COMMENTS: * Lost some resin on transfer.

** Front and Back tubes corrected for the mean EHLB archive and Field XAD-7
blanks of 0.05 ± 0.02 µg MIC/ tube.

DATA SHEET FOR PESTICIDES

COMPOUND: METHYL ISOCYANATE (MIC)

Date Samples Submitted: August 29, 1995 Submitted by: Don Fitzell

Dates Samples Analyzed: Aug. 31. to Oct. 3, 1995

Analysts: M. Fracchia and D. Pon

| <u>Sample ID</u> | <u>MIC</u> <u>µg</u> | | <u>TOTAL</u> <u>MIC</u> <u>µg</u> | <u>TOTAL MIC**</u> <u>Blank corrected</u> <u>µg</u> |
|------------------|-------------------------|------------------|---|---|
| | <u>Front Tube</u> | <u>Back Tube</u> | | |
| <u>4WX</u> | 0.13 | < 0.02 | 0.13 | 0.08 |
| <u>4SX-1</u> | 0.14 | 0.02 | 0.16 | 0.09 |
| <u>42S-2</u> | 0.15 | 0.02 | 0.17 | 0.10 |
| <u>4EX</u> | 0.45 | 0.03 | 0.48 | 0.40 |
| <u>4NX</u> | 0.33 | 0.03 | 0.36 | 0.28 |
| <u>5WX</u> | 0.17 | 0.03 | 0.20 | 0.12 |
| <u>5SX-1</u> | 0.15 | 0.03 | 0.18 | 0.10 |
| <u>5SX-2</u> | 0.17 | 0.04 | 0.21 | 0.12 |
| <u>5EX*</u> | 0.07 | 0.19 | 0.26 | 0.16 |
| <u>5NX</u> | 0.16 | 0.02 | 0.18 | 0.11 |

COMMENTS: * Front and back tubes appear to have been switched. Double checking the labels and the dates of extraction for these two XAD-7 tubes confirms that EHLB received the samples as shown above. Regardless of the labeling, the total MIC for 5EX is correct.

**Front and back tubes corrected for the mean EHLB archive and field XAD-7 blanks of 0.05 ± 0.02 µg MIC/tube.

Control No: C94-046A
Lab Number: 50405

DATA SHEET FOR PESTICIDES

COMPOUND: METHYL ISOCYANATE (MIC)

Date Samples Submitted: August 29, 1995 Submitted by: Don Fitzell

Dates Samples Analyzed: Aug. 31, to Oct. 3, 1995

Analysts: M. Fracchia and D. Pon

| <u>Sample ID</u> | <u>MIC</u> <u>µg</u> | | <u>TOTAL</u> <u>MIC</u> <u>µg</u> | <u>TOTAL MIC**</u> <u>Blank corrected</u> <u>µg</u> |
|------------------|-------------------------|------------------|---|---|
| | <u>Front Tube</u> | <u>Back Tube</u> | | |
| <u>6WX</u> | 0.15 | 0.03 | 0.18 | 0.10 |
| <u>6SX-1</u> | 0.09 | 0.03 | 0.12 | 0.04 |
| <u>6SX-2</u> | 0.18 | 0.03 | 0.21 | 0.13 |
| <u>6EX</u> | 0.17 | 0.03 | 0.20 | 0.12 |
| <u>6NX*</u> | 0.13 | 0.02 | 0.15 | 0.08 |

COMMENTS: * Lost about 50% of resin during transfer. The tube broke in the middle while removing the cap.

**Front and back tubes corrected for the mean EHLB archive and field blanks of 0.05 ± 0.02 µg MIC/ tube.

Control No: C94-046A
Lab Number: 50405

**DATA SHEET FOR PESTICIDES
QUALITY CONTROL SAMPLES**
TARGET CONCENTRATION - 0.200 µg/ mL

COMPOUND: METHYL ISOCYANATE (MIC)

Analysts: M. Fracchia and D. Pon

| Sample ID | Date Analyzed | MIC- µg/ mL |
|-------------|---------------|-------------|
| EHLB QC 1 | 09/ 13/ 1995 | 0.21 |
| EHLB QC 2 | 09/ 14/ 1995 | 0.20 |
| EHLB QC 3 | 09/ 15/ 1995 | 0.19 |
| EHLB QC 4 | 09/ 19/ 1995 | 0.19 |
| EHLB QC 5 | 09/ 21/ 1995 | 0.19 |
| EHLB QC 6 | 09/ 22/ 1995 | 0.20 |
| EHLB QC 7 | 09/ 26/ 1995 | 0.19 |
| EHLB QC 8 | 09/ 27/ 1995 | 0.20 |
| EHLB QC 9 | 09/ 28/ 1995 | 0.20 |
| EHLB QC 10 | 09/ 29/ 1995 | 0.20 |
| EHLB QC 11 | 10/ 02/ 1995 | 0.20 |
| EHLB QC 12 | 10/ 03/ 1995 | 0.21 |
| EHLB QC 13 | 10/ 06/ 1995 | 0.20 |
| MEAN | | 0.20 |
| CV % | | 3.5% |

Control No: C94-046A

Lab Number: 50405

**DATA SHEET FOR PECTICIDE (MIC)
EHLB SPIKE SAMPLES**

COMPOUND: METHYL ISOCYANATE (MIC)

Submitted by: Don Fitzell

Analysts: M. Fracchia and D. Pon

| Sample ID | Date Analyzed | MIC - µg | MIC Blank Corrected* µg | Target Concentration µg |
|-------------|---------------|----------|-------------------------------|-------------------------------|
| EHLB SPIKE | 09/ 13/ 1995 | 0.91 | 0.86 | 0.96 |
| EHLB SPIKE | 09/ 14/ 1995 | 0.96 | 0.91 | 0.96 |
| EHLB SPIKE | 09/ 15/ 1995 | 0.96 | 0.91 | 0.96 |
| EHLB SPIKE | 09/ 19/ 1995 | 0.91 | 0.86 | 0.96 |
| EHLB SPIKE | 09/ 21/ 1995 | 0.93 | 0.88 | 0.96 |
| EHLB SPIKE | 09/ 22/ 1995 | 0.92 | 0.87 | 0.96 |
| FIELD SPIKE | 09/ 13/ 1995 | 0.92 | 0.87 | 0.96 |
| FIELD SPIKE | 09/ 14/ 1995 | 0.94 | 0.89 | 0.96 |
| FIELD SPIKE | 09/ 15/ 1995 | 0.95 | 0.90 | 0.96 |
| FIELD SPIKE | 09/ 19/ 1995 | 0.92 | 0.87 | 0.96 |
| FIELD SPIKE | 09/ 21/ 1995 | 0.95 | 0.90 | 0.96 |
| FIELD SPIKE | 09/ 22/ 1995 | 0.94 | 0.89 | 0.96 |
| EHLB SPIKE | 09/ 26/ 1995 | 1.82 | 1.77 | 1.92 |
| EHLB SPIKE | 09/ 27/ 1995 | 1.96 | 1.91 | 1.92 |
| EHLB SPIKE | 09/ 28/ 1995 | 1.92 | 1.87 | 1.92 |
| FIELD SPIKE | 08/ 31/ 1995 | 2.13 | 2.08 | 1.92 |
| FIELD SPIKE | 09/ 26/ 1995 | 1.81 | 1.76 | 1.92 |
| FIELD SPIKE | 09/ 27/ 1995 | 1.95 | 1.90 | 1.92 |
| FIELD SPIKE | 09/ 28/ 1995 | 1.96 | 1.91 | 1.92 |
| FIELD SPIKE | 09/ 29/ 1995 | 1.90 | 1.85 | 1.92 |
| FIELD SPIKE | 10/ 02/ 1995 | 1.86 | 1.81 | 1.92 |

OVERALL RECOVERY

95.4%

COMMENTS: * Corrected for the mean EHLB archive and field blanks of 0.05 ± 0.02 µg MIC/tube.

Control No: C94-046A
Lab Number: 50484

**DATA SHEET FOR PESTICIDES
AUDIT SAMPLES**

COMPOUND: METHYL ISOCYANATE (MIC)

Submitted by: Don Fitzell

Analysts: M. Fracchia and D. Pon

| Sample ID | Date Analyzed | MIC- µg/ Tube | MIC-µg/Tube* Blank Corrected |
|-----------|---------------|---------------|---------------------------------|
| MIC 1A | 09/ 26/ 1995 | 0.09 | 0.04 |
| MIC 2A | 09/ 27/ 1995 | 0.06 | 0.01 |
| MIC 3A | 09/ 28/ 1995 | 0.05 | < 0.02 |
| MIC 4A | 09/ 29/ 1995 | 0.05 | < 0.02 |
| MIC 5A | 10/ 02/ 1995 | 0.05 | < 0.02 |
| MIC 6A | 10/ 03/ 1995 | < 0.02 | < 0.02 |
| MIC 1B | 09/ 26/ 1995 | 0.09 | 0.04 |
| MIC 2B | 09/ 27/ 1995 | 0.04 | < 0.02 |
| MIC 3B | 09/ 28/ 1995 | 0.02 | < 0.02 |
| MIC 4B | 09/ 29/ 1995 | 0.04 | < 0.02 |
| MIC 5B | 10/ 02/ 1995 | 0.03 | < 0.02 |
| MIC 6B | 10/ 03/ 1995 | < 0.02 | < 0.02 |

COMMENTS: * Corrected for the mean EHLB archive blanks and field blanks of 0.05 ± 0.02 µg MIC/tube.

**DATA SHEET FOR PESTICIDES
AUDIT SAMPLES
SECOND SET***

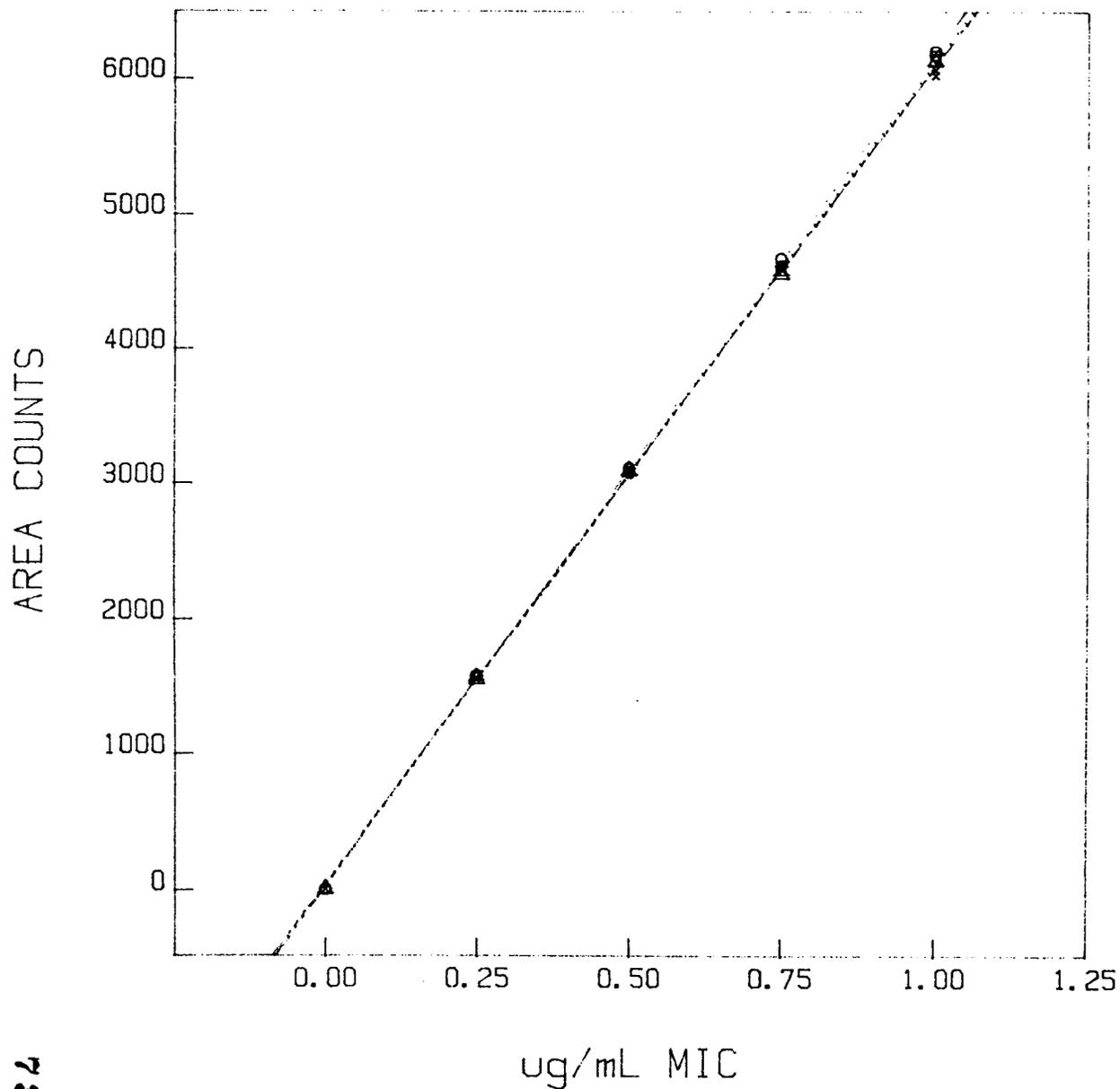
COMPOUND: METHYL ISOCYANATE (MIC)Analysts: M. Fracchia and D. Pon

| Sample ID | Date Analyzed | MIC- µg/ Tube | MIC-µg Blank Corrected | Target Concentration µg/ tube |
|--------------------|---------------|---------------|---------------------------|----------------------------------|
| XAD-7 TUBES | | | | |
| ARB A1 | 10/ 06/ 1995 | < 0.02 | < 0.02 | 0.04 |
| ARB A2 | 10/ 06/ 1995 | < 0.02 | < 0.02 | 0.04 |
| EHLB 1 | 10/ 06/ 1995 | < 0.02 | < 0.02 | 0.04 |
| EHLB 2 | 10/ 06/ 1995 | < 0.02 | < 0.02 | 0.04 |
| ARB B1 | 10/ 06/ 1995 | < 0.02 | < 0.02 | 0.08 |
| ARB B2 | 10/ 06/ 1995 | < 0.02 | < 0.02 | 0.08 |
| EHLB 3 | 10/ 06/ 1995 | 0.03 | < 0.02 | 0.08 |
| EHLB 4 | 10/ 06/ 1995 | 0.04 | < 0.02 | 0.08 |
| SOLUTIONS | | | | |
| | | MIC-µg/ mL | | MIC-µg/mL |
| ARB 1 | 10/ 06/ 1995 | 0.76 | | 2.00 |
| ARB 2 | 10/ 06/ 1995 | 0.78 | | 2.00 |
| EHLB 5 | 10/ 06/ 1995 | 1.67 | | 1.54 |
| EHLB 6 | 10/ 06/ 1995 | 1.62 | | 1.54 |

COMMENTS * This second set of spiked tubes and a portion of the liquid spiking standard were provided by ARB to confirm the initial audit tube results.

** Corrected for the mean EHLB archive blanks and field blanks of 0.05 ± 0.02 µg MIC/tube.

FIGURE 1.
MIC UREA DERIVATIVE COMPARISON



OLD EHLB (1993)
 SYMBOL=○
 LINETYPE=- - - - -
 $y=a+b*x$
 n=10
 $a=12.2250$ $s_a=12.2731$
 $b=6180.0580$ $s_b=20.0418$
 $s_{y,x}=22.4074$ $r=1.0000$

NEW EHLB (1995)
 SYMBOL=△
 LINETYPE=.....
 $y=a+b*x$
 n=10
 $a=15.5200$ $s_a=12.7643$
 $b=6106.5440$ $s_b=20.8439$
 $s_{y,x}=23.3042$ $r=1.0000$

OSHA LAB (1982)
 SYMBOL=x
 LINETYPE=- . - . -
 $y=a+b*x$
 n=10
 $a=31.7740$ $s_a=21.3855$
 $b=6057.4140$ $s_b=34.9224$
 $s_{y,x}=39.0444$ $r=0.9999$

DATA SHEET FOR PESTICIDES

COMPOUND: METHYL ISOTHIOCYANATE (MITC)

Date Samples Submitted: August 29, 1995

Submitted by: Don Fitzell

Dates Samples Analyzed: September 6-20, 1995

Analyst: Paul Larkin

| <u>Sample ID</u> | <u>MITC</u> <u>µg</u> | | <u>Total</u> <u>µg</u> |
|------------------|--------------------------|---------------------|---------------------------|
| | <u>Front Section</u> | <u>Back Section</u> | |
| OWC | 0.743 | <0.147 | 0.743 |
| OSC-1 | 0.342 | <0.147 | 0.342 |
| OSC-2 | 0.623 | <0.147 | 0.623 |
| OEC | 0.644 | <0.147 | 0.644 |
| ONC | 0.736 | <0.147 | 0.736 |
| 1WC | 0.553 | <0.147 | 0.553 |
| 1SC-1 | 12.45 | <0.147 | 12.45 |
| 1SC-2 | 17.15 | <0.147 | 17.15 |
| 1EC | 4.840 | <0.147 | 4.840 |
| 1NC | 0.445 | <0.147 | 0.445 |

COMMENTS: _____

DATA SHEET FOR PESTICIDES

COMPOUND: METHYL ISOTHIOCYANATE (MITC)

| <u>Sample ID</u> | <u>MITC</u> | | <u>Total</u> <u>µg</u> |
|------------------|-------------------------------------|---------------------|---------------------------|
| | <u>Front Section</u> | <u>Back Section</u> | |
| 2BC | <0.057 | <0.120 | <0.120 |
| 2WC | 99.70 | <0.147 | 99.70 |
| 2SC-1 | <i>sample not received - "lost"</i> | | |
| 2SC-2 | <i>sample not received - "lost"</i> | | |
| 2EC | 57.95 | <0.147 | 57.95 |
| 2NC | 350.4 | <0.147 | 350.4 |
| 3WC | 1.354 | <0.120 | 1.354 |
| 3SC-1 | 13.84 | <0.120 | 13.84 |
| 3SC-2 | 22.33 | <0.057 | 22.33 |
| 3EC | 26.48 | <0.057 | 26.48 |
| 3NC | 10.49 | <0.057 | 10.49 |
| 4WC | 1.506 | <0.153 | 1.506 |
| 4SC-1 | 2.827 | <0.153 | 2.827 |
| 4SC-2 | 3.686 | <0.153 | 3.686 |
| 4EC | 303.5 | <0.153 | 303.5 |
| 4NC | 252.0 | <0.153 | 252.0 |

DATA SHEET FOR PESTICIDES

COMPOUND: METHYL ISOTHIOCYANATE (MITC)

MITC
µg

| <u>Sample ID</u> | <u>Front Section</u> | <u>Back Section</u> | <u>Total µg</u> |
|------------------|----------------------|---------------------|---------------------|
| 5WC | 1.123 | <0.153 | 1.123 |
| 5SC-1 | 2.805 | <0.153 | 2.805 |
| 5SC-2 | 2.504 | <0.276 | 2.504 |
| 5EC | 5.377 | <0.276 | 5.377 |
| 5NC | 3.568 | <0.276 | 3.568 |
| 6WC | 3.335 | <0.276 | 3.335 |
| 6SC-1 | 1.793 | <0.276 | 1.793 |
| 6SC-2 | 1.681 | <0.084 | 1.681 |
| 6EC | 11.27 | <0.084 | 11.27 |
| 6NC | 29.43 | <0.084 | 29.43 |

BLANK RESULTS

Control No. C94-046A
Lab Number: 50404

COMPOUND: METHYL ISOTHIOCYANATE (MITC)

| Sample ID | Date Analyzed | MITC µg/Tube |
|------------------|---------------|-----------------|
| SOLUTIONS | | |
| CS2 BLANK | 6-Sep-95 | <0.147 |
| CS2 BLANK | 7-Sep-95 | <0.051 |
| CS2 BLANK | 11-Sep-95 | <0.120 |
| CS2 BLANK | 12-Sep-95 | <0.057 |
| CS2 BLANK | 13-Sep-95 | <0.153 |
| CS2 BLANK | 14-Sep-95 | <0.057 |
| CS2 BLANK | 14-Sep-95 | <0.276 |
| CS2 BLANK | 14-Sep-95 | <0.156 |
| CS2 BLANK | 20-Sep-95 | <0.096 |
| CS2 BLANK | 21-Sep-95 | <0.084 |
| CS2 BLANK | 3-Oct-95 | <0.066 |
| CS2 BLANK | 4-Oct-95 | <0.247 |
| CS2 BLANK | 10-Oct-95 | <0.072 |

Each value = average of 4 injections

CHARCOAL TUBE

| | | |
|------------|----------|--------|
| EHLB Blank | 3-Oct-95 | <0.066 |
| EHLB Blank | 3-Oct-95 | <0.066 |

**DATA SHEET FOR PESTICIDE
QUALITY CONTROL SAMPLES**
TARGET CONCENTRATION: 1.000 µg/ mL

Compound: Methyl Isothiocyanate (MITC)

| Sample ID | Date Analyzed | MITC µg/mL |
|----------------|---------------|---------------|
| QC 43 | 6-Sep-95 | 1.101 |
| QC 44 | 11 Sept. 95 | 1.037 |
| QC 47 | 11-Sep-95 | 1.070 |
| QC 51 | 13-Sep-95 | 0.967 |
| QC 53 | 14-Sep-95 | 1.087 |
| QC 55 | 14-Sep-95 | 1.255 |
| QC 57 | 15-Sep-95 | 1.125 |
| QC 59 | 20-Sep-95 | 0.901 |
| QC 61 | 21-Sep-95 | 0.998 |
| QC 71 | 4-Oct-95 | 0.829 |
| QC 75 | 10-Oct-95 | 0.951 |
| QC 79 | 12-Oct-95 | 1.302 |
| Average | | 1.052 |
| CV % | | 13.0 |

**DATA SHEET FOR PESTICIDE
QUALITY CONTROL SAMPLES**
TARGET CONCENTRATION: 0.200 µg/ mL

Compound: Methyl Isothiocyanate (MITC)

| Sample ID | Date Analyzed | MITC µg/mL |
|----------------|---------------|---------------|
| QC 45 | 6-Sep-95 | 0.193 |
| QC 46 | 7-Sep-95 | 0.197 |
| QC 48 | 11-Sep-95 | 0.156 |
| QC 50 | 12-Sep-95 | 0.155 |
| QC 52 | 13-Sep-95 | 0.176 |
| QC 54 | 14-Sep-95 | 0.158 |
| QC 56 | 14-Sep-95 | 0.172 |
| QC 60 | 20-Sep-95 | 0.113 |
| QC 62 | 21-Sep-95 | 0.147 |
| QC 64 | 2-Oct-95 | 0.139 |
| QC 66 | 3-Oct-95 | 0.084 |
| Average | | 0.153 |
| CV % | | 21.7 |

**DATA SHEET FOR PESTICIDE (MITC)
SPIKE SAMPLES**

| Sample ID | Date Analyzed | MITC µg | Target Concentration µg |
|---------------------|---------------|------------|----------------------------|
| Tube 25 Field Spike | 6 Sept. 95 | 0.754 | 1.000 |
| Tube 27 Field Spike | 7 Sept. 95 | 0.837 | 1.000 |
| Tube 29 Field Spike | 11 Sept. 95 | 0.632 | 1.000 |
| Tube 31 Field Spike | 12 Sept. 95 | 0.903 | 1.000 |
| Tube 33 Field Spike | 13 Sept. 95 | 0.724 | 1.000 |
| Tube 35 Field Spike | 14 Sept. 95 | 0.669 | 1.000 |
| | | | |
| Tube 37 Field Spike | 14 Sept. 95 | 0.099 | 0.200 |
| Tube 39 Field Spike | 15 Sept. 95 | 0.177 | 0.200 |
| Tube 41 Field Spike | 20 Sept. 95 | 0.102 | 0.200 |
| Tube 43 Field Spike | 21 Sept. 95 | 0.086 | 0.200 |
| | | | |
| Tube 45 EHLB Spike | 2 Oct. 95 | 0.132 | 0.200 |
| Tube 46 EHLB Spike | 2 Oct. 95 | 0.139 | 0.200 |

OVERALL RECOVERY:**73.0%**

Comments: All prepared on 17 Aug. 95

**DATA SHEET FOR PESTICIDES
AUDIT SAMPLES**

COMPOUND: METHYL ISOTHIOCYANATE (MITC)

Submitted by: Don Fitzell

Analyst: Paul Larkin

MITC - μg

| <u>Sample ID</u> | <u>Front Section</u> | <u>Back Section</u> | <u>Total</u> |
|------------------|----------------------|---------------------|--------------|
| MITC - 1 | 0.098 | <0.074 | 0.098 |
| MITC - 2 | 0.075 | <0.074 | 0.075 |
| MITC - 3 | 0.109 | <0.074 | 0.109 |
| MITC - 4 | 0.092 | <0.074 | 0.092 |
| MITC - 5 | <0.074 | <0.074 | <0.074 |
| MITC - 6 | <0.074 | <0.074 | <0.074 |

Comments: Analysis of ARB spiking solution yielded results two to three times higher than the nominal concentration. These results were quantified against standard stock solutions prepared by two different analysts on two different days, and cross checked against a new lot of MITC.

**APPENDIX VI
QMOSB AUDIT REPORT**

**STATE OF CALIFORNIA AIR RESOURCES BOARD
MONITORING AND LABORATORY DIVISION
QUALITY ASSURANCE SECTION**

**SYSTEM AUDIT REPORT
METHYL ISOCYANATE AND METHYL ISOTHIOCYANATE MONITORING
IN
KERN COUNTY**

DECEMBER 1996

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SYSTEM AUDIT REPORT
METHYL ISOCYANATE AND METHYL ISOTHIOCYANATE MONITORING
IN
KERN COUNTY

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2. Flow Rate Audit Procedures for Air Samplers Used in Pesticide Monitoring
3. Performance Audit Procedures for the Laboratory Analysis of Methyl Isocyanate and Methyl Isothiocyanate

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T10N09P6-12/96-SJN

I. EXECUTIVE SUMMARY

In August 1995, the Engineering and Laboratory Branch (ELB) of the Air Resources Board (ARB) conducted a three-day source impacted ambient air monitoring program for an application of metam sodium to a field in Kern County. This monitoring was conducted to determine if methyl isocyanate (MIC), a breakdown product of metam sodium's primary breakdown product, methyl isothiocyanate (MITC), could be detected and measured in ambient air. The samples were collected by the ELB and analyzed by the Environmental Health Laboratory Branch (EHLB) of the Department of Health Services.

The Quality Assurance Section (QAS) of the ARB's Monitoring and Laboratory Division (MLD) conducted a system audit of the field and laboratory operations to review the sample handling and storage procedures, analytical methodology, and method validation. In general, the laboratory practices were consistent with the Quality Assurance Plan for Pesticide Monitoring (ARB, February 4, 1994).

Additionally, the QAS staff conducted performance audits of the air monitoring samplers. The performance audits of the air monitoring samplers were conducted to evaluate the flow rate accuracy. The difference between the reported and assigned flow rates for MIC sampling averaged -0.3% with a range of -3.9% to 5.3%. The difference between the reported and assigned flow rates for MITC sampling averaged 3.5% with a range of 2.3% to 4.9%.

To determine the effectiveness of the analytical procedure, laboratory performance audits were also conducted. On September 21, 1995, 18 QAS audit samples spiked with known amounts of MIC and MITC were submitted to the EHLB for analysis. The samples were prepared from MIC and MITC standard solutions obtained from Chem Service.

The first set of 12 QAS audit samples spiked on September 21, 1995 were MIC audit samples (Six were primary MIC sample tubes and six secondary MIC sample tubes). The samples were analyzed between September 26, 1995 and October 3, 1995 at the EHLB facility. The EHLB essentially did not detect any MIC from the spiked audit samples. On October 5, 1995, the QAS spiked a second set of four MIC samples and submitted these samples to the EHLB for analysis. During the analysis of these four samples, the EHLB experienced a computer equipment failure and the results were lost.

The EHLB staff conducted an investigation to determine the cause of the low recovery results during the QAS analytical performance audit performed September 26, 1995 through October 3, 1995. The EHLB found inconsistencies when analyzing QAS's audit standard solution. The EHLB determined the Chem Service standard solution had a concentration of 38.8% of its reported value.

To verify the integrity of the EHLB results, the EHLB conducted a stability analysis using a fresh batch of MITC-derivative prepared from fresh MITC and 1,2-pyridylpiperazine (1,2-PP) and an independent source of the MITC-derivative obtained from the federal Occupational Safety & Health Administration laboratory (OSHA) in Salt Lake City, Utah. These two standards were analyzed, plotted, and compared with the EHLB's standard. The standard curves from all three sources were in close agreement. The percent difference between the assigned masses and the reported masses for the three standards were an average of 0.3% and ranged from -1.3% to 4.0%. Based on these validation studies, the QAS has decided to invalidate the audit samples used during the analytical performance audit.

The remaining six of the 18 QAS audit samples spiked on September 21, 1995 were MITC audit samples. In addition to these samples, on October 5, 1995, the QAS spiked a second set of five MITC samples and submitted these samples along with the QAS's standard solution to the EHLB for analysis.

The five MITC audit samples spiked on October 5, 1995 were not analyzed because the samples were misplaced at the EHLB. This problem has been associated to the fact that the ARB and the EHLB chain-of-custody protocols were not properly followed. The six MITC audit samples (spiked on September 21, 1995) were analyzed by the EHLB on October 10, 1995. MITC was quantitated in four of the five audit samples which had been spiked with an assigned amount of MITC. Of the two samples that were reported to have no MITC above the limit of detection (LOD), one audit sample was a blank and the other was assigned an amount 0.001 ug above the LOD. The average percent difference between the assigned and the reported total mass for the four audit samples, MITC-1 through MITC-4, was -25.2% with a range of -38.7% to 0.0%. This -25% difference was in close agreement with the average 73% recovery for the MITC spiked charcoal tubes the EHLB determined during the method validation studies.

The EHLB conducted two separate stability analyses on the QAS audit samples. Using the EHLB's MITC standards and the ARB supplied QAS MITC standard solution, the first analysis was conducted on October 12, 1995 by comparing the QAS standard solution to the EHLB calibration standard solution, and another EHLB standard solution, prepared by an independent chemist, from EHLB's MITC stock. The second analysis was conducted on October 30, 1995 by comparing the QAS standard solution to the EHLB standard solution (received 7/92), a new EHLB standard solution (received 10/95), and the EHLB standard solution, prepared by an independent chemist, from EHLB's stock.

The results of these two EHLB stability studies indicated the EHLB standards were stable and the QAS standard solution was unstable. There was an average 5.6% difference between the reported masses and the assigned masses for the EHLB's standard solutions. The results of the comparison indicated the QAS's standard

solution had an average concentration 2.32 times its nominal value. After discussions with the EHLB's staff and ARB's Engineering Laboratory Branch, the increase in concentration of the QAS standard solution may be attributed to the use of carbon disulfide as the solvent. Due to its high volatility, the carbon disulfide may have evaporated during the spiking process and/or during the storage and transporting of the standard solution. For these reasons, the level of MITC in the QAS standard solution would increase in concentration.

The QAS analytical performance audit results for MITC indicated good agreement between the spiked sample mass levels and the reported mass levels. The high concentration level of the QAS standard solution was first identified within three weeks of the expiration date of the solution and near the end of the MIC/MITC study. Therefore, the QAS analytical performance audit results for MITC most likely was not influenced by the questionable stability of the analyte in solution. The high concentration level of the QAS standard solution had no impact on the ambient data.

A QAS review of all of EHLB's trip spikes, blanks and in-house QC laboratory spikes resulted in good recovery levels.

The reported levels of concentration for both the MIC and MITC were discussed with Chem Service. Chem Service stated they had reviewed the data and issued a certificate of analysis prior to sending the standard solutions to ARB. Chem Service had assigned an expiration date of two months to both solutions due to the questionable stability of the analytes in solution. Chem service was not able to study the standard solutions after the EHLB analysis due to the fact that the solution had expired. No definite cause or explanation for the low MIC and high MITC concentration levels has been determined by Chem Service.

II. CONCLUSIONS

Operation

The records for field operations, sample handling and storage procedures, analytical methodology, and method validation were in general in agreement with the Quality Assurance Plan for Pesticide Monitoring. The ARB and EHLB have chain-of-custody procedures established within each of their facilities. However, five QAS audit samples did not have the necessary chain-of-custody documentation during the transfer from ARB and the receipt into EHLB facility. All ambient air monitoring field samples had chain-of-custody documentation.

Field Flow Rates

The results of the reported flow rates for the ambient air monitoring samplers were in good agreement with the actual flow rates measured by the QAS staff.

Laboratory Accuracy

The QAS review of all of EHLB's trip spikes, blanks, and in-house laboratory spikes resulted in good recovery levels. However, the results of the QAS analytical performance audit showed little or no detection of MIC. Based on the validation studies comparing the levels of concentrations for a number of standard solutions and discussions with the EHLB, ELB, and Chem Service, the results of these studies indicates the Chem Service's MIC standard solution attributed to the low or no detection levels. The QAS has invalidated the MIC audit samples used during the analytical performance audit. The MIC ambient data can be used without adjustment.

Results of the MITC laboratory performance audit indicate an average percent difference between the assigned and the reported total mass for the audit samples were -25.2% with a range of -38.7% to 0.0%.

The EHLB archive and spiked charcoal tubes were prepared by EHLB using crystalline MITC of 97% purity. The EHLB recovery studies in 1992 gave values of approximately 75%. The EHLB archive and field spike for this current 1995 set had an average recovery of 73%. Based on the QAS audit sample results and the EHLB recovery studies, the level of MITC detected could be 25% higher for the reported ambient field data.

III. RECOMMENDATIONS

1. The ARB and the EHLB personnel should review and follow their chain-of-custody procedures. Sample analysis request and chain-of-custody forms should be utilized for all sample transfers.
2. The QAS should investigate alternative sources for procuring standard solutions and/or investigating the possibility of using an independent laboratory to verify the concentrations of standard solutions procured by the QAS.
3. The QAS should develop a protocol for transporting audit material (spikes, solutions, etc) and marking the meniscus so it can be determined whether the solvent volatilized during transport.

IV. INTRODUCTION

In August 1995, the Engineering and Laboratory Branch (ELB) of the Air Resources Board (ARB) conducted a three-day source impacted ambient air monitoring program for an application of metam sodium to a field in Kern County, California. This monitoring was conducted to determine if methyl isocyanate (MIC), a breakdown product of metam sodium's primary breakdown product, methyl isothiocyanate (MITC), could be detected and measured in ambient air. The samples were collected by the ELB and analyzed by the Environmental Health Laboratory Branch (EHLB) of the Department of Health Services. The ARB's Monitoring and Laboratory Division's (MLD) Quality Assurance Section (QAS) staff conducted a system audit of the field and laboratory operations, and performance audits of the air samplers' flow rates and of the analytical method.

V. AUDIT OBJECTIVE

The system audit was conducted to determine whether the quality control practices followed in the handling and storage of samples, analytical methodology, and method validation were consistent with the Quality Assurance Plan for Pesticide Monitoring (ARB, February 4, 1994). Performance audits were conducted to evaluate the accuracy of the air samplers' flow rate and the analytical method.

VI. FIELD AND LABORATORY OPERATIONS

A system audit of the field and laboratory operations was initiated in September 1995 through a questionnaire submitted to EHLB staff. Also, the protocol, "Methyl Isocyanate and Methyl Isothiocyanate Monitoring After a Application of Metam Sodium During the Summer 1995" was reviewed.

Sample Handling and Storage

Samples were collected by drawing ambient air at measured rates through sample tubes containing either charcoal for MITC sampling or XAD-7 treated with 1,2-pyridylpiperazine (1,2-PP) for MIC sampling. The MITC charcoal tubes were 8 mm x 110 mm and contained a 400 mg charcoal primary section and a 200 mg charcoal secondary section. The MIC XAD-7 tubes were 8 mm x 110 mm and contained a 175 mg of XAD-7. A pair of XAD-7 tubes (tube A as primary, tube B as secondary) were placed in series. The treated XAD-7 tubes were stored either in a freezer or on dry ice until used in the field. The air samplers consisted of one sample holder, connected with Teflon tubing to an in-line rotometer and an air pump. The sampling assembly was supported by a two meter section of galvanized steel tube (Attachment I). The samplers' rotometers were set to an indicated flow rate of 2.0

liters per minute (LPM) for the charcoal tubes and 70 cc per minute for the XAD-7 tubes.

Sampling was conducted following the schedule specified in the sampling protocol. After sampling, the tubes were then removed from the sample train, end caps were installed on both ends, and identification labels were affixed to each tube. Each tube was then placed in a culture tube with a screw cap and stored with dry ice until delivery to the ELB laboratory in Sacramento. Samples were stored in a freezer for up to seven days until delivery to the EHLB in Berkeley.

Upon receipt at the EHLB, the samples were stored in their original boxes in a freezer for less than four weeks until extraction and analyses were conducted.

Sample Analysis

The analytical method used to analyze the MIC samples was developed by the EHLB, and is described in the EHLB Method No. 104 (modified Occupational Safety & Health Administration Method 54). The MIC XAD-7 tubes were extracted with 4 mL of acetonitrile (ACN). The analysis was performed on a Hewlett Packard HPLC liquid chromatograph with a fluorescence detector. The MITC sample analysis were performed using the Stauffer, Inc. Method RRC-82-35, modified by substituting larger capacity sorbent tubes for the smaller sampling tubes specified. The charcoal in the primary and secondary sections of each sample tube was extracted with carbon disulfide (CS₂). The analysis of the MITC was performed on a Varian 6000 gas chromatograph with a nitrogen/phosphorous detector (NPD).

The following quality control activities were performed to monitor and document the quality of the data: field control blanks were analyzed with every analytical run; laboratory spikes were analyzed in replicate with every analytical run; and every sample was analyzed in replicate to document analytical precision. Precision checks of the data were less than $\pm 10\%$ difference. Field duplicates from collocated sites were collected once each sampling day. A portion of the samples were analyzed by GC/Mass Spectroscopy Selective Ion monitoring to confirm the identity of the analyte.

Method Validation

The limit of detection criteria was determined by using the EPA technique based on multiple determinations of low concentrations of MIC or MITC. The LOD was calculated as 0.03 ug MIC per mL ACN and 0.01 ug MITC per mL CS₂. A daily LOD was calculated and reported for each daily standard curve. Due to the Perkin-Elmer gas chromatograph NPD sensitivity, the daily LOD for MITC varied from 0.05 to 0.28 ug/sample. All ambient MITC monitoring data were reported as greater than the daily LOD.

Trapping efficiency was determined as 100% total mass recovery for MIC and MITC. No breakthrough was detected at a mass load of 5.0 ug MIC over 24 hours at a flow rate of 0.075 LPM. No breakthrough was detected at a mass load of 230 ug MITC over six hours at a flow rate of 2.0 LPM.

Recovery studies were conducted by the EHLB using archived and spiked charcoal tubes that were prepared by EHLB using crystalline MITC of 97% purity. The EHLB recovery studies in 1992 gave values of approximately 75%. The EHLB archive and field spike for this current 1995 set had an average recovery of 73%. Sample stability studies for the MITC samples stored for two weeks under refrigeration (4° Celsius) were within 15% relative to the initial analysis.

The recovery studies for the MIC archive and field spike had an average recovery of 95%. Sample stability studies were conducted and the integrity of the MIC sample was determined to have 98% recovery relative to the initial analysis after being stored for 18 days at 21° Celsius and 100% recovery relative to the initial analysis after being stored for 18 days at 4° Celsius.

Documentation

Field data sheets containing the sample collection information accompanied each sample. The information recorded on the field data sheets included sampler location, sampling date, start and stop times, log number, identification number, description, job name, date, job number, and initials of the field technician.

All of the ARB field samples were accompanied by chain-of-custody records prior to transferring these samples into the EHLB's internal chain-of-custody system. However, the QAS and the EHLB neglected to properly document the transfer and receipt of five QAS MITC audit samples. These five MITC samples were misplaced at the EHLB.

Laboratory and instrument maintenance logs were kept in bound notebooks with numbered pages. The entries made in the laboratory book included sample number, sample type, date sample was received, date of analysis, results of analysis, and analyst. The raw analytical data were recorded on electronic files and will be kept indefinitely by the EHLB.

VII. PERFORMANCE AUDITS

NOTE: The percent difference listed on each Table used the following formula:

$$\text{Percent Difference} = \frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

FLOW RATE AUDIT

The flow rate of each sampler used was audited on July 21, 1995 following the procedures outlined in Attachment II. The audit was conducted with a 0 to 30 LPM mass flow meter traceable to the National Institute of Standards and Technology (NIST). The percent difference between the reported and true flow rates averaged -0.3% and ranged from -3.9% to 5.3% for MIC (Table 1). For MITC, the percent difference between reported and true flow rates averaged 3.5% and ranged from 2.3% to 4.9% (Table 2).

Table 1
Results of the Flow Audit of the Samplers Used in the
Monitoring of Methyl Isocyanate

| Sampler Number | Reported Flow (cc/min) | True Flow (cc/min) | Percent Difference |
|----------------|------------------------|--------------------|--------------------|
| 1 | 90 | 85.5 | 5.3 |
| 2 | 90 | 89.9 | 0.0 |
| 3 | 90 | 92.9 | -3.1 |
| 4 | 90 | 93.7 | -3.9 |
| 5 | 90 | 89.9 | 0.0 |

Table 2
Results of the Flow Rate Audit of the Samplers Used in the
Monitoring of Methyl Isothiocyanate

| Sampler Number | Reported Flow (LPM) | True Flow (LPM) | Percent Difference |
|----------------|---------------------|-----------------|--------------------|
| 1 | 1.9 | 1.81 | 4.9 |
| 2 | 1.9 | 1.84 | 3.5 |
| 3 | 1.9 | 1.85 | 2.5 |
| 4 | 1.9 | 1.86 | 2.3 |
| 5 | 1.9 | 1.82 | 4.4 |

LABORATORY PERFORMANCE AUDIT

The accuracy of the analytical method was evaluated by submitting a set of 18 QAS audit samples spiked with measured amounts of MIC and MITC for analysis. The QAS standard solutions were prepared by Chem Service and samples were spiked by QAS staff on September 21, 1995 following the procedures outlined in Attachment III.

MIC Analytical Performance Audit

The first set of 12 MIC audit samples were analyzed by the EHLB. Six were primary section MIC samples (Table 3) and six secondary section MIC samples (Table 4). Samples were analyzed between September 26, 1995 and October 3, 1995. The EHLB essentially did not detect any MIC from the spiked audit samples. On October 5, 1995, the QAS spiked a second set of four MIC samples (Table 5) and submitted these samples to the EHLB for analysis. During the analysis of these four samples, the EHLB experienced a computer equipment failure and the results were lost.

Table 3
Results of Analyses of the Methyl Isocyanate Audit Samples
(Primary Tube)

| Sample ID | Assigned Mass (ug) | Uncorrected Reported Mass (ug) | Reported Mass (ug) Blank Corrected | Percent Difference |
|-----------|--------------------|--------------------------------|------------------------------------|--------------------|
| MIC-1A | 0.08 | 0.09 | 0.04 | -50 |
| MIC-2A | 0.04 | 0.06 | 0.01 | -75 |
| MIC-3A | 0.04 | 0.05 | <0.02 | -100 |
| MIC-4A | 0.08 | 0.05 | <0.02 | -100 |
| MIC-5A | 0.08 | 0.05 | <0.02 | -100 |
| MIC-6A | 0.00 | <0.05 | <0.02 | --- |

Table 4
Results of Analyses of the Methyl Isocyanate Audit Samples
(Secondary Tube)

| Sample ID | Assigned Mass (ug) | Uncorrected Reported Mass (ug) | Reported Mass (ug) Blank Corrected | Percent Difference |
|-----------|--------------------|--------------------------------|------------------------------------|--------------------|
| MIC-1B | 0.08 | 0.09 | 0.04 | -50 |
| MIC-2B | 0.00 | 0.04 | <0.02 | --- |
| MIC-3B | 0.00 | 0.02 | <0.02 | --- |
| MIC-4B | 0.04 | 0.04 | <0.02 | -100 |
| MIC-5B | 0.04 | 0.03 | <0.02 | -100 |
| MIC-6B | 0.00 | <0.02 | <0.02 | --- |

Note: Tables 3 and 4 are corrected for the mean EHLB archive blanks and field blanks of 0.05 ± 0.02 ug MIC/tube.

Table 5
Results of Analyses of the Methyl Isocyanate Audit Samples
(Spiked October 5)

| Sample ID | Assigned Mass (ug) | Reported Mass (ug) | Percent Difference |
|-----------|--------------------|--------------------|--------------------|
| MIC-6C | 0.20 | N/A | ---- |
| MIC-7C | 0.20 | N/A | ---- |
| MIC-8C | 0.08 | N/A | ---- |
| MIC-9C | 0.40 | N/A | ---- |

The EHLB staff conducted an investigation to determine the cause of the low recovery results during the QAS analytical performance audit performed September 26, 1995 through October 3, 1995. The EHLB found inconsistencies when analyzing the QAS's audit standard solution. The EHLB determined the Chem Service standard solution had a concentration of 38.8% of its reported value (Table 6). This reported level of concentration was discussed with Chem Service. Chem Service stated they had reviewed the data and issued a certificate of analysis prior to sending the standard solution to ARB. Chem Service had assigned an expiration date of two months to this solution due to the questionable stability of the analytes in solution. Chem Service was not able to study the standard solution after the EHLB analysis due to the fact that the solution had expired. No definite cause or explanation for the low concentration level has been determined by Chem Service.

Table 6
Purity of the QAS Methyl Isocyanate Spiking Solution

| Sample ID | Sample Amount (ug/mL) | Percent Purity |
|-----------|-----------------------|----------------|
| ARB-1 (1) | 0.190 | 38.0 |
| ARB-1 (2) | 0.195 | 39.0 |
| ARB-2 (1) | 0.197 | 39.4 |
| ARB-2 (2) | 0.194 | 38.8 |

To verify the integrity of the EHLB results, the EHLB conducted a stability analysis using a fresh batch of MIC-derivative prepared from fresh MIC (EHLB 1995) and 1,2-PP and an independent source of the MIC-derivative obtained from the federal OSHA laboratory in Salt Lake City, Utah. These two standards were analyzed, plotted, and compared with the EHLB's standard (EHLB 1993) (Table 7). The standard curves from all three sources were in close agreement. The percent difference between the assigned masses and the reported masses for the EHLB 1993

calibration standard, the EHLB 1995 calibration standard, and the OSHA standard were an average of 0.3% and ranged from -1.3% to 4.0%. Based on these validation studies, the QAS has decided to invalidate the audit samples used during the analytical performance audit. The MITC ambient data can be used without adjustment.

Table 7
Results of Analyses Comparing EHLB and OSHA
Methyl Isocyanate Standard Solutions

| Sample ID | Assigned Mass (ug) | Reported Mass (ug) | Percent Difference |
|-----------|-----------------------|-----------------------|-----------------------|
| EHLB 1993 | 0.25 | 0.26 | 4.0 |
| | 0.50 | 0.50 | 0.0 |
| | 0.75 | 0.76 | 1.3 |
| | 1.00 | 1.01 | 1.0 |
| EHLB 1995 | 0.25 | 0.25 | 0.0 |
| | 0.50 | 0.50 | 0.0 |
| | 0.75 | 0.74 | -1.3 |
| | 1.00 | 1.00 | 0.0 |
| OSHA | 0.25 | 0.25 | 0.0 |
| | 0.50 | 0.50 | 0.0 |
| | 0.75 | 0.75 | 0.0 |
| | 1.00 | 0.99 | -1.0 |

MITC Analytical Performance Audit

On October 5, 1995, the QAS spiked a second set of five MITC samples (Table 8) and submitted these samples to the EHLB for analysis. These were not analyzed due to the fact that the ARB and the EHLB chain-of-custody protocol for transferring and receiving pesticide samples were not properly followed. These five MITC samples were misplaced at the EHLB. The six MITC audit samples (spiked on September 21, 1995) were analyzed by the EHLB (Table 9) on October 10, 1995. MITC was quantitated in four of the five audit samples which had been spiked with an assigned amount of MITC. Of the two samples that were reported to have no MITC above the LOD, one audit sample was a blank and the other was assigned an amount 0.001 ug above the LOD. The average percent difference between the assigned and the reported total mass for the four audit samples, MITC-1 through MITC-4, was -25.2% with a range of -38.7% to 0.0%. The EHLB did not detect any MITC from the back section of the audit samples. The QAS did not spike the back section of the audit tubes.

Table 8
Results of Analyses of the Methyl Isothiocyanate

| Sample ID | Assigned Mass (ug) | Reported Mass (ug) | Percent Difference |
|-----------|--------------------|--------------------|--------------------|
| MITC-1C | 0.00 | N/A | ---- |
| MITC-2C | 0.075 | N/A | ---- |
| MITC-3C | 0.075 | N/A | ---- |
| MITC-4C | 0.15 | N/A | ---- |
| MITC-5C | 0.15 | N/A | ---- |

Table 9
Results of Analyses of the Methyl Isothiocyanate

| Sample ID | Assigned Mass (ug) | Reported Mass Front Sec.(ug) | Reported Mass Back Sec.(ug) | Front Section Percent Difference |
|-----------|--------------------|------------------------------|-----------------------------|----------------------------------|
| MITC-1 | 0.15 | 0.098 | <0.074 | -34.7 |
| MITC-2 | 0.075 | 0.075 | <0.074 | 0.0 |
| MITC-3 | 0.15 | 0.109 | <0.074 | -27.3 |
| MITC-4 | 0.15 | 0.092 | <0.074 | -38.7 |
| MITC-5 | 0.00 | <0.074 | <0.074 | --- |
| MITC-6 | 0.075 | <0.074 | <0.074 | --- |

The EHLB conducted two separate stability analyses on the QAS audit samples. Using the EHLB's MITC standards and the ARB supplied QAS MITC standard solution, the first analysis was conducted on October 12, 1995 by comparing the QAS standard solution to the EHLB calibration standard solution (MITC), and another EHLB standard solution, prepared by an independent chemist, from EHLB's MITC stock (MF MITC). Results are shown on Table 10. The second analysis was conducted on October 30, 1995 by comparing the QAS standard solution to EHLB standard solution (Old MITC, received 7/92), a new EHLB standard solution (New MITC, received 10/95), and the EHLB standard solution, prepared by an independent chemist, from EHLB's stock (MF MITC). Results are shown on Table 11.

The results of these studies indicated an average 5.6% difference between the reported masses and the assigned masses for the EHLB's standard solutions. The results of the comparison also indicated the QAS's standard solution had an average concentration 2.32 times its nominal value. This reported level of concentration was discussed with Chem Service. Chem Service stated they had reviewed the data and issued a certificate of analysis prior to sending the standard solution to ARB. Chem Service assigned an expiration date of two months to this solution due to the questionable stability of the analytes in solution. Chem Service was not able to study the standard solution after the EHLB analysis due to the fact that the solution had expired. No definite cause or explanation for the high concentration has been determined by Chem Service.

After discussions with the EHLB's staff and ARB's Engineering Laboratory Branch, the increase in concentration of the QAS standard solution may be attributed to the carbon disulfide usage as the solvent. Due to its high volatility, the carbon disulfide may have evaporated during the spiking process and/or during the storage and transporting of the standard solution. For these reasons, the level of MITC in the standard solution would increase in concentration.

The QAS analytical performance audit results indicated good agreement between the spiked sample mass levels and the reported mass levels. The high concentration level of the QAS standard solution was first identified within three weeks of the expiration date of the solution and near the end of the MIC/MITC study. Therefore, the QAS analytical performance audit results for MITC most likely was not influenced by the questionable stability of the analyte in solution. The high concentration level of the QAS standard solution had no impact on the ambient data.

A QAS review of all of EHLB's trip spikes, blanks and in-house QC laboratory spikes resulted in good recovery levels.

Table 10
Results of Analyses Comparing the QAS and the EHLB
Methyl Isothiocyanate Standard Solutions

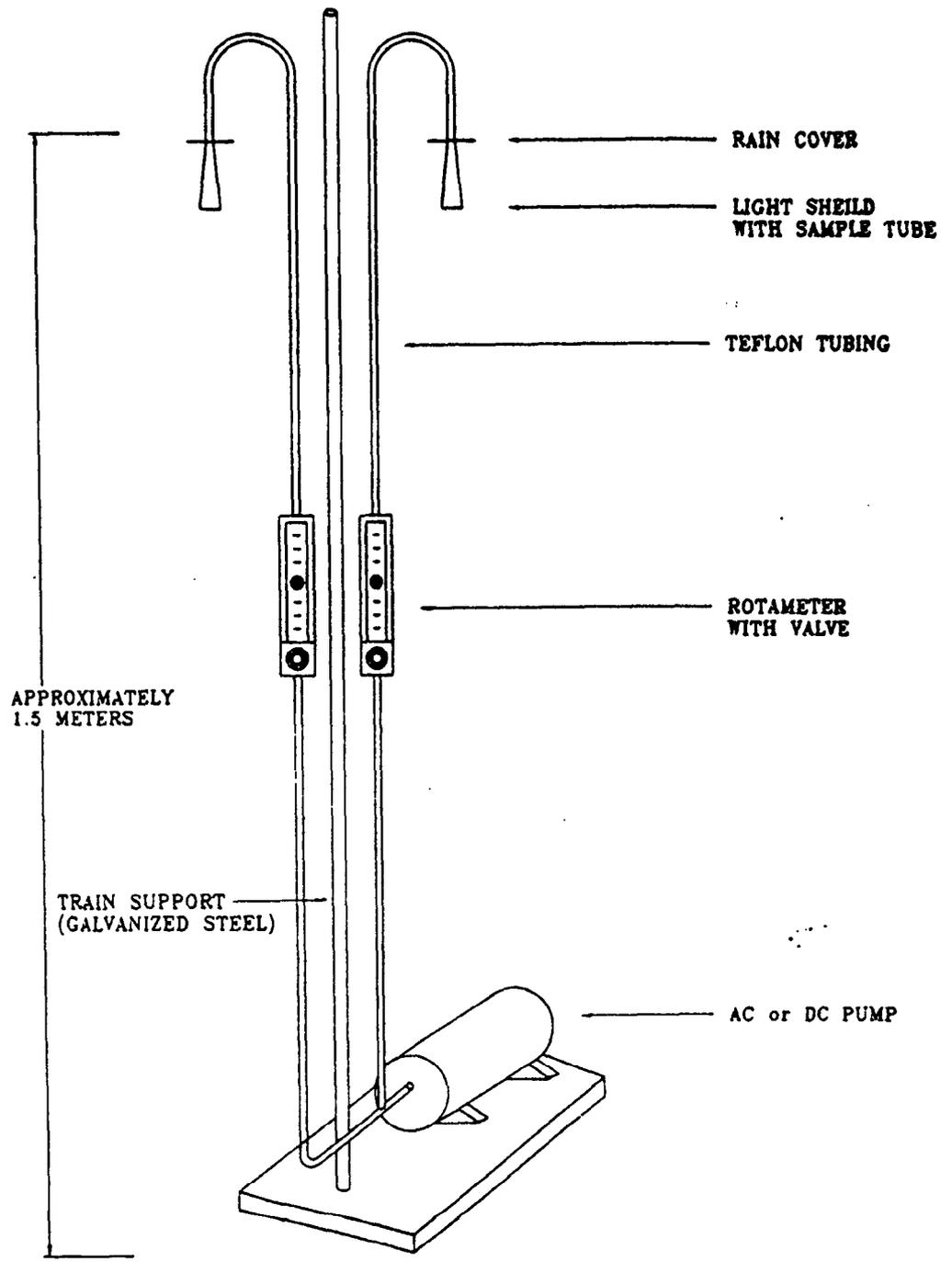
| Sample ID | Assigned Mass (ug) | Reported Mass(ug) | Percent Difference |
|-----------|--------------------|-------------------|--------------------|
| MITC | 1.00 | 1.12 | 12.0 |
| ARB Stock | 1.00 | 2.22 | 122.0 |
| MF MITC | 1.00 | 1.07 | 7.0 |

Table 11
Results of Analyses Comparing the QAS, EHLB, and Aldrich
Methyl Isothiocyanate Standard Solutions

| Sample ID | Assigned Mass (ug) | Reported Mass (ug) | Percent Difference |
|-----------|-----------------------|-----------------------|-----------------------|
| Old MITC | 1.00 | 1.23 | 23.0 |
| New MITC | 1.00 | 0.99 | -1.0 |
| ARB Stock | 1.00 | 2.42 | 142.0 |
| MF MITC | 1.00 | 0.87 | -13.0 |

Results of the MITC laboratory performance audit indicate an average percent difference between the assigned and the reported total mass for the audit samples were -25.2% with a range of -38.7% to 0.0%. The EHLB archive and spiked charcoal tubes were prepared by EHLB using crystalline MITC of 97% purity. The EHLB recovery studies in 1992 gave values of approximately 75%. The EHLB archive and field spike for this current 1995 set had an average recovery of 73%. Based on the QAS audit sample results and the EHLB recovery studies, the level of MITC detected could be 25% higher for the reported ambient field data.

AIR SAMPLER USED IN MONITORING
OF
METHYL ISOCYANATE AND METHYL ISOTHIOCYANATE



ATTACHMENT II

**FLOW RATE AUDIT PROCEDURES FOR AIR SAMPLERS
USED IN PESTICIDE MONITORING**

Introduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST-traceable flow calibrator. The audit device is connected in series with the sampler's flow meter, and the flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's corrected flow is then compared to the true flow, and a percent difference is determined.

Equipment

The basic equipment required for the air sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST-traceable mass flow meter.
2. Calibrated differential pressure gauge with laminar flow element.
3. 1/4" O.D. Teflon tubing.
4. 1/4", stainless steel, Swagelock fittings.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 VAC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.
2. Connect the inlet port of the audit device to the outlet port of the sampler's flow control valve with a 5 ft. section of Teflon tubing and Swagelock fittings.
3. Connect the outlet port of the audit device to the pump with another 5 ft. section of Teflon tubing and Swagelock fittings.
4. Allow the flow to stabilize for at least 1-2 minutes and record the flow rate indicated by the sampler and the audit device's response.
5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the corrected measured flow rate.

**PERFORMANCE AUDIT PROCEDURES
FOR THE
LABORATORY ANALYSIS OF METHYL ISOCYANATE
AND METHYL ISOTHIOCYANATE**

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory to measure the ambient concentrations and determine if methyl isocyanate (MIC) is a breakdown product of metam sodium's primary breakdown product, methyl isothiocyanate (MITC). The audit is conducted by submitting audit samples spiked with known concentrations of MIC and MITC. The analytical laboratory reports the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Methyl isocyanate at 0.008 ug/ul in Dry Hexane, Chem Service, Analysis Lot #156-78B.
2. Methyl isothiocyanate at 0.015 ug/ul in Carbon Disulfide, Chem Service, Analysis Lot #156-78A.
3. Charcoal Sample Tubes, SKC catalog #226-09, Lot #120.
4. XAD-7 Sample Tubes, SKC catalog #226-97, XAD-7 treated with 1,2-pyridylpiperazine (1,2-PP) supplied by EHLB.

Safety Precautions

Prior to handling any chemical, read the manufacturer's Material Safety Data Sheets (MSDS). Avoid direct physical contact with chemicals. Avoid breathing vapors. Use only under a fume hood. Wear rubber gloves, safety glasses, and protective clothing.

Preparation of Audit Samples

Prepare eleven MITC audit samples and sixteen MIC audit samples by spiking the charcoal sample tubes and the XAD-7 sample tubes treated with 1,2-PP with the volume of MITC and MIC solution indicated in Table 1 and Table 2 below. Using a microsyringe, slowly expel the solution into the sample tubes (primary section of the MITC charcoal tubes), move the syringe so that the solution is applied evenly throughout the sample. Avoid contact of the spiking solution with the tube walls.

Table 1

| Sample ID | MITC Total Spiked, (ug) into Charcoal Tubes | MIC Total Spiked, (ug) into XAD-7 Tubes |
|-----------|---|---|
| MITC-1 | 0.15 | --- |
| MITC-2 | 0.075 | --- |
| MITC-3 | 0.15 | --- |
| MITC-4 | 0.15 | --- |
| MITC-5 | 0.00 | --- |
| MITC-6 | 0.075 | --- |
| MIC-1A | --- | 0.08 |
| MIC-2A | --- | 0.04 |
| MIC-3A | --- | 0.04 |
| MIC-4A | --- | 0.08 |
| MIC-5A | --- | 0.08 |
| MIC-6A | --- | 0.00 |
| MIC-1B | --- | 0.08 |
| MIC-2B | --- | 0.00 |
| MIC-3B | --- | 0.00 |
| MIC-4B | --- | 0.04 |
| MIC-5B | --- | 0.04 |
| MIC-6B | --- | 0.00 |

Table 2

| Sample ID | MITC Total Spiked, (ug) into Charcoal Tubes | MIC Total Spiked, (ug) into XAD-7 Tubes |
|-----------|---|---|
| MITC-1C | 0.00 | --- |
| MITC-2C | 0.075 | --- |
| MITC-3C | 0.075 | --- |
| MITC-4C | 0.15 | --- |
| MITC-5C | 0.15 | --- |
| MIC-1C | --- | 0.2 |
| MIC-2C | --- | 0.2 |
| MIC-3C | --- | 0.08 |
| MIC-4C | --- | 0.4 |

APPENDIX VII
CDFA CONFIRMATION REPORT

DEPARTMENT OF FOOD AND AGRICULTURE

Center for Analytical Chemistry
3292 Meadowview Road
Sacramento, CA 95832



REQUEST FOR MASS SPECTRAL ANALYSIS

(Please Print)

Requester: Don Fitzell Sample (I.D.): 1-8 Commodity: 1-2PP-MIC

Organization (Program): Air Resources Board

Nature of Analysis:

Confirmation on tentative findings; Tentative I.D. 1-2PP-MIC

Identification of Unknown Analytical Response; Mode of Analysis Requested: _____

Mass Spectral Characterization; Compound: _____

Any specific Analysis Request? LC/MS using CN-column-

A column-CN is provided with HPLC chromatogram & conditions

Whole Sample Subsample Extract/Solvent Clean up (Mode) _____

For Confirmation and Identification of Compounds, please attach copies of chromatogram, any spectral information, detailed sample preparation, and chromatographic conditions.

Other Information: _____ Sample Conc: varied

Approved by _____

Date: _____

RESULTS & DISCUSSION

MS Conditions:

GC HPLC DIRECT PROBE DIRECT INFUSION

EI (70 eV) EI _____ eV CI/CH₄ CI/C₂H₁₀ CI/NH₃ CI/ _____

APCI Electrospray Thermospray Gas Analysis FAB/ _____

Resolution: 1000-3000 Range (m/z): SIR or Limit Scan Tune Compound: Caffeine
m/z 100-250

Calib Standard: PEG/Caffeine ISTD: NIL ESTD: ME 1-2PP-MIC

FINDING (Identification or Confirmation): 1-2PP-MIC

Calculated m/z: 221.140236 Observed m/z: 221.1402 Molecular Formula: C₁₁H₁₇ON₄
(m+H) (m+H) (m+H)

Scanned Selected Ion Monitoring Link Scan Neutral Analysis

Analyst: Alce Chung Date: 5/20/96 Reviewer: Mark Lee Date: 5/21/96



Table of Content

- A. HPLC CHROMATOGRAM : 1-2PP-MIC, SAMPLE #8 (1-2PP-MIC + 1-2PP REAGENT), AND SAMPLE #1 (COMPOSITE FIELD SAMPLE)
- B. MASS SPECTRUM OF 1-2PP-MIC STANDARD : DIRECT INFUSION
- C. ACCURATE MASS MEASUREMENT APCI - HPLC/MS : THE PARENT ION OF 1-2PP-MIC (10 ng/ μ L) STANDARD
- D. SINGLE ION REACTION MONITORING (m/z 221.1402) APCI - HPLC/MS : 1-2PP-MIC (5 ng/ μ L) STANDARD AND SOLVENT BLANK
- E. SINGLE ION REACTION MONITORING (m/z 221.1402) APCI - HPLC/MS : SAMPLE #1 (COMPOSITE FIELD SAMPLE) AND SOLVENT BLANK
- F. SINGLE ION REACTION MONITORING (m/z 221.1402) APCI - HPLC/MS : SAMPLE #2 (COMPOSITE FIELD FORTIFICATION)
- G. MULTIPLE IONS REACTION MONITORING (MS/MS) APCI - HPLC/MS/MS : SAMPLE #1 (COMPOSITE FIELD SAMPLE) AND SOLVENT BLANK.

Results and Discussion

- A. HPLC Chromatogram : 1-2PP-MIC, Sample #8 (1-2PP-MIC + 1-2PP Reagent), and Sample #1 (Composite Field Sample)

HPLC conditions were provided by Mario Fracchia and repeated without any change. The observed R_t for pure 1-2PP-MIC is 12.2 min while the sample #8 has four(4) peaks (R_t of 10.6, 12.7, 15.5 and 30.3 min. The chromatogram from Mario indicated that R_t of 1-2PP-MIC to be 15.6 min, an unknown oxidation product of reagent at 12.5 min, and the unreacted reagent at ~ 29 min. The peak at 15.6 min is absent in sample #1 and sample #2 but the both samples contained the peak at 12.8 min. According to the retention time of the pure standard and the subsequent analysis, 1-2PP-MIC elutes around 12 to 13 min and not 15.5 min.

- B. Mass Spectrum of 1-2PP-MIC Standard : Direct Infusion

A direct infusion of sample gave the full EI spectrum of 1-2PP-MIC. The full EI spectrum has three fragment ions: m/z 221 [M^+H], 164 [$C_9H_{14}N_3$]⁺, (Base Peak), and 121. The Base peak represents the derivatizing agent, 1-(2-pyridyl)piperazine.

- C. Accurate Mass Measurement APCI- HPLC/MS : the Parent Ion of 1-2PP-MIC (10 ng/ μ L) Standard

An experiment was carried out to determine the accurate mass of m/z 221 when a sample was introduced via HPLC with APCI interface. The experimental values of the parent and base ions are 221.1520 and 163.6543, respectively while the corresponding calculated values are 221.140236 and 163.110948. The experimental values of these two ions matched to their theoretical values. This experiment demonstrated that the LC/MS is properly calibrated and we were observing the correct fragment ions. The retention time of the parent ion is at 12.4 min.

- D. Single Ion Reaction Monitoring (m/z 221.1402) APCI- HPLC/MS : 1-2PP-MIC (5 ng/ μ L) Standard and Solvent Blank

The parent ion (m/z 221.1402) of 1-2PP-MIC was monitored at 3000 resolution via APCI, LC/MS. An injection of 20 μ L 1-2PP-MIC standard (5 ng/ μ L) gave a peak well distinguished from background noise at the anticipated retention time of 12.2 min. An analysis of solvent blank showed no detectable peak around the anticipated retention time range.

E. Single Ion Reaction Monitoring (m/z 221.1402) APCI - HPLC/MS : Sample #1
(Composite Field Sample) and Solvent Blank

Under the same condition as the Section D, there was not any distinguishable peak (m/z 221.1402) around the anticipated retention time (12 - 13 min) although a hump is present.

F. Single Ion Reaction Monitoring (m/z 221.1402) APCI- HPLC/MS : Sample #2
(Composite Field Fortification)

The sample #2 was analyzed under the same conditions as the Section D. The sample #2 which is a field spike sample with a higher concentration of 1-2PP-MIC showed a well distinguished peak at R_t 12.4 min. A solvent blank did not contain any peak.

G. Multiple Ions Reaction Monitoring (MS/MS) APCI - HPLC/MS/MS : Sample #1
(Composite Field Sample) and Solvent Blank.

To further clarify the hump detected in the Sample #1, a tandem mass spectrometric experiment was conducted. The first MS (magnetic sector) was set at an accurate mass of 221.1402 to act as a mass filter while the second MS (quadrupole) was set to monitor the daughter ions of 1-2PP-MIC (m/z 221 and 165). The Sample #1 showed well distinguished daughter ion peaks at the retention time of 12.4 min.

Conclusion

HPLC/MS analyses of 1-2PP-MIC, field spike sample and the field sample (Sample #1) indicated a positive presence of 1-(2-pyridyl) piperazine derivative of methyl isocyanate. The correct retention time for 1-2PP-MIC appears to be 12.2-12.4 min and not 15.6 min as suggested. We did not make any attempt to quantify the analyte of interest since it was outside of this study's scope.



S. Mark Lee, Ph.D.
Research Agricultural Chemist

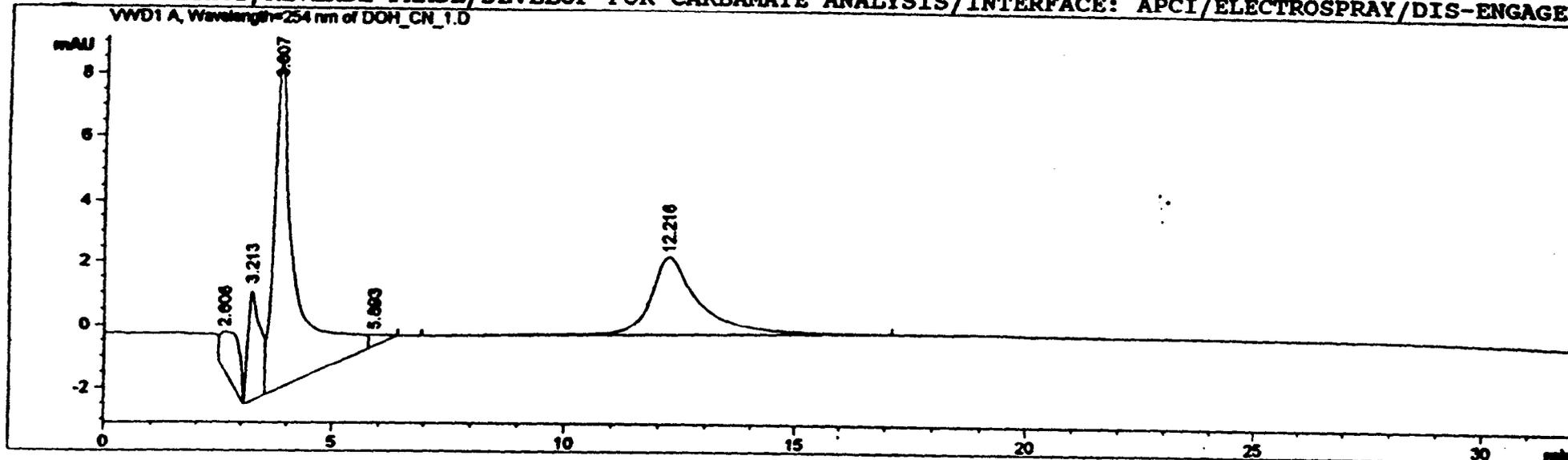
May 22, 1996

DEPT OF HEALTH 1,2-PP-MIC/20UL INJ ISOCALATIC/ ACN(15) :
WATER(85):NH4Ac(.8gm/L)/pH=6.1-6.5/CN 240 X 4.5 mm COLU
MN/LAMDA=254nm/LC RATE=1.0/MIN

109

| | | | |
|----------------|----------------------|------------|-----------|
| Acq. Method | : ACX_LCMS.M | Seq. Line | : - |
| Acq. Operator | : ACC | Vial | : 1 |
| Injection Date | : 5/7/96 10:10:07 AM | Inj | : - |
| Sample Name | : 1,2-pp-mic/5NG | Inj Volume | : Unknown |

Analysis Method : C:\HPCHEM\1\METHODS\ACX_LCMS.M
ACX LCMS METHOD/REVERSE PHASE/DEVELOP FOR CARBAMATE ANALYSIS/INTERFACE: APCI/ELECTROSPRAY/DIS-ENGAGED



Area Percent Report

Sorted by Signal
Multiplier : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RT [min] | Type | Width [min] | Area [mAU*sec] | Height [mAU] | Area t |
|----------|----------|------|-------------|----------------|--------------|---------|
| 1 | 2.608 | VV | 0.448 | 43.88736 | 1.23490 | 6.8009 |
| 2 | 3.213 | PV | 0.248 | 64.02580 | 3.56468 | 9.9215 |
| 3 | 3.807 | VV | 0.426 | 339.99466 | 10.69508 | 52.6861 |
| 4 | 5.893 | VB | 0.400 | 8.66835 | 3.61254e-1 | 1.3433 |
| 5 | 12.216 | BV | 1.060 | 188.74518 | 2.46047 | 29.2482 |
| Totals : | | | | 645.32135 | 18.31639 | |

*** End of Report ***

110

DEPT OF HEALTH 1,2-PP-MIC/10NG/UL/20UL INJ ISOCLATIC/ A
CN(15) :WATER(85):NH4Ac(.8gm/L)/pH=6.1-6.5/CN 240 X 4.5
mm COLUMN/LAMDA=254nm/LC RATE=1.0/MIN

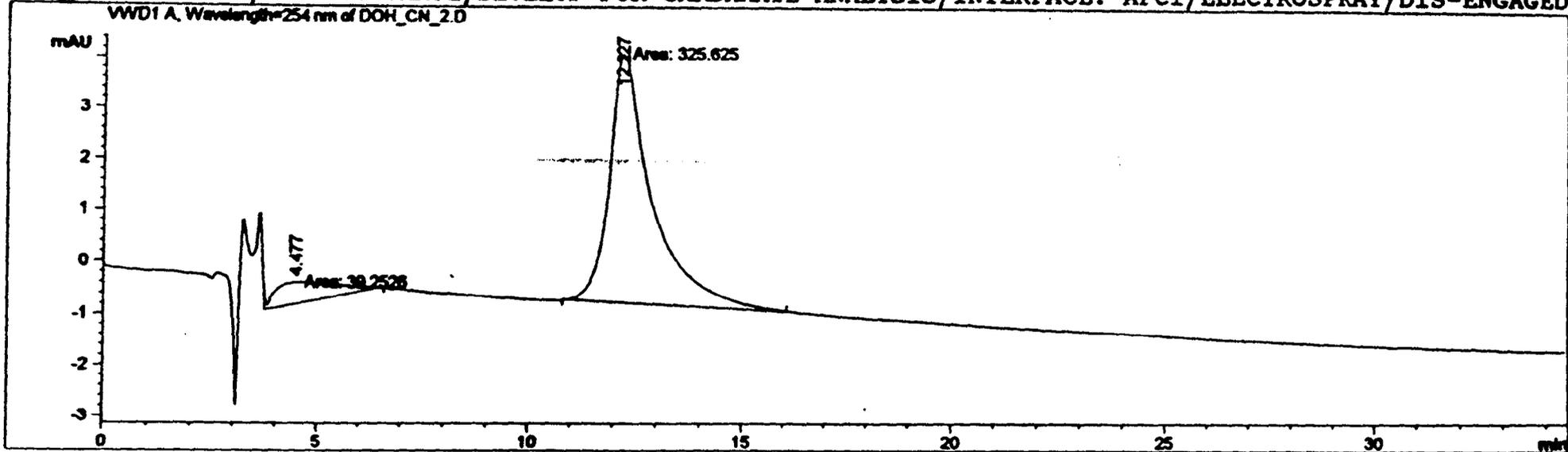
111

```

=====
Acq. Method      : ACX_LCMS.M                      Seq. Line : -
Acq. Operator    : ACC                            Vial      : 1
Injection Date   : 5/7/96 10:44:23 AM             Inj       : -
Sample Name      : 1,2-pp-mic/10NG                Inj Volume: Unknown
=====

```

Analysis Method : C:\HPCHEM\1\METHODS\ACX_LCMS.M
 ACX LCMS METHOD/REVERSE PHASE/DEVELOP FOR CARBAMATE ANALYSIS/INTERFACE: APCI/ELECTROSPRAY/DIS-ENGAGED



=====
 Area Percent Report
 =====

Sorted by Signal
 Multiplier : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RT [min] | Type | Width [min] | Area [mAU*sec] | Height [mAU] | Area % |
|----------|----------|------|-------------|----------------|--------------|---------|
| 1 | 4.477 | MM | 1.600 | 39.25262 | 4.08877e-1 | 10.7577 |
| 2 | 12.227 | MM | 1.120 | 325.62503 | 4.84729 | 89.2423 |
| Totals : | | | | 364.87766 | 5.25617 | |

*** End of Report ***

DEPT OF HEALTH SAMPLE 8/1:1 DIL(S/B 5NG 1,2PP-MIC)/20UL
INJ ISOCALATIC/ ACN(15) :WATER(85):NH4Ac(.8gm/L)/pH=6.1
-6.5/CN 240 X 4.5 mm COLUMN/LAMDA=254nm/LC RATE=1.0/MIN

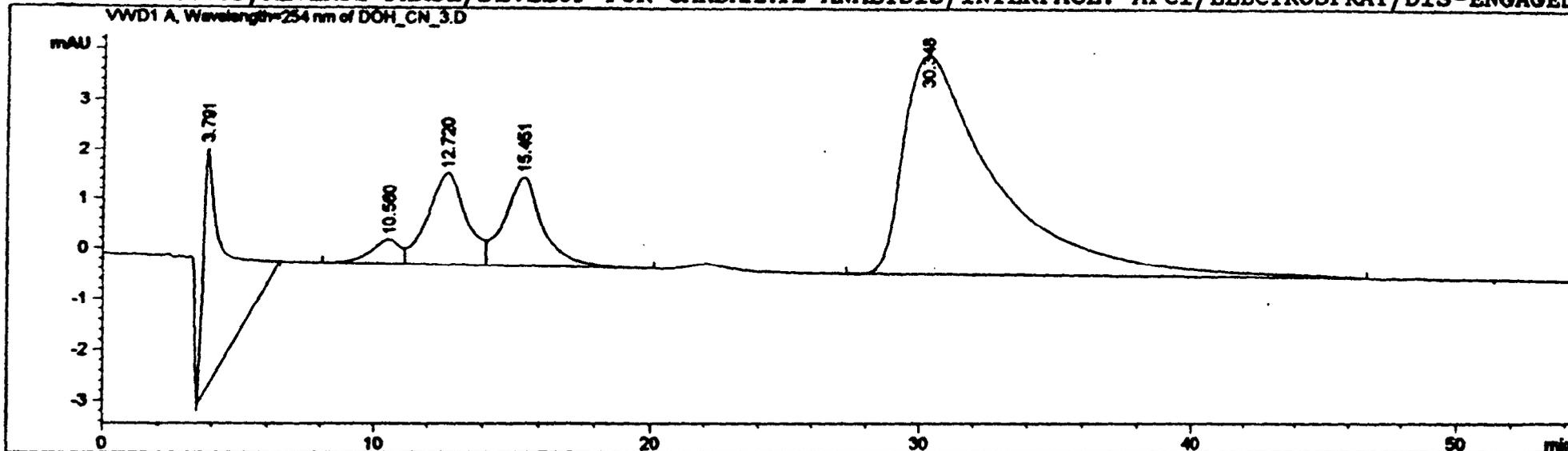
113

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=====
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Acq. Operator    : ACC                               Vial      : 1
Injection Date   : 5/7/96 11:22:03 AM              Inj       : -
Sample Name      : SAMPLE 8                         Inj Volume: Unknown
=====

```

Analysis Method : C:\HPCHEM\1\METHODS\ACX_LCMS.M
ACX_LCMS METHOD/REVERSE PHASE/DEVELOP FOR CARBAMATE ANALYSIS/INTERFACE: APCI/ELECTROSPRAY/DIS-ENGAGED



Area Percent Report

Sorted by Signal
Multiplier : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RT [min] | Type | Width [min] | Area [nAU*sec] | Height [nAU] | Area % |
|----------|----------|------|-------------|----------------|--------------|---------|
| 1 | 3.791 | PB | 0.751 | 286.29871 | 4.79800 | 16.6192 |
| 2 | 10.560 | BV | 1.018 | 35.85710 | 4.82567e-1 | 2.0814 |
| 3 | 12.720 | VV | 1.395 | 178.51314 | 1.84632 | 10.3624 |
| 4 | 15.451 | VB | 1.369 | 168.66745 | 1.78593 | 9.7909 |
| 5 | 30.348 | BB | 3.350 | 1053.36548 | 4.39256 | 61.1461 |
| Totals : | | | | 1722.70190 | 13.30538 | |

*** End of Report ***

DEPT OF HEALTH/SAMPLE 1/20UL INJ ISOCALATIC/ ACN(15) :WA
TER(85):NH4Ac(.8gm/L)/pH=6.1-6.5/CN 240 X 4.5 mm COLUMN
/LAMDA=254nm/LC RATE=1.0/MIN

117

```

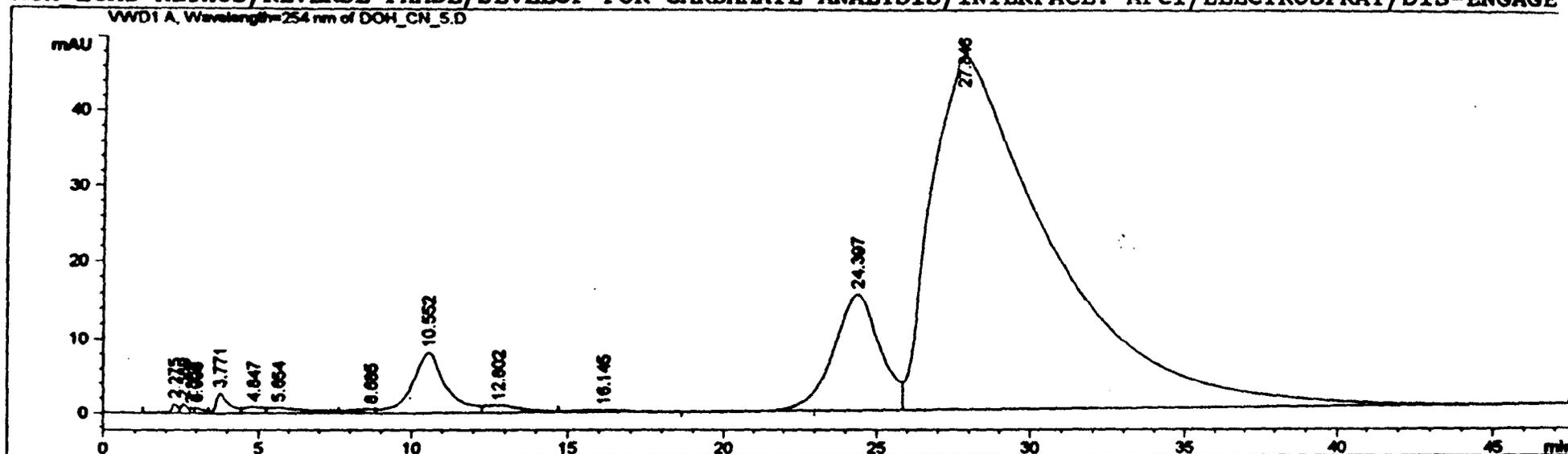
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Acq. Method      : ACX_LCMS.M                      Seq. Line : -
Acq. Operator    : ACC                            Vial      : 1
Injection Date   : 5/7/96 2:19:40 PM              Inj       : -
Sample Name      : SAMPLE 1                       Inj Volume: Unknown
=====

```

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Analysis Method : C:\HPCHEM\1\METHODS\ACX_LCMS.M
ACX LCMS METHOD/REVERSE PHASE/DEVELOP FOR CARBAMATE ANALYSIS/INTERFACE: APCI/ELECTROSPRAY/DIS-ENGAGE
=====

```



```

=====
Area Percent Report
=====

```

```

Sorted by Signal
Multiplier      :      1.000000

```

Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RT [min] | Type | Width [min] | Area [mAU*sec] | Height [mAU] | Area % |
|----------|----------|------|-------------|----------------|--------------|---------|
| 1 | 2.275 | BV | 0.222 | 20.71617 | 1.29306 | 0.1330 |
| 2 | 2.589 | VV | 0.208 | 19.30731 | 1.32825 | 0.1240 |
| 3 | 2.852 | VV | 0.135 | 5.89657 | 7.30212e-1 | 0.0379 |
| 4 | 3.003 | VV | 0.328 | 15.08941 | 7.66414e-1 | 0.0969 |
| 5 | 3.771 | PV | 0.376 | 77.89178 | 2.81093 | 0.5002 |
| 6 | 4.847 | VV | 0.590 | 40.98449 | 9.36924e-1 | 0.2632 |
| 7 | 5.654 | VV | 1.185 | 79.17915 | 8.17719e-1 | 0.5084 |
| 8 | 8.685 | VV | 0.735 | 33.52475 | 5.59172e-1 | 0.2153 |
| 9 | 10.552 | VV | 1.072 | 625.52777 | 8.24149 | 4.0166 |
| 10 | 12.802 | VV | 1.255 | 92.35477 | 1.03875 | 0.5930 |
| 11 | 16.145 | VV | 1.583 | 41.58356 | 3.26283e-1 | 0.2670 |
| 12 | 24.397 | PV | 1.590 | 1662.73901 | 15.64039 | 10.6767 |
| 13 | 27.846 | VB | 3.588 | 12858.71289 | 47.27868 | 82.5679 |
| Totals : | | | | 15573.50781 | 81.76827 | |

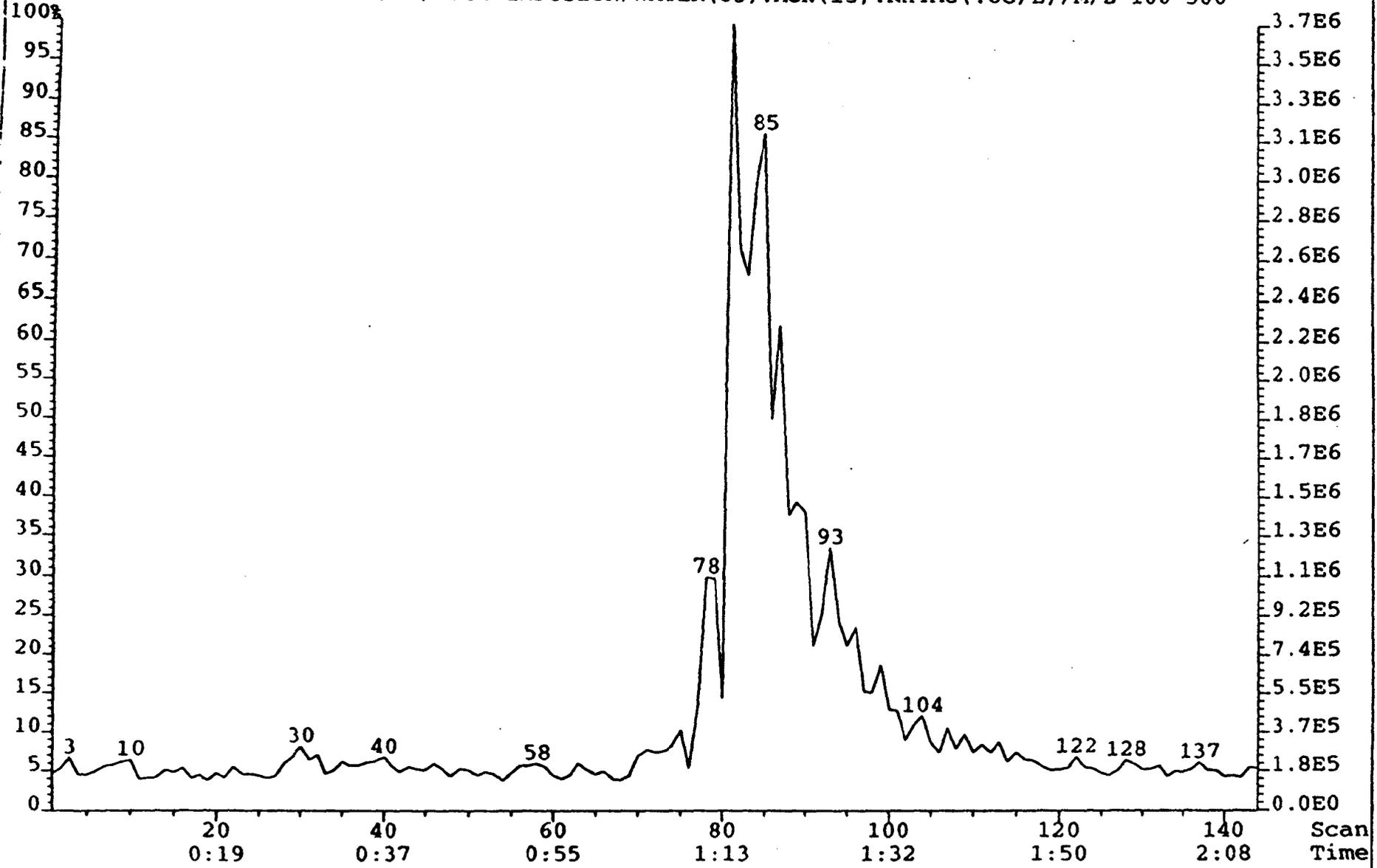
=====
 *** End of Report ***

Experiment: ACX_MAGNET (1 Functions)

Operator : User
Date : 9-MAY-1996 07:52:52
Instrument : Autospec-UltimaEQ

Function 1
Type : Magnet
Calibration file used : PEG100_500H
High mass : 500.0
Low mass : 100.0
Resolution : 1000
Time (s/dec) : 1.12
Delay (secs) : 0.12
Ionisation mode : API+
Accelerating Voltage : 4000.0V
Magnet 1 control : Current
Start Time : 0:00
End Time : 120:00
Data type : Continuum

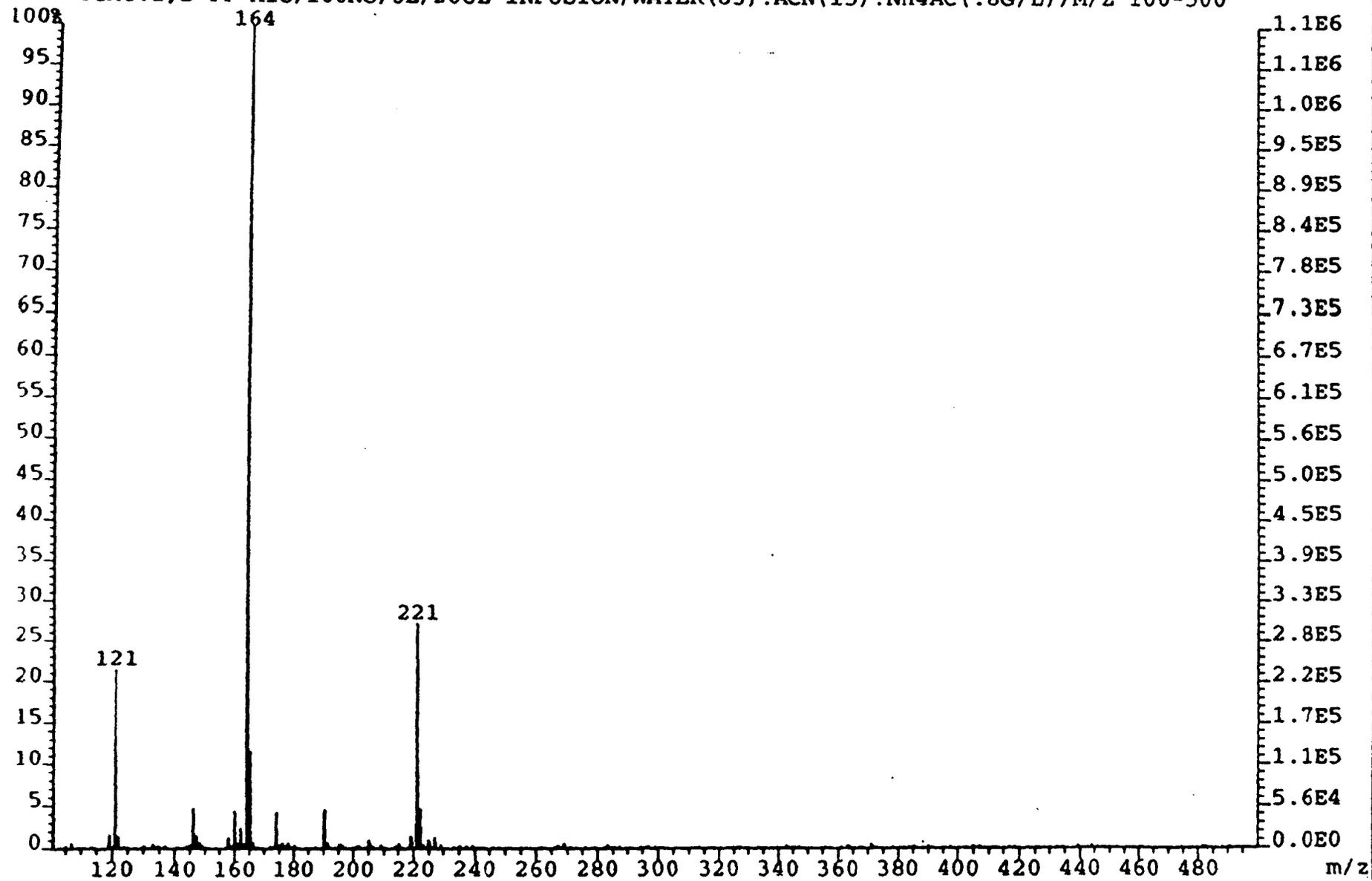
File:DOH12PPMIC_A #1-144 Acq: 9-MAY-1996 07:55:31 Septum API+ Magnet Autospec-UltimaEQ
TIC (+RP) Exp:ACX_MAGNET
File Text:1,2-PP-MIC/100NG/UL/20UL INFUSION/WATER(85):ACN(15):NH4AC(.8G/L)/M/Z 100-500



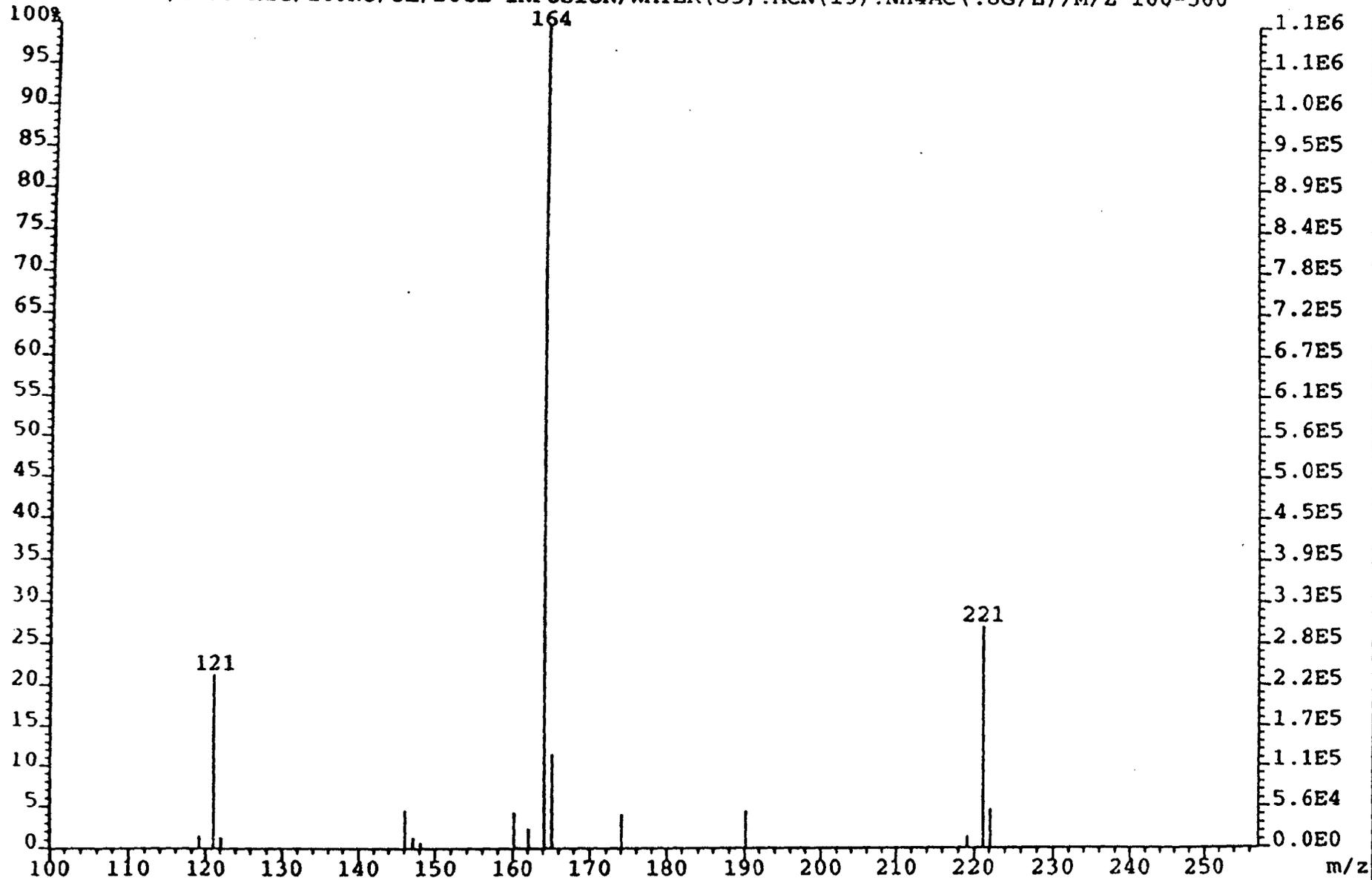
File:DOH12PPMIC_A Ident:77_103-47_62-113_124 Acq: 9-MAY-1996 07:55:31 +1:53 Cal:PEG100_500H

Autospec-UltimaEQ API+ Magnet BpI:1115973 TIC:31679336

File Text:1,2-PP-MIC/100NG/UL/20UL INFUSION/WATER(85):ACN(15):NH4AC(.8G/L)/M/Z 100-500



File:DOH12PPMIC_A Ident:77_103-47_62-113_124 PKD(9,4,9,0.50%,0.0,0.00%,F,F) SPEC(Heights, Centro»
Autospec-UltimaEQ API+ Magnet BpI:1115973 TIC:31679336 Flags:NORM
File Text:1,2-PP-MIC/100NG/UL/20UL INFUSION/WATER(85):ACN(15):NH4AC(.8G/L)/M/Z 100-500



Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RT [min] | Type | Width [min] | Area [mAU*sec] | Height [mAU] | Area % |
|----------|----------|------|-------------|----------------|--------------|---------|
| 1 | 3.231 | PV | 0.254 | 103.30537 | 5.77138 | 9.8847 |
| 2 | 3.591 | VV | 0.244 | 112.20395 | 6.28061 | 10.7362 |
| 3 | 4.794 | VB | 1.342 | 191.82225 | 1.73048 | 18.3544 |
| 4 | 12.463 | BV | 1.029 | 625.26208 | 8.35349 | 59.8277 |
| 5 | 16.315 | VB | 1.127 | 12.51028 | 1.85047e-1 | 1.1970 |
| Totals : | | | | 1045.10388 | 22.32101 | |

*** End of Report ***

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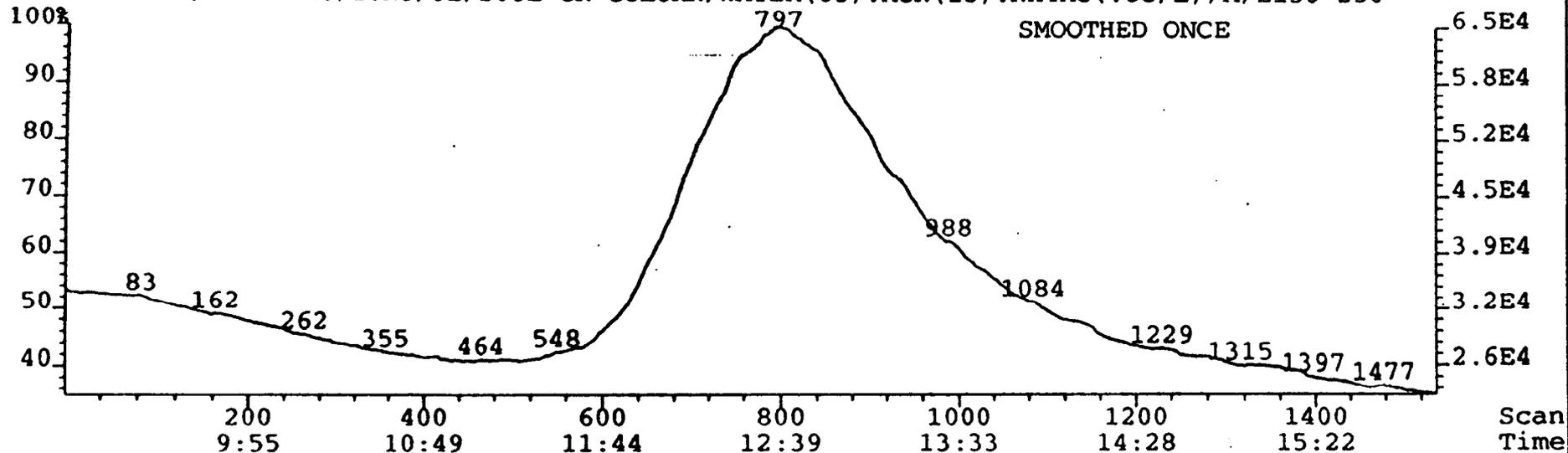
Experiment: ACX_MAGNET (1 Functions)

Operator : User
Date : 9-MAY-1996 10:10:35
Instrument : Autospec-UltimaEQ

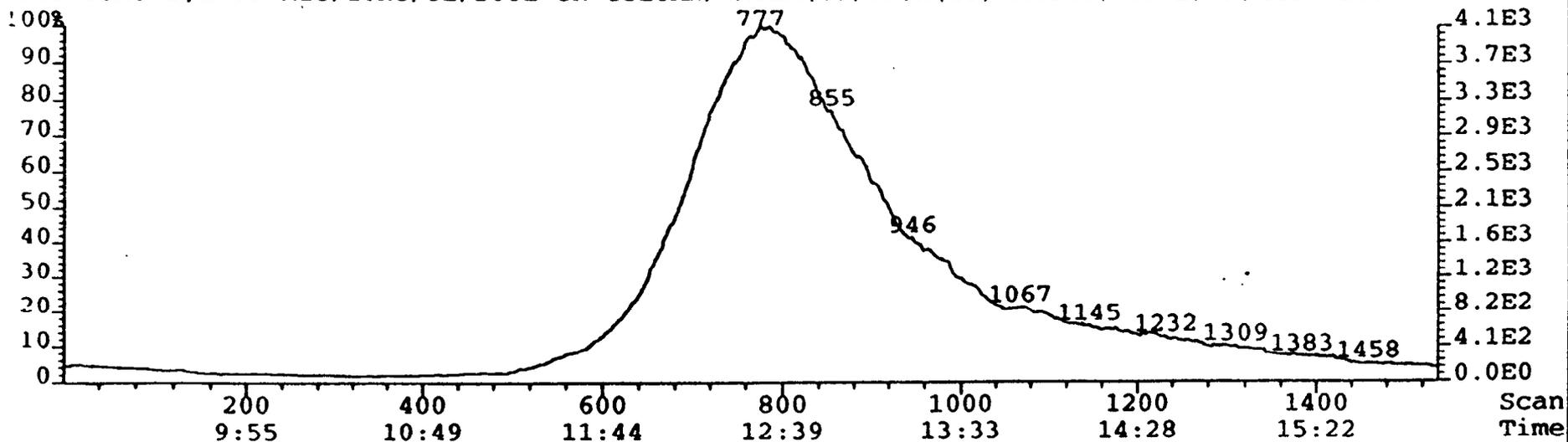
Function 1

Type : Magnet
Calibration file used : PEG100_500H
High mass : 250.0
Low mass : 150.0
Resolution : 1000
Time (s/dec) : 0.85
Delay (secs) : 0.08
Ionisation mode : API+
Accelerating Voltage : 4000.0V
Magnet 1 control : Current
Start Time : 9:00
End Time : 120:00
Data type : Continuum

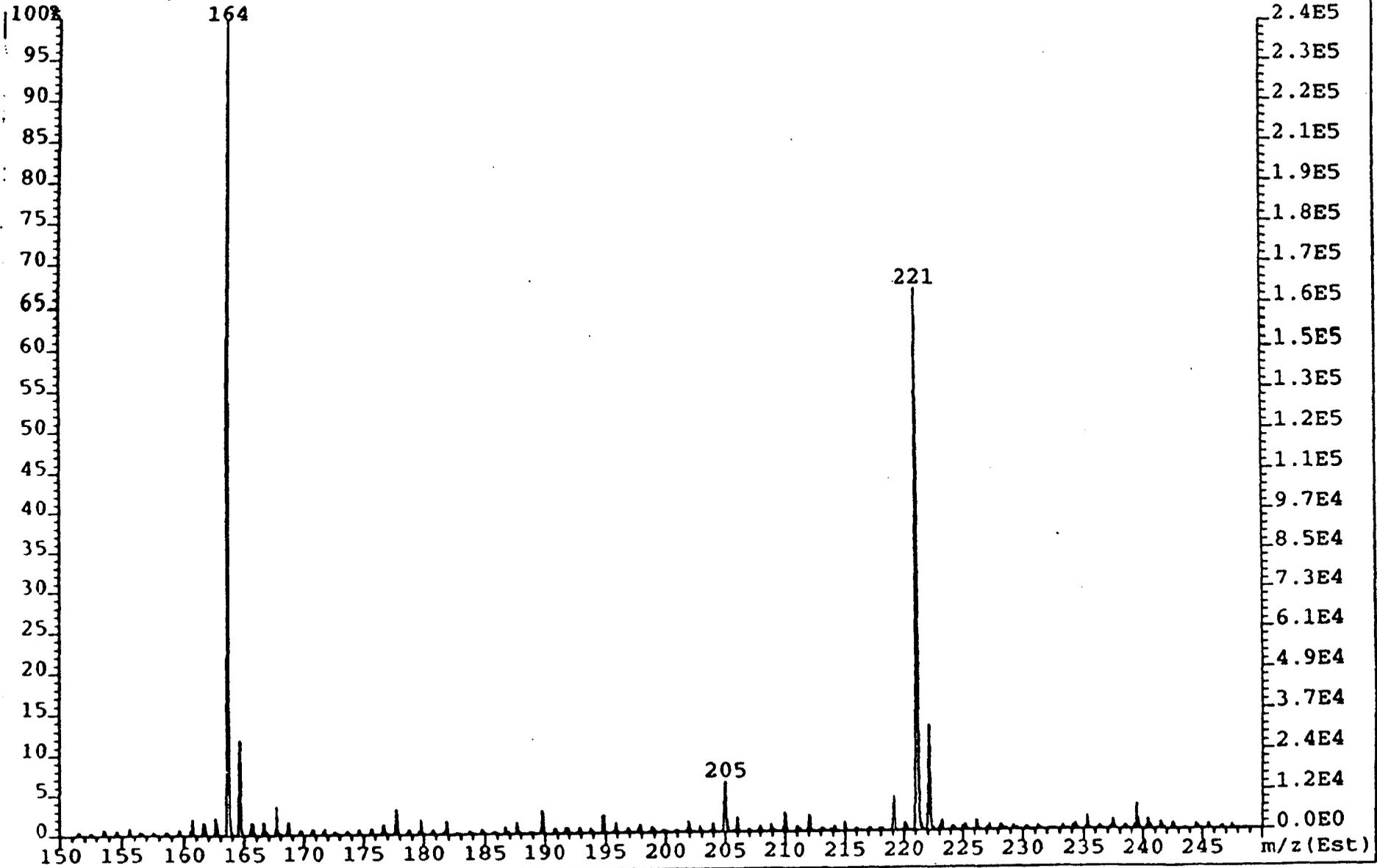
File:DOH_CN_8 #1-1537 Acq: 9-MAY-1996 10:24:02 Septum API+ Magnet Autospec-UltimaEQ
FIC (+RP) SMO(1,165) Exp:ACX_MAGNET
File Text:1,2-PP-MIC/10NG/UL/20UL CN-COLUMN/WATER(85):ACN(15):NH4AC(.8G/L)/M/Z150-250



File:DOH_CN_8 #1-1537 Acq: 9-MAY-1996 10:24:02 Septum API+ Magnet Autospec-UltimaEQ
21 Win 1000PPM SMO(1,137) Exp:ACX_MAGNET
File Text:1,2-PP-MIC/10NG/UL/20UL CN-COLUMN/WATER(85):ACN(15):NH4AC(.8G/L)/M/Z150-250



File: DOH_CN_8 Ident: 698_896-434_515-1016_1035 Acq: 9-MAY-1996 10:24:02 +13:43 Cal: PEG100_500H(n)
Autospec-UltimaEQ API+ Magnet BpI: 243574 TIC: 8089223
File Text: 1,2-PP-MIC/10NG/UL/20UL CN-COLUMN/WATER(85):ACN(15):NH4AC(.8G/L)/M/Z150-250



```

: Listing of raw data for
: data file DCH_CN_8
: data ident 698_896-134_516-1016-1035 FNDU7.4.7.0.50X,0.0.0.00X,F,F) SPRO(Heights, Centroid)
: Axis display range X_MASS (150.00, 250.00)
: Normalising intensity 2.43035E+05 at buffer index 1
: Data threshold 2.00X of normalising intensity

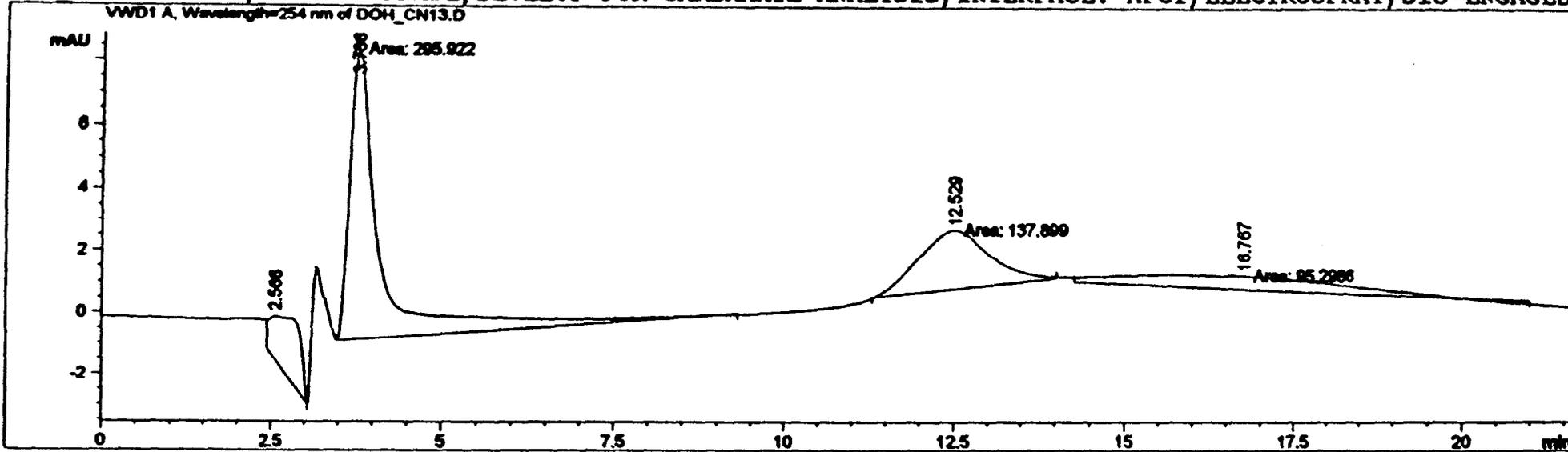
```

| MASS | TIME | ABS HEIGHT | REL HEIGHT(%) | FLAGS |
|----------|-----------|-------------|---------------|-------|
| 163.6543 | 8934.0166 | 2.43035E+05 | 100.00 | |
| 164.6620 | 8804.5781 | 2.85554E+04 | 11.75 | |
| 177.7112 | 7196.4985 | 7.68827E+03 | 3.16 | |
| 204.9776 | 4186.7324 | 1.52181E+04 | 6.26 | |
| 219.0773 | 3784.0471 | 1.02919E+04 | 4.23 | |
| 221.1520 | 2585.2996 | 1.61996E+05 | 66.66 | |
| 222.1729 | 2488.1897 | 3.16005E+04 | 13.00 | |

DEPT OF HEALTH/1,2-PP-MIC/5NG/UL/20UL INJ ISOCLATIC[ABS
=20NG]/ ACN(15) :WATER(85):NH4Ac(.8gm/L)/pH=6.1-6.5/CN
240 X 4.5 mm COLUMN/LAMDA=254nm/LC RATE=1.0/MIN/SIR/RP=
3000

Acq. Method : ACX_LCMS.M Seq. Line : -
Acq. Operator : ACC Vial : 1
Injection Date : 5/10/96 7:12:14 AM Inj : -
Sample Name : DOH/12PP-MIC/5NG Inj Volume : Unknown

Analysis Method : C:\HPCHEM\1\METHODS\ACX_LCMS.M
ACX_LCMS METHOD/REVERSE PHASE/DEVELOP FOR CARBAMATE ANALYSIS/INTERFACE: APCI/ELECTROSPRAY/DIS-ENGAGED



Area Percent Report

Sorted by Signal
Multiplier : 1.000000

Experiment: AMX_SIR_VOLT_JK (1 Functions)

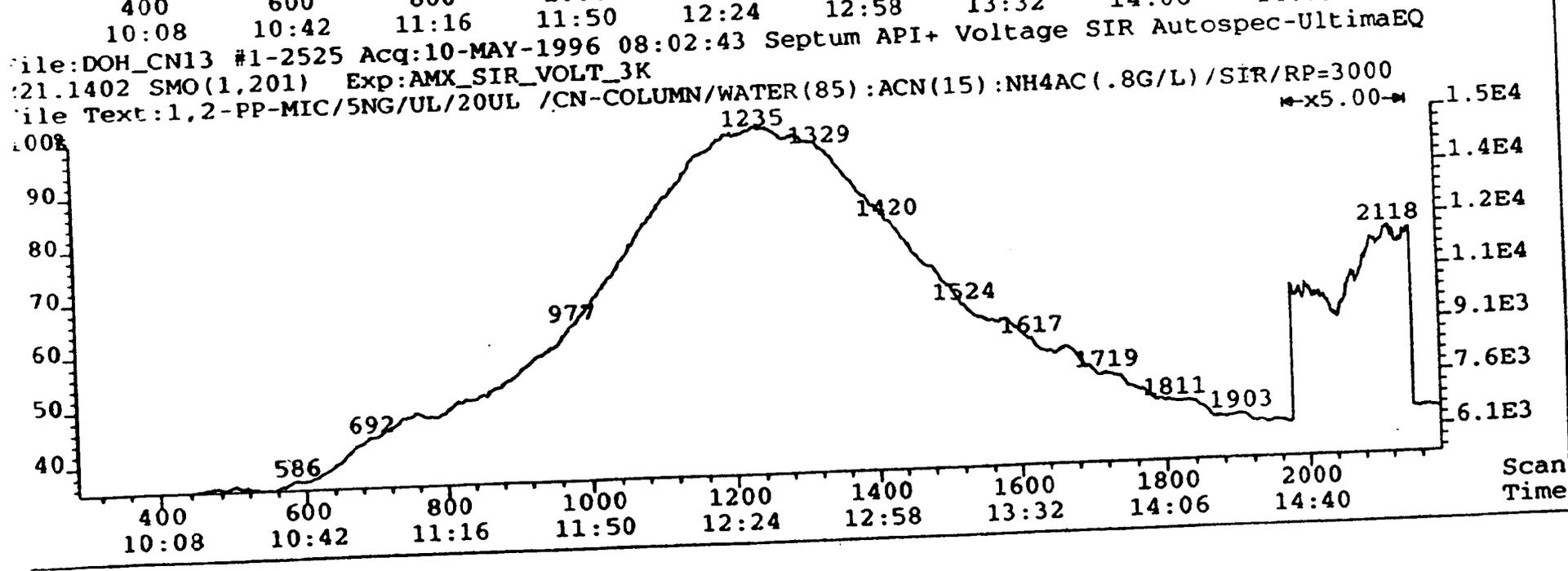
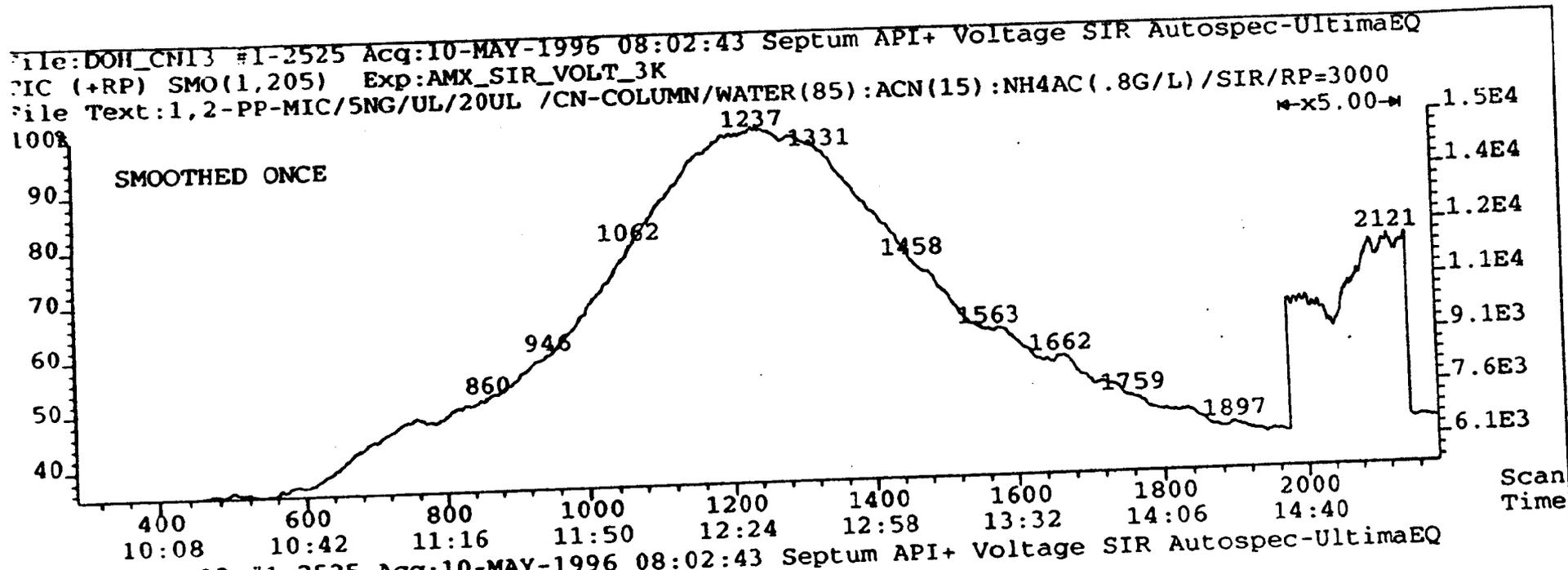
 Operator : User
 Date : 10-MAY-1996 08:02:26
 Instrument : Autospec-UltimaEQ

Function 1

Type : SIR Voltage
 Calibration file used : DOH_CN13_1
 High mass : 239.1
 Low mass : 221.1
 Resolution : 3000
 Ionisation mode : API+
 Accelerating Voltage : 4000.0V
 Magnet 1 control : Current
 Start Time : 9:00
 End Time : 120:00
 Fast lock : On
 Number of channels : 2
 Cycle time (ms) : 160

| Channel | Mass | Ch Time (ms) | I/ch Time (ms) |
|----------|----------|--------------|----------------|
| 1 | 221.1402 | 80 | 20 |
| 2 (Lock) | 239.1495 | 40 | 20 |

Primary Span Lock (Peaks) 2.00
 Secondary Span Lock (Peaks) 2.00
 Lock Level (mV) 0
 Step Lock (Peaks) 0.020



Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RT [min] | Type | Width [min] | Area [MAU*sec] | Height [MAU] | Area % |
|--------|----------|------|-------------|----------------|--------------|----------|
| 1 | 3.789 | PV | 0.489 | 189.67567 | 5.11729 | 100.0000 |

Totals : 189.67567 5.11729

=====
 *** End of Report ***

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Experiment: AMX_SIR_VOLT_3K (1 Functions)

Operator : User
Date : 10-MAY-1996 10:24:43
Instrument : Autospec-UltimaEQ

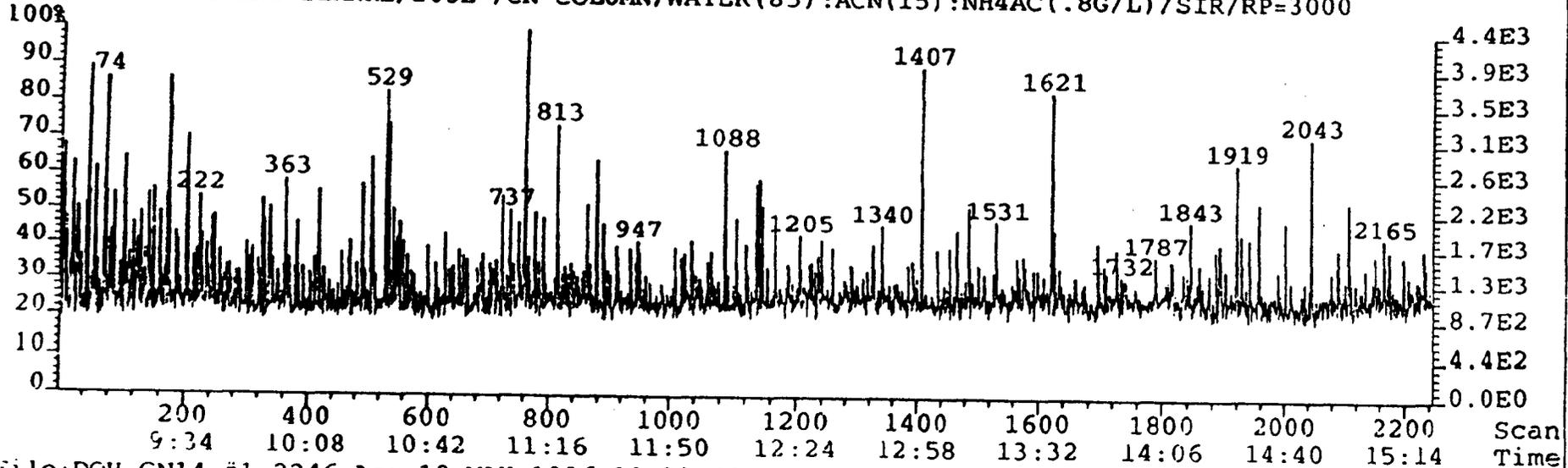
Function 1

Type : SIR Voltage
Calibration file used : DOH_CN13_1
High mass : 239.1
Low mass : 221.1
Resolution : 3000
Ionisation mode : API+
Accelerating Voltage : 4000.0V
Magnet 1 control : Current
Start Time : 9:00
End Time : 120:00
Fast lock : On
Number of channels : 2
Cycle time (ms) : 160

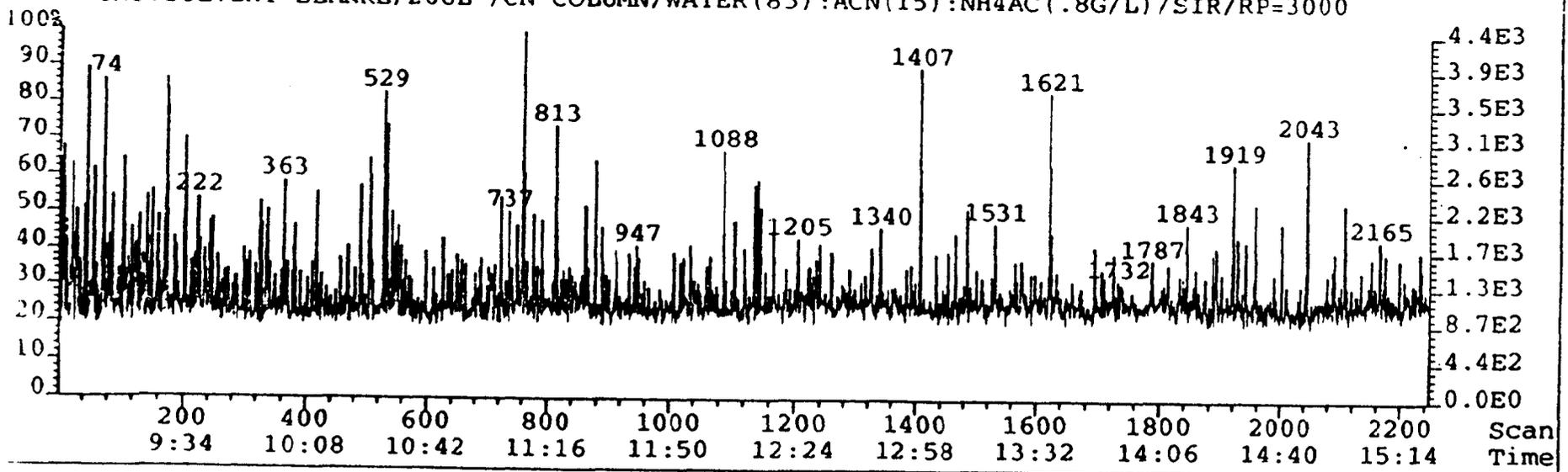
| Channel | Mass | Ch Time (ms) | I/ch Time (ms) |
|----------|----------|-----------------|-------------------|
| 1 | 221.1402 | 80 | 20 |
| 2 (Lock) | 239.1495 | 40 | 20 |

Primary Span Lock (Peaks) 2.00
Secondary Span Lock (Peaks) 2.00
Lock Level (mV) 0
Step Lock (Peaks) 0.020
Repeats : 1

File:DOH_CN14 #1-2246 Acq:10-MAY-1996 10:29:41 Septum API+ Voltage SIR Autospec-UltimaEQ
FIC (+RP) Exp:AMX_SIR_VOLT_3K
File Text:SOLVENT BLANKL/20UL /CN-COLUMN/WATER(85):ACN(15):NH4AC(.8G/L)/SIR/RP=3000



File:DOH_CN14 #1-2246 Acq:10-MAY-1996 10:29:41 Septum API+ Voltage SIR Autospec-UltimaEQ
21.1402 Exp:AMX_SIR_VOLT_3K
File Text:SOLVENT BLANKL/20UL /CN-COLUMN/WATER(85):ACN(15):NH4AC(.8G/L)/SIR/RP=3000

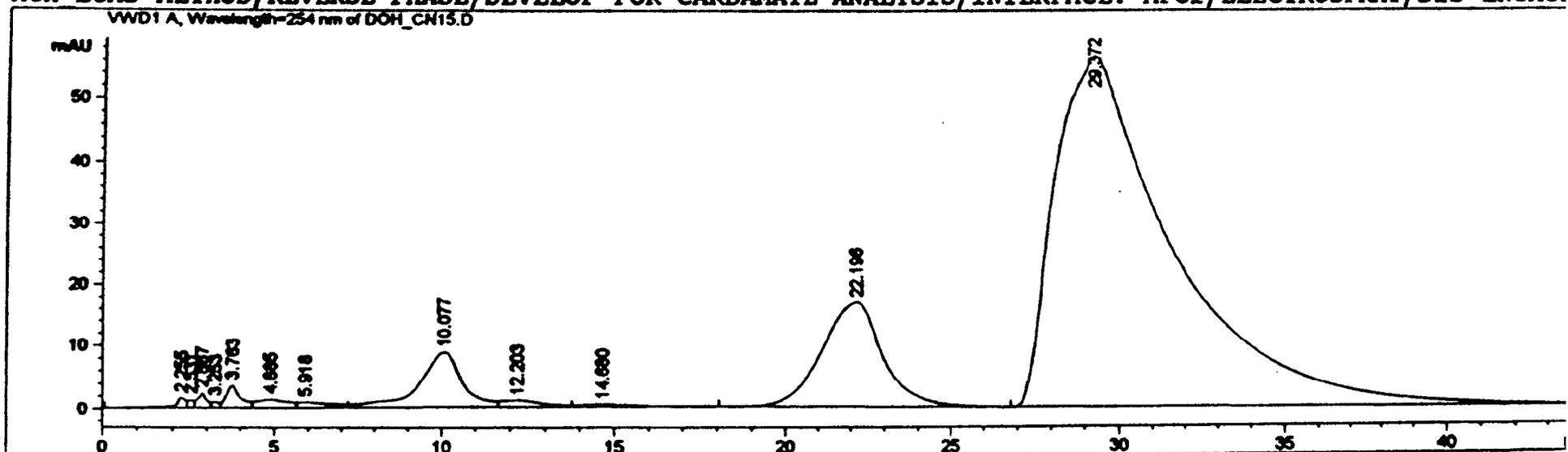


DEPT OF HEALTH/SAMPLE-1/20UL INJ ISOCALATIC/ ACN(15) :WA
TER(85):NH4Ac(.8gm/L)/pH=6.1-6.5/CN 240 X 4.5 mm COLUMN
/LAMBDA=254nm/LC RATE=1.0/MIN/SIR/RP=3000

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Acq. Method : ACX_LCMS.M Seq. Line : -
Acq. Operator : ACC Vial : 1
Injection Date : 5/10/96 9:58:05 AM Inj : -
Sample Name : DOH/SAMPLE 1/SIR Inj Volume : Unknown

Analysis Method : C:\HPCHEM\1\METHODS\ACX_LCMS.M
ACX_LCMS_METHOD/REVERSE PHASE/DEVELOP FOR CARBAMATE ANALYSIS/INTERFACE: APCI/ELECTROSPRAY/DIS-ENGAGE



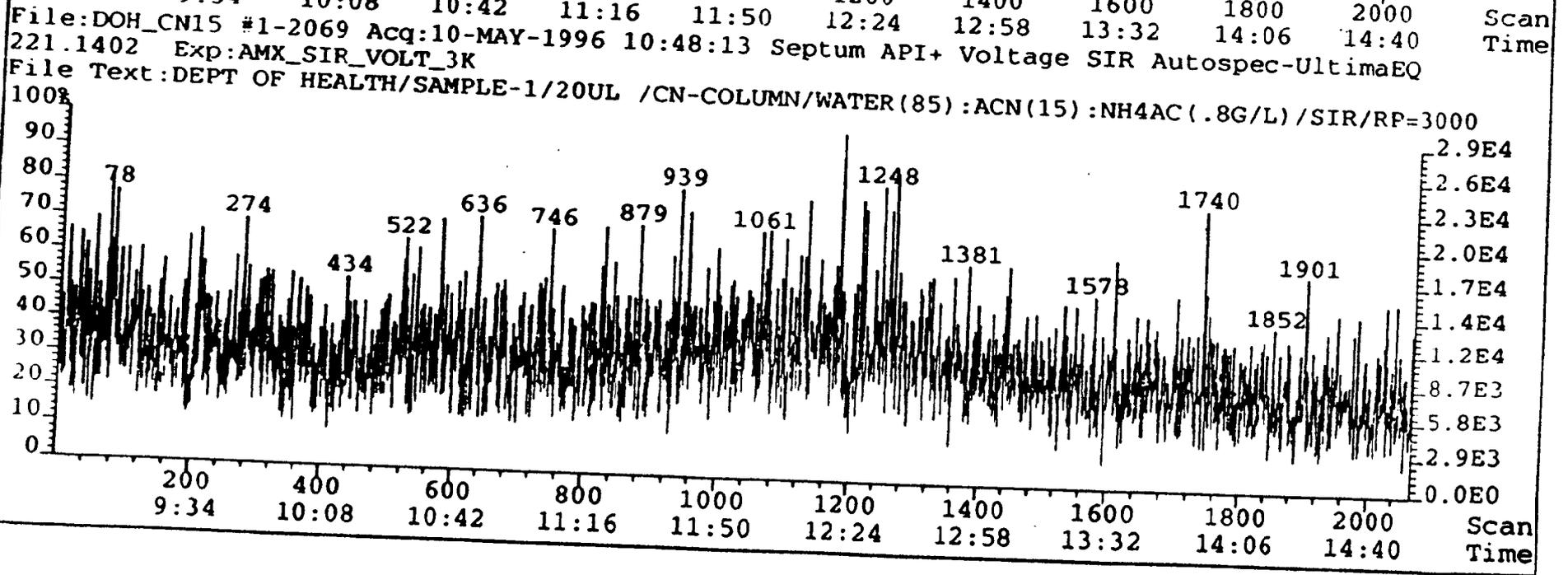
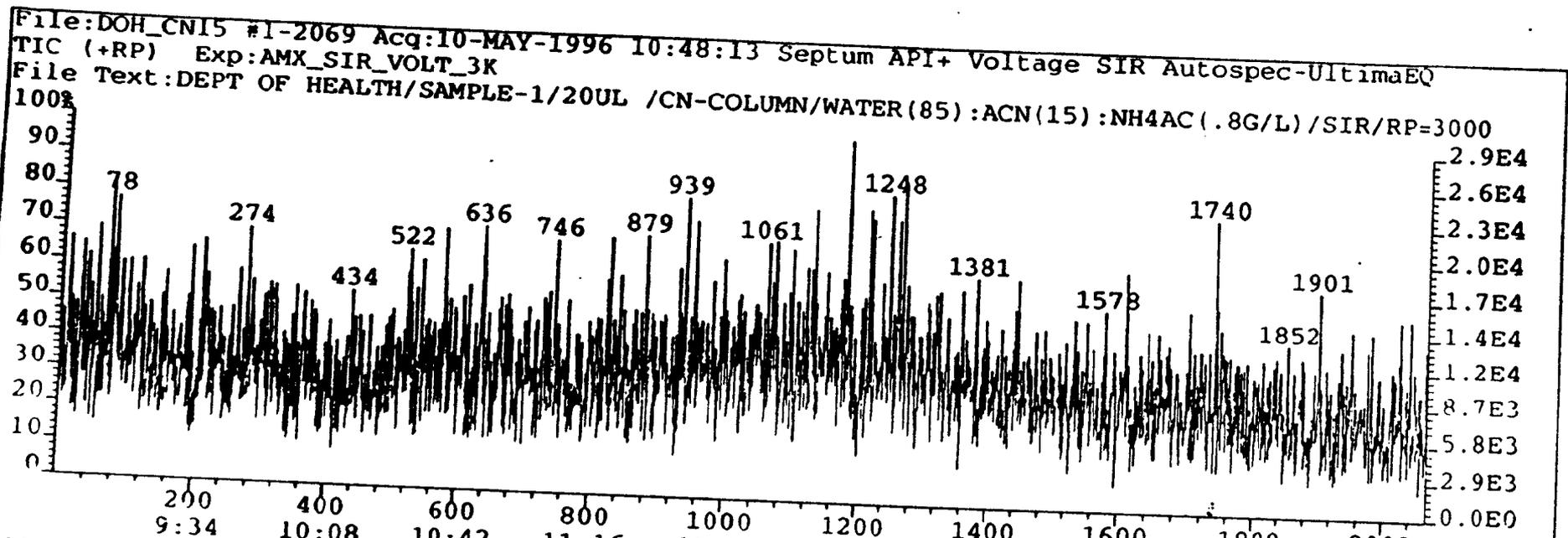
Area Percent Report

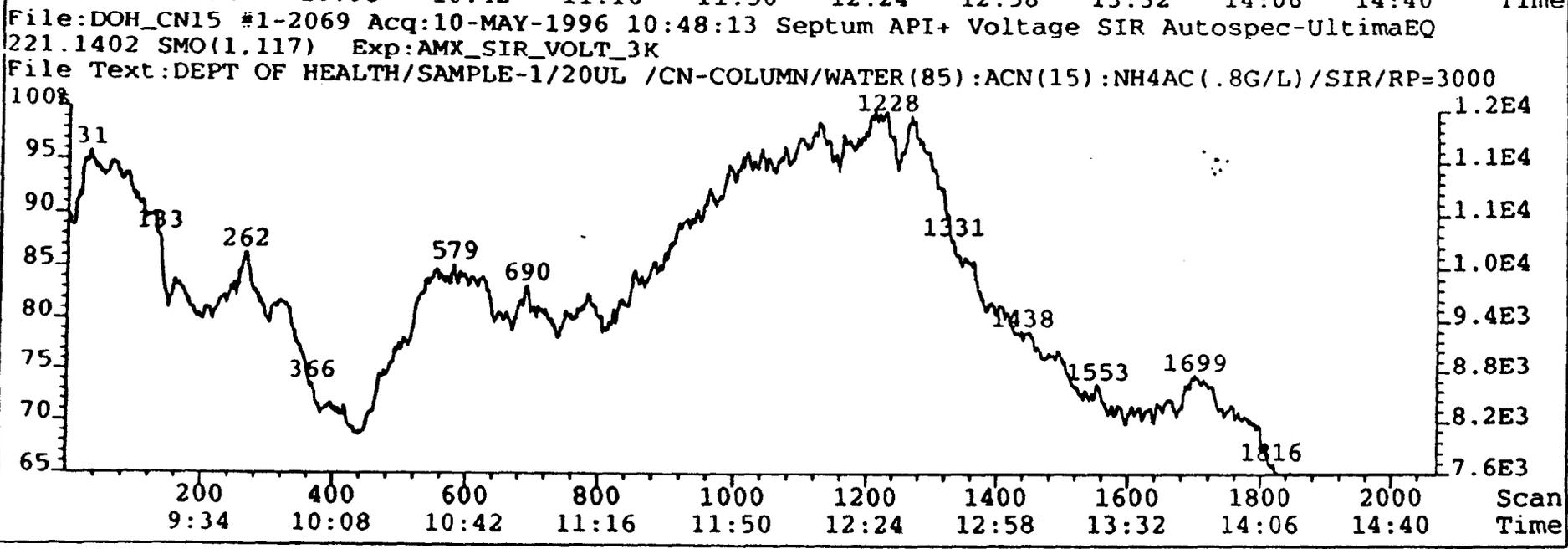
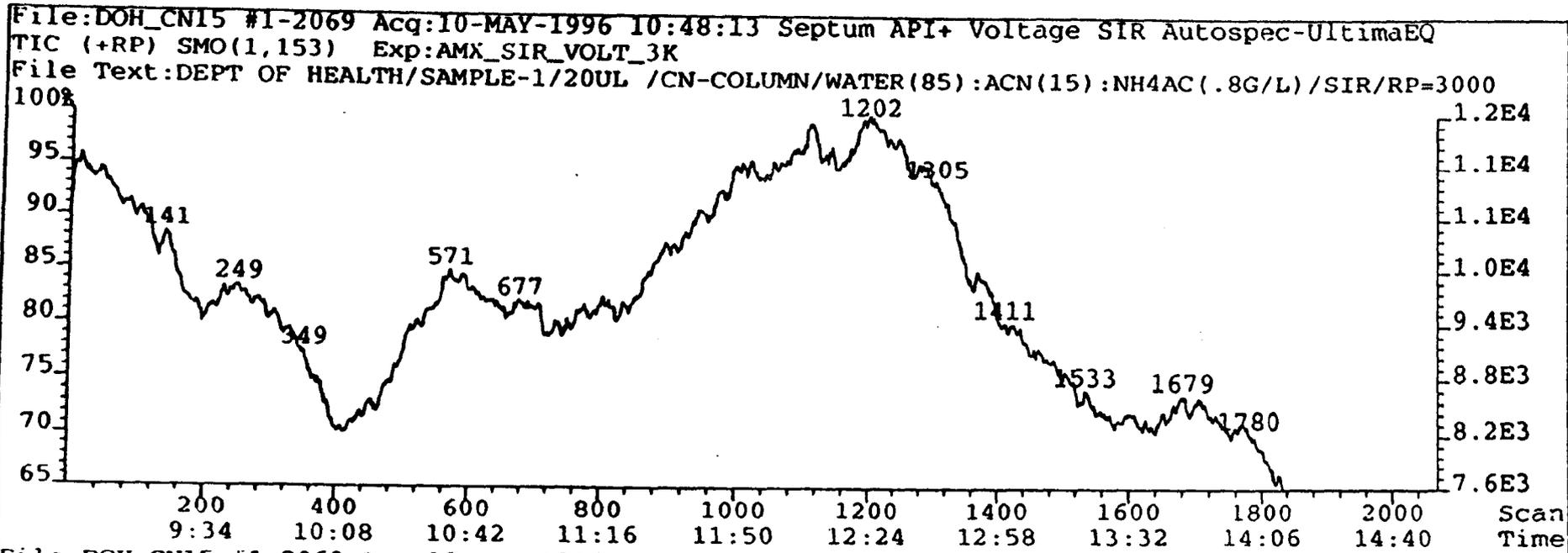
Sorted by Signal
Multiplier : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RT [min] | Type | Width [min] | Area [MAU*sec] | Height [MAU] | Area % |
|----------|----------|------|-------------|----------------|--------------|---------|
| 1 | 2.255 | BV | 0.307 | 38.31689 | 1.65937 | 0.2212 |
| 2 | 2.531 | VV | 0.172 | 15.37489 | 1.28191 | 0.0888 |
| 3 | 2.867 | VV | 0.258 | 45.28702 | 2.39662 | 0.2614 |
| 4 | 3.253 | VV | 0.203 | 15.57010 | 1.07858 | 0.0899 |
| 5 | 3.763 | VV | 0.402 | 104.25579 | 3.57917 | 0.6019 |
| 6 | 4.885 | VV | 0.864 | 87.78448 | 1.35857 | 0.5068 |
| 7 | 5.918 | VV | 1.026 | 68.54021 | 9.03679e-1 | 0.3957 |
| 8 | 10.077 | VV | 1.277 | 789.75226 | 8.77847 | 4.5591 |
| 9 | 12.203 | VV | 1.191 | 97.14459 | 1.11284 | 0.5608 |
| 10 | 14.680 | VB | 1.499 | 50.14759 | 4.29233e-1 | 0.2895 |
| 11 | 22.196 | BV | 1.915 | 2160.99634 | 16.85944 | 12.4751 |
| 12 | 29.372 | PBA | 3.113 | 13849.31738 | 56.63867 | 79.9499 |
| Totals : | | | | 17322.48828 | 96.07655 | |

*** End of Report ***





Experiment: AMX_SIR_VOLT_3K (1 Functions)

Operator : User
Date : 10-MAY-1996 11:13:22
Instrument : Autospec-UltimaEQ

Function 1

Type : SIR Voltage
Calibration file used : DOH_CN13_1
High mass : 239.1
Low mass : 221.1
Resolution : 3000
Ionisation mode : API+
Accelerating Voltage : 4000.0V
Magnet 1 control : Current
Start Time : 9:00
End Time : 120:00
Fast lock : On
Number of channels : 2
Cycle time (ms) : 160
Channel

| Channel | Mass | Ch Time (ms) | I/ch Time (ms) |
|-----------------------------|----------|-----------------|-------------------|
| 1 | 221.1402 | 80 | 20 |
| 2 (Lock) | 239.1495 | 40 | 20 |
| Primary Span Lock (Peaks) | 2.00 | | |
| Secondary Span Lock (Peaks) | 2.00 | | |
| Lock Level (mV) | 0 | | |
| Step Lock (Peaks) | 0.020 | | |
| Repeats | : 1 | | |

Experiment: AMX_SIR_VOLT_3K (1 Functions)

Operator : User
Date : 10-MAY-1996 12:06:25
Instrument : Autospec-UltimaEQ

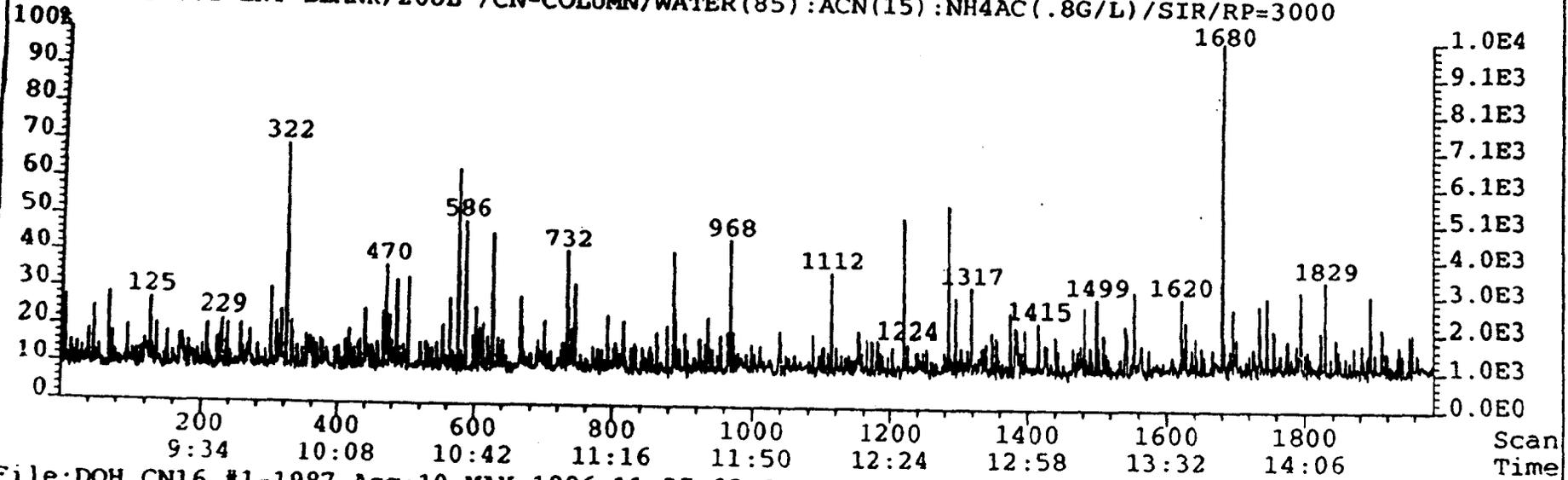
Function 1

Type : SIR Voltage
Calibration file used : DOH_CN13_1
High mass : 239.1
Low mass : 221.1
Resolution : 3000
Ionisation mode : API+
Accelerating Voltage : 4000.0V
Magnet 1 control : Current
Start Time : 9:00
End Time : 120:00
Fast lock : On
Number of channels : 2
Cycle time (ms) : 160

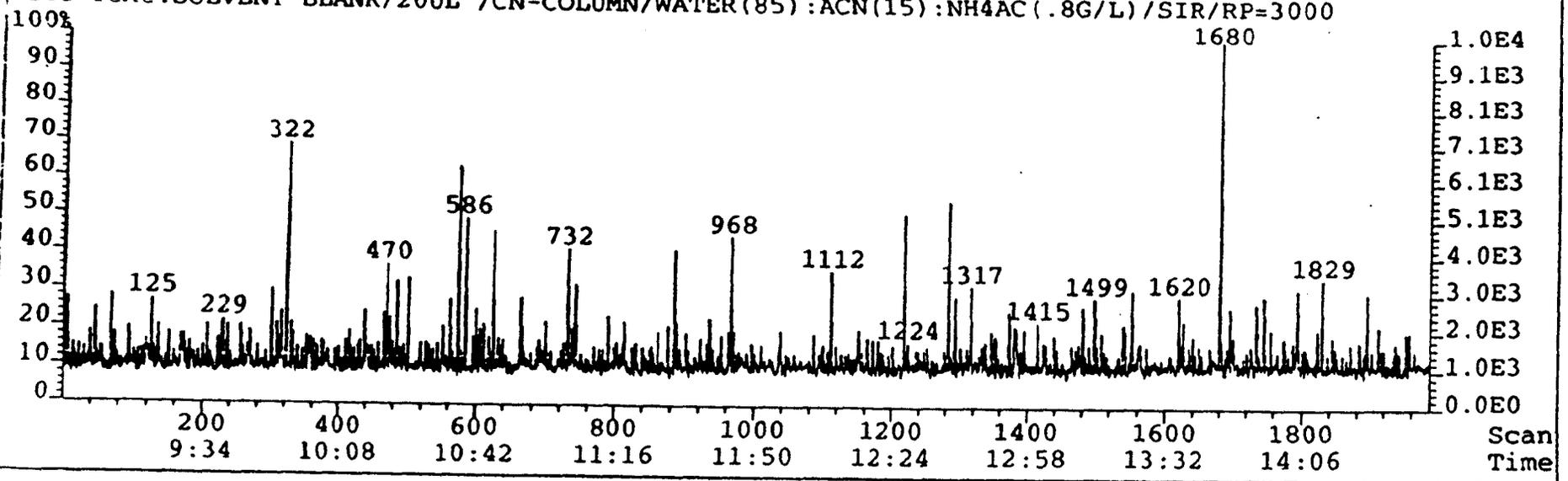
| Channel | Mass | Ch Time (ms) | I/ch Time (ms) |
|----------|----------|-----------------|-------------------|
| 1 | 221.1402 | 80 | 20 |
| 2 (Lock) | 239.1495 | 40 | 20 |

Primary Span Lock (Peaks) 2.00
Secondary Span Lock (Peaks) 2.00
Lock Level (mV) 0
Step Lock (Peaks) 0.020
Repeats : 1

File:DOH_CN16 #1-1987 Acq:10-MAY-1996 11:35:02 Septum API+ Voltage SIR Autospec-UltimaEQ
TIC (+RP) Exp:AMX_SIR_VOLT_3K
File Text:SOLVENT BLANK/20UL /CN-COLUMN/WATER(85):ACN(15):NH4AC(.8G/L)/SIR/RP=3000



File:DOH_CN16 #1-1987 Acq:10-MAY-1996 11:35:02 Septum API+ Voltage SIR Autospec-UltimaEQ
221.1402 Exp:AMX_SIR_VOLT_3K
File Text:SOLVENT BLANK/20UL /CN-COLUMN/WATER(85):ACN(15):NH4AC(.8G/L)/SIR/RP=3000



Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RT [min] | Type | Width [min] | Area [MAU*sec] | Height [MAU] | Area % |
|----------|----------|------|-------------|----------------|--------------|---------|
| 1 | 2.529 | BV | 0.261 | 114.82564 | 6.04223 | 0.6993 |
| 2 | 2.900 | VV | 0.214 | 73.96062 | 4.92165 | 0.4505 |
| 3 | 3.364 | VV | 0.239 | 48.43895 | 2.81850 | 0.2950 |
| 4 | 3.786 | VV | 0.391 | 92.39291 | 3.36418 | 0.5627 |
| 5 | 5.260 | VV | 0.966 | 59.32596 | 8.01242e-1 | 0.3613 |
| 6 | 10.539 | VV | 1.398 | 611.87726 | 6.29309 | 3.7266 |
| 7 | 12.840 | VV | 1.736 | 387.66367 | 3.14851 | 2.3611 |
| 8 | 15.544 | VV | 3.821 | 409.52756 | 1.34580 | 2.4942 |
| 9 | 31.038 | PBA | 3.493 | 14621.08984 | 53.30045 | 89.0493 |
| Totals : | | | | 16419.10156 | 82.03564 | |

*** End of Report ***

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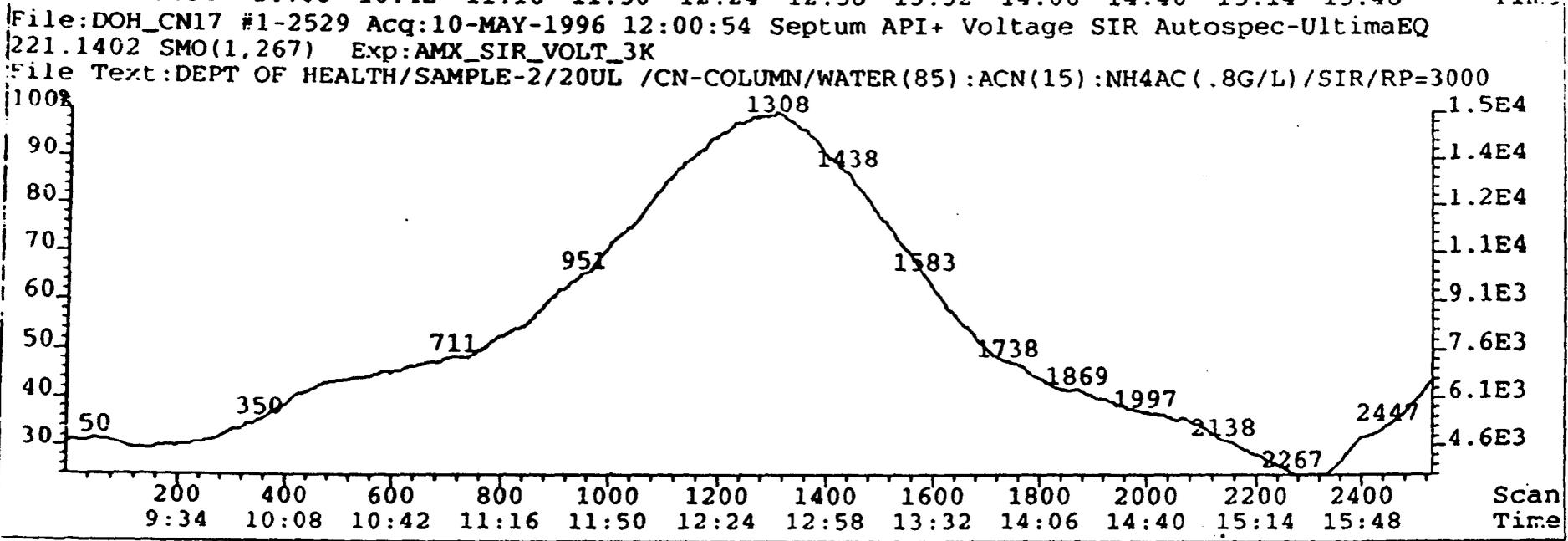
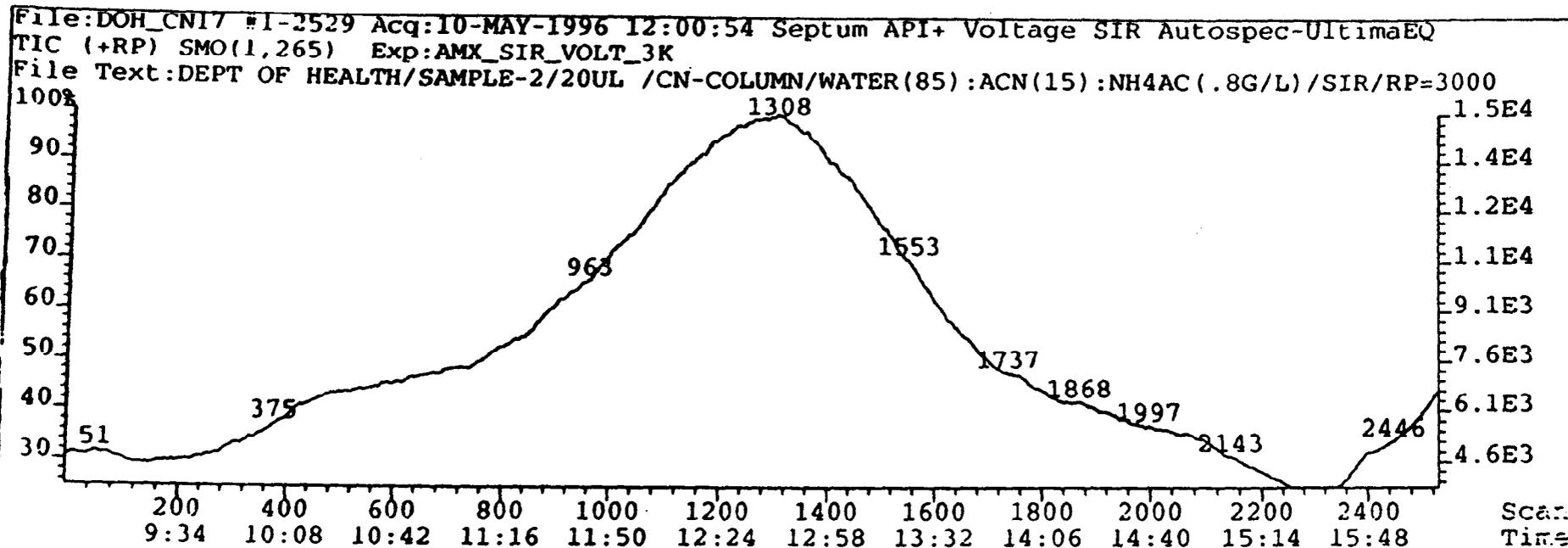
Experiment: AMX_SIR_VOLT_3K (1 Functions)

Operator : User
Date : 10-MAY-1996 12:06:46
Instrument : Autospec-UltimaEQ

Function 1

Type : SIR Voltage
Calibration file used : DOH_CN13_1
High mass : 239.1
Low mass : 221.1
Resolution : 3000
Ionisation mode : API+
Accelerating Voltage : 4000.0V
Magnet 1 control : Current
Start Time : 9:00
End Time : 120:00
Fast lock : On
Number of channels : 2
Cycle time (ms) : 160

| Channel | Mass | Ch Time (ms) | I/ch Time (ms) |
|----------------------------------|----------|-----------------|-------------------|
| 1 | 221.1402 | 80 | 20 |
| 2 (Lock) | 239.1495 | 40 | 20 |
| Primary Span Lock (Peaks) 2.00 | | | |
| Secondary Span Lock (Peaks) 2.00 | | | |
| Lock Level (mV) 0 | | | |
| Step Lock (Peaks) 0.020 | | | |
| Repeats | : 1 | | |

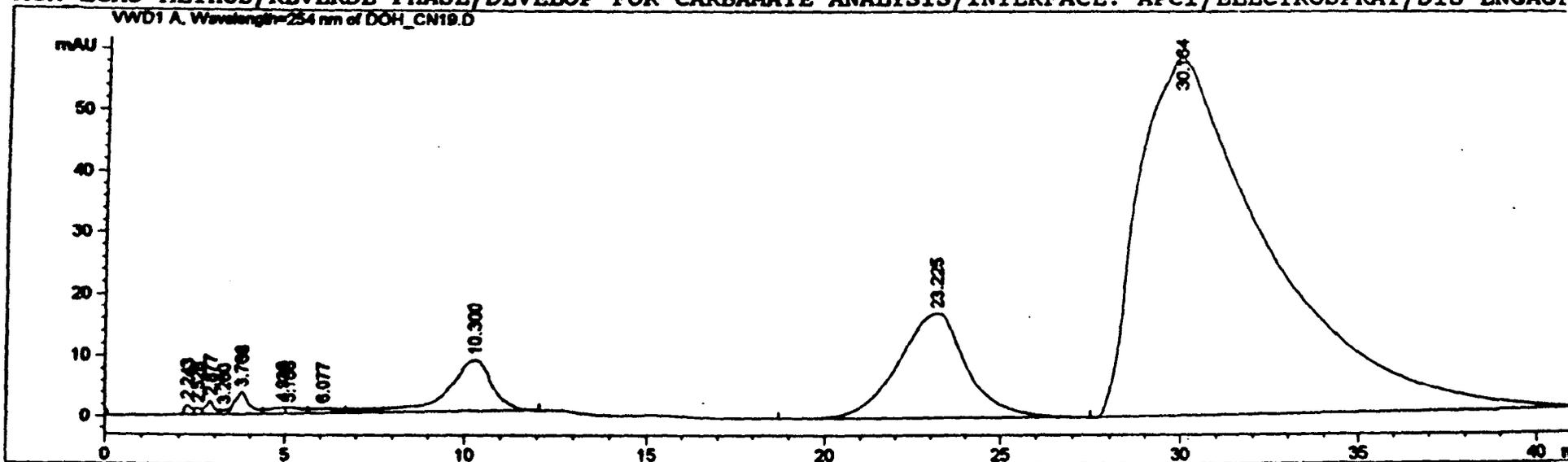


DEPT OF HEALTH/SAMPLE-1/20UL INJ ISOCLATIC/ ACN(15) :WA
TER(85):NH4Ac(.8gm/L)/pH=6.1-6.5/CN 240 X 4.5 mm COLUMN
/LAMDA=254nm/LC RATE=1.0/MIN/MRM_Q

150

Acq. Method : ACX_LCMS.M Seq. Line : -
Acq. Operator : ACC Vial : 1
Injection Date : 5/10/96 1:47:55 PM Inj : -
Sample Name : DOH/SAMPLE-1/MRM Inj Volume : Unknown

Analysis Method : C:\HPCHEM\1\METHODS\ACX_LCMS.M
ACX_LCMS METHOD/REVERSE PHASE/DEVELOP FOR CARBAMATE ANALYSIS/INTERFACE: APCI/ELECTROSPRAY/DIS-ENGAGE



Area Percent Report

Sorted by Signal
Multiplier : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RT [min] | Type | Width [min] | Area [MAU*sec] | Height [MAU] | Area % |
|----------|----------|------|-------------|----------------|--------------|---------|
| 1 | 2.243 | BV | 0.182 | 19.87410 | 1.59023 | 0.1084 |
| 2 | 2.528 | VV | 0.180 | 13.82428 | 1.10513 | 0.0754 |
| 3 | 2.877 | VV | 0.237 | 37.54073 | 2.20494 | 0.2047 |
| 4 | 3.260 | VV | 0.205 | 10.02090 | 7.44291e-1 | 0.0546 |
| 5 | 3.768 | VV | 0.385 | 103.28820 | 3.69528 | 0.5632 |
| 6 | 4.938 | VV | 0.474 | 34.60483 | 1.04129 | 0.1887 |
| 7 | 5.108 | VV | 0.553 | 33.99940 | 1.02485 | 0.1854 |
| 8 | 6.077 | VV | 0.791 | 46.59855 | 8.09095e-1 | 0.2541 |
| 9 | 10.300 | VV | 1.270 | 753.40643 | 8.52757 | 4.1082 |
| 10 | 23.225 | BV | 2.017 | 2357.97681 | 17.18229 | 12.8576 |
| 11 | 30.164 | PBA | 3.250 | 14928.09375 | 58.81927 | 81.3998 |
| Totals : | | | | 18339.22852 | 96.74424 | |

*** End of Report ***

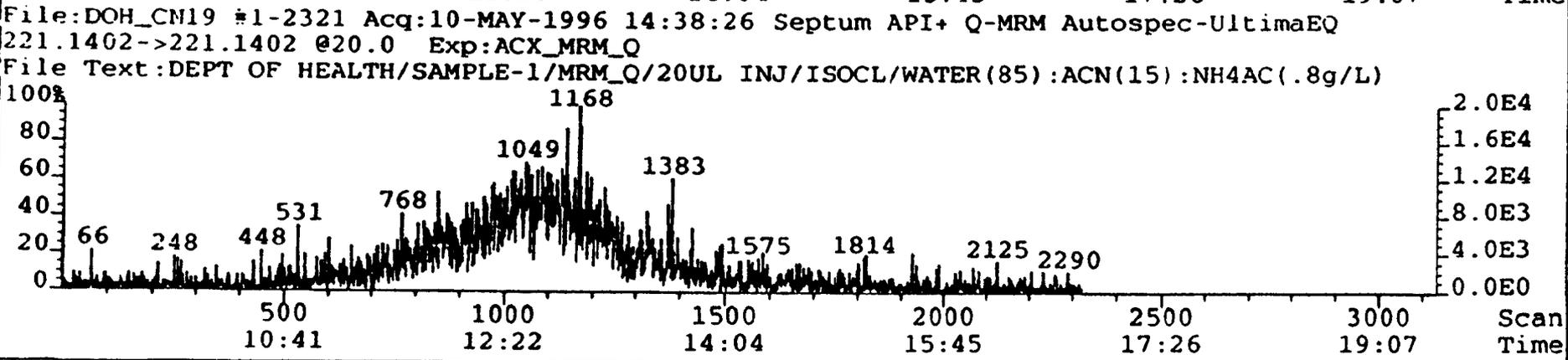
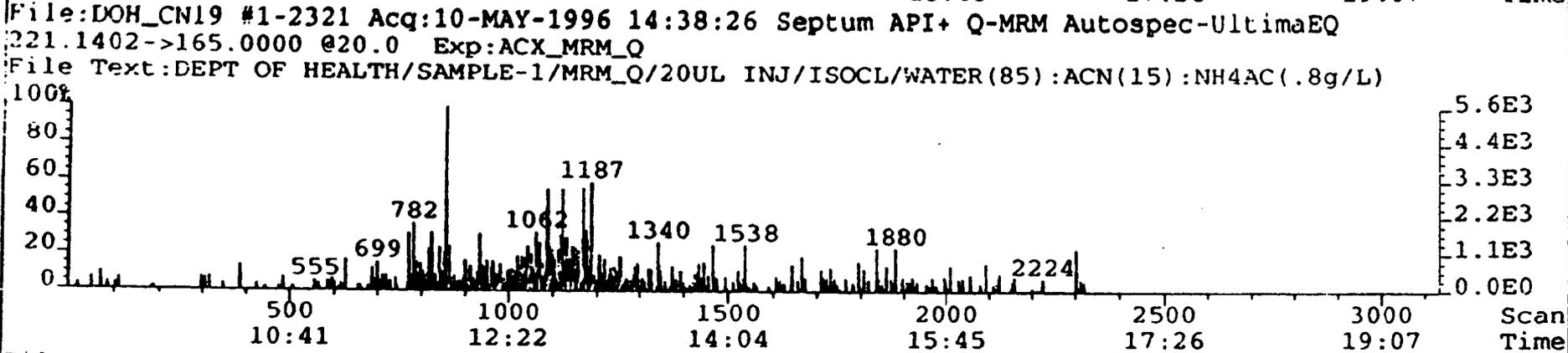
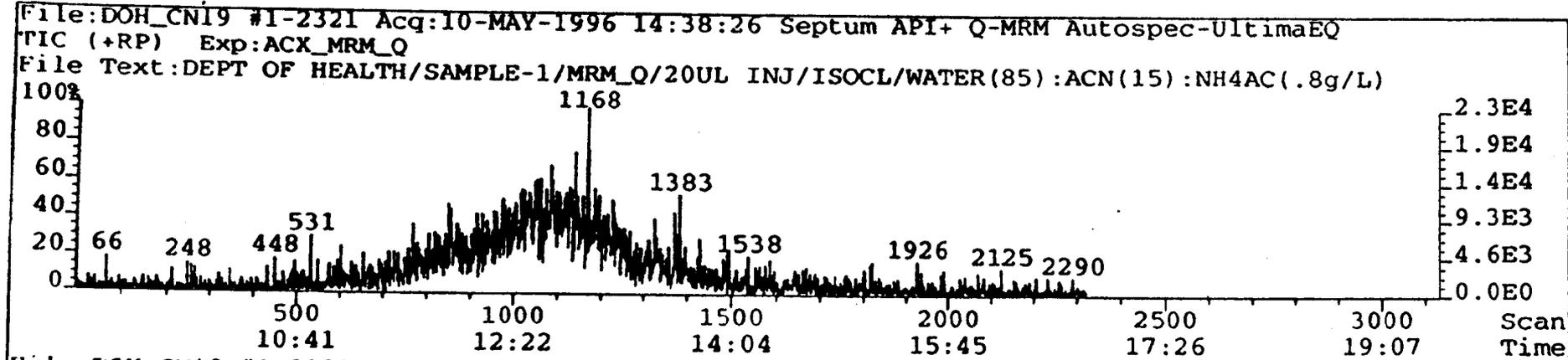
Experiment: ACX_MRM_Q (1 Functions)

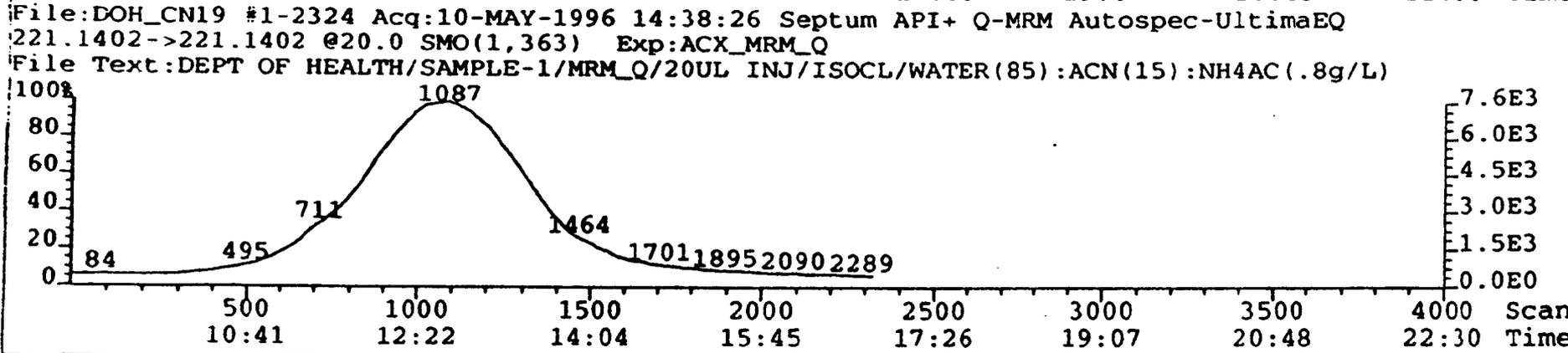
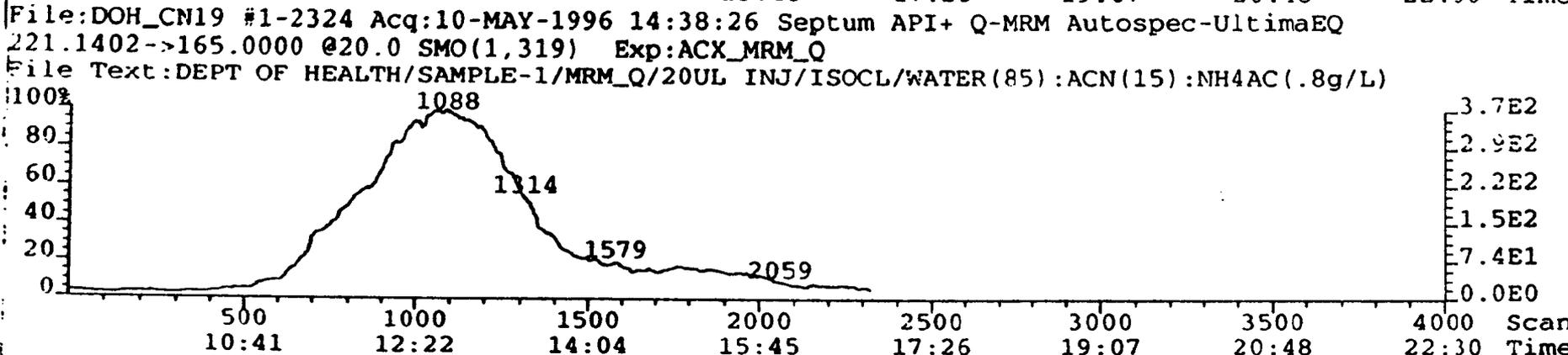
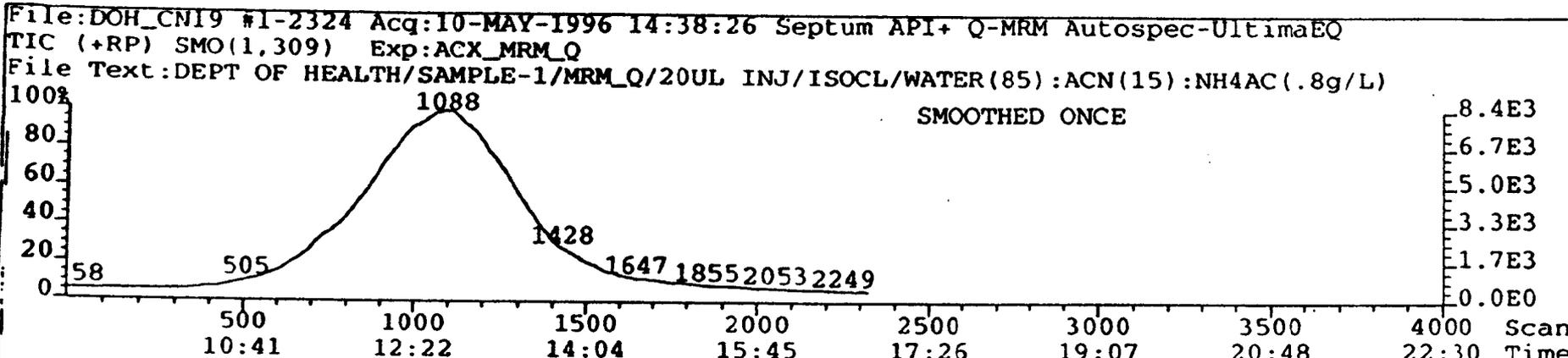
Operator : User
Date : 10-MAY-1996 14:38:18
Instrument : Autospec-UltimaEQ

Function 1

Type : MRM Q
Calibration file used : MRMQ_MIC_1
High mass : 221.1
Low mass : 221.1
Resolution : 1000
Ionisation mode : API+
Accelerating Voltage : 4000.0V
Magnet 1 control : Current
Start Time : 9:00
End Time : 60:00
Number of channels : 2
Cycle time (ms) : 200
Channel

| Channel | Parent Mass | Daughter Mass | Ch Time (ms) | I/ch Time (ms) | Collision Energy |
|---------|-------------|---------------|--------------|----------------|------------------|
| 1 | 221.1402 | 165.0000 | 80 | 20 | 20.0 |
| 2 | 221.1402 | 221.1402 | 80 | 20 | 20.0 |





Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RT [min] | Type | Width [min] | Area [mAU*sec] | Height [mAU] | Area % |
|----------|----------|------|-------------|----------------|--------------|----------|
| 1 | 3.796 | PB | 0.601 | 279.87070 | 6.02348 | 100.0000 |
| Totals : | | | | 279.87070 | 6.02348 | |

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*** End of Report ***

Experiment: ACX_MRM_Q (1 Functions)

Operator : User
Date : 10-MAY-1996 14:17:25
Instrument : Autospec-UltimaEQ

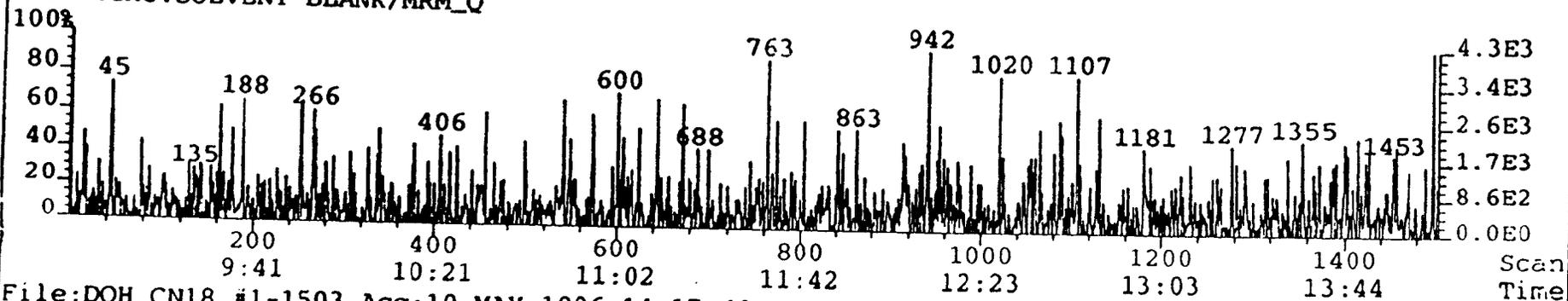
Function 1

Type : MRM Q
Calibration file used : NRMQ_MIC_1
High mass : 221.1
Low mass : 221.1
Resolution : 1000
Ionisation mode : API+
Accelerating Voltage : 4000.0V
Magnet 1 control : Current
Start Time : 9:00
End Time : 60:00
Number of channels : 2
Cycle time (ms) : 200
Channel

| Channel | Parent Mass | Daughter Mass | Ch Time (ms) | I/ch Time (ms) | Collision Energy |
|---------|-------------|---------------|--------------|----------------|------------------|
| 1 | 221.1402 | 165.0000 | 80 | 20 | 20.0 |
| 2 | 221.1402 | 221.1402 | 80 | 20 | 20.0 |

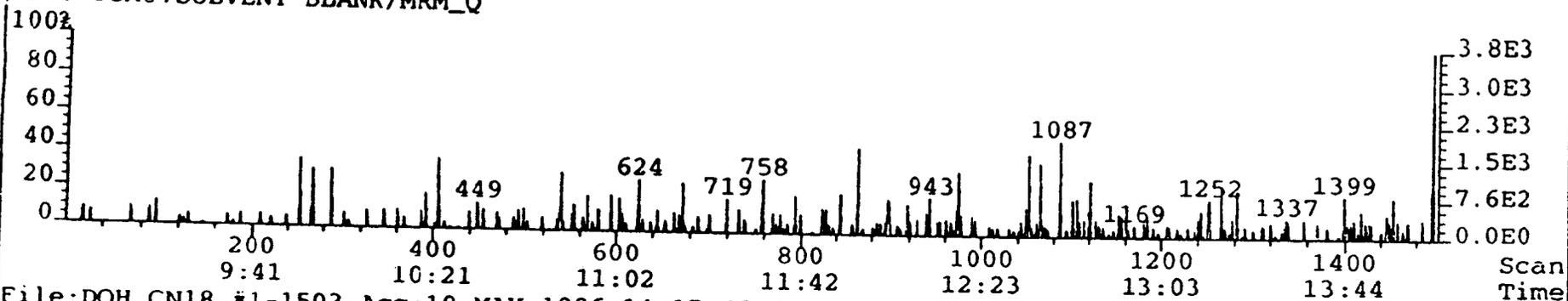
File:DOH_CN18 #1-1503 Acq:10-MAY-1996 14:17:49 Septum API+ Q-MRM Autospec-UltimaEQ
 TIC (+RP) Exp:ACX_MRM_Q

File Text:SOLVENT BLANK/MRM_Q



File:DOH_CN18 #1-1503 Acq:10-MAY-1996 14:17:49 Septum API+ Q-MRM Autospec-UltimaEQ
 221.1402->165.0000 @20.0 Exp:ACX_MRM_Q

File Text:SOLVENT BLANK/MRM_Q



File:DOH_CN18 #1-1503 Acq:10-MAY-1996 14:17:49 Septum API+ Q-MRM Autospec-UltimaEQ
 221.1402->221.1402 @20.0 Exp:ACX_MRM_Q

File Text:SOLVENT BLANK/MRM_Q

