CL-052R

ANALYSIS OF CHEMICAL AGENTS IN DAAMS BY GAS CHROMATOGRAPHY

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1.0 Scope and Application

This method provides procedures for analyzing chemical agents tabun: ethyl N,N-dimethylphosphoroamidocyanidate (GA), sarin: isopropyl methylphosphonofluoridate (GB), soman: pinacolyl methylphosphonofluoridate (GD), cyclohexyl methylphosphonoflouridate (GF), mustard, distilled: bis-2-chloroethyl sulfide (HD), tris-2-chloroethylamine (HN3), and o-ethyl s-(2-diisopropylaminoethyl) methylphosphonthioate (VX) collected on Depot Area Air-Monitoring System (DAAMS) sorbent tubes using gas chromatography (GC) and GC/mass spectrometry. This method is applicable to solid wastes and safety air monitoring regulated by the regulatory compliance program at US Amy Dugway Proving Ground (DPG).

General quality control (QC) guidelines for sampling, sampling equipment, and chain-of-custody (COC) are found in the DPG Waste Permit, Attachment 1-10, *Central Hazardous Waste Storage Facility* (*CHWSF) Quality Assurance Program Plan* (QAPP). A method schematic and accompanying analytical sequence is provided in Figures 1 and 2 respectively.

2.0 Scientific Basis

Samples adsorbed on DAAMS tubes are thermally desorbed by heating each tube and aspirating air through the tube and onto a three mm concentrator tube. The concentrator tube is thermally desorbed onto a capillary column equipped GC system. DAAMS tubes and concentrator tubes filled with Chromosorb 106 (C-106) are used for GA, GB, GD, GF, and VX. DAAMS tubes and concentrator tubes filled with Tenax® TA are used for HD, and HN3. Sample components are separated by traditional GC techniques. Detection is achieved with a flame photometric detector (FPD) equipped with an appropriate optical bandpass filter for the nerve agents or HD, or a mass selective detector (MSD). HN3 is detected using a flame ionization detector (FID) or MSD. Analyte identification is predicated upon four independent criteria: analyte volatility, sorption by the sorbent sampling tube, GC retention time, and detector response, as well as diagnostic ion signals for HN3 (base ion 154 and confirmation ions 156, 92, and 63).

Positive interferences are generally limited to volatile pesticides or other organic compounds applied as part of the test procedure from which the waste originated or related to airborne organics sources.

3.0 Terminology

This section lists in alphabetical order all terms, abbreviations, and acronyms unique to understanding this method.

- %R – percent recovery
- AgF – silver fluoride
- C-106 – Chromosorb 106 polymer adsorbent
- Calibration Standard – A solution used to prepare a series of concentrations, including the Hazard Level, which will be used to calibrate the GC.
- CAS® – Chemical Abstracts Number®
- CCV – continuing calibration verification
- CC – calibration check

- Chemical Agent – Any of several highly toxic chemical compounds (including GA, GB, GD, GF, HD, HN3, and VX) that are intended for use in military operations.
- COC – chain-of-custody
- DAAMS – Depot Area Air-Monitoring System
- Decontamination – The process of decreasing the amount of chemical agent on any person, object, or area by absorbing, neutralizing, destroying, ventilating, or removing chemical agents.
- DPG – US Army Dugway Proving Ground
- FID – flame ionization detector
- FPD – flame photometric detector
- GA – tabun: ethyl N,N-dimethylphosphoroamidocyanidate, CAS® 77-81-6, a nerve agent
- GB – sarin: isopropyl methylphosphonofluoridate, CAS® 107-44-8, a nerve agent
- GC – gas chromatograph
- GD – soman: pinacolyl methylphosphonofluoridate, CAS® 96-64-0, a nerve agent
- GF – cyclohexyl methylphosphonoflouridate, CAS® 329-99-7, a nerve agent
- HL – hazard level. A concentration in mg/m^3 equivalent to the WPL exposure limits for a given analyte as indicated in the following table:

Agent	Hazard Level (mg/m^3)
GA	0.00003
GB	0.00003
GD	0.00003
GF	0.00003
HD	0.0004
HN3	0.0004
VX	0.000001

- HD – mustard, distilled: bis-2-chloroethyl sulfide, CAS® 505-60-2, a blister agent
- HN3 – tris-2-chloroethylamine**,** CAS® 555-77-1 a blister agent
- MB – method blank. A negative control prepared in the laboratory to establish that the analytical system is free of interference and contamination.
- MDL – method detection limit. Estimate of the lowest level of an analyte that a method can distinguish from noise.
- MSD – mass selective detector
- NA – not applicable
- NO_x – nitrogen oxide
- QAPP – Quality Assurance Program Plan
- QC Standard – A standard, prepared at the HL concentration, which verifies that the analytical system is operating as designed and is capable of detecting and quantifying chemical agent at the required concentrations.
- QC – quality control
- QL – quality laboratory
- QL Standard – A standard used to verify the calibration. QL standards are prepared in the laboratory by spiking unexposed DAAMS tubes with a solution of dilute chemical agent and,

aspirating with laboratory air to remove residual solvent. QL standards are not aspirated with sample air.

- QP – quality plant
- QP Standard – A QC standard used to verify the sampling process. QP standards are prepared (in duplicate) in the laboratory by spiking unexposed DAAMS tubes with a solution of dilute chemical agent and, if necessary aspirating with laboratory air to remove residual solvent. QP standards are sent into the field with the sample tubes and aspirated with sample air.
- RPD – relative percent difference
- SA – spike amount
- SDS – safety data sheet
- SOP – standing operating procedure
- SSR – spiked sample result
- TWA – Time Weighted Average
- VX – o-ethyl s-(2-diisopropylaminoethyl) methylphosphonthioate, CAS® 50782-69-9, a nerve agent
- WPL – worker population limit
- XXXX – Four X level of decontamination equivalent to the WPL

4.0 Safety

Generally, regulatory compliance samples received by the laboratory have been exposed to chemical agent and subsequently decontaminated. Handle all samples with caution until negative test results have been released. For all operations involving chemical agents, comply with all laboratory chemical agent safety rules and regulations. Be familiar with and follow safety guidelines contained in Safety Data Sheets (SDS) for the chemicals being used or analyzed.

5.0 Apparatus and Reagents

To perform the procedures in this method, obtain the apparatus and DAAMS tubes described in the following sections.

5.1 Apparatus

Ensure that the following items are available to analyze chemical agents in DAAMS by GC:

- GC system with a computer interface
- Detectors: an FPD equipped with an appropriate optical bandpass filter, an FID, or an MSD
- 30-m capillary columns: Columns typically include DB-1, DB-5, DB-1701, or DB-210
- DAAMS tubes filled with C-106 to analyze for nerve agents (GA, GB, GD, GF, and VX) or Tenax® TA to analyze for blister agents (HD and HN3)
- 10-µL precision syringes
- Dust filter pads
- Silver fluoride (AgF) pads
- Nitrogen oxide (NO_x) filters
- Calibrated flow meter

Document the configuration and maintenance for each instrument in a bound maintenance logbook.

5.2 Sorbent Tube Evaluation

Each shipment of new vendor-produced DAAMS tubes will be tested for absence of contamination and agent tested [at least 75% recovery of a 1.0 worker population limit (WPL) spike] using the lot acceptance criteria in Table 1. The tubes will also be pressure drop tested using the acceptance criteria in Table 2. If the lot fails acceptance, each tube from the lot must be cleaned and certified as such before use. Records will be maintained documenting the performance of the evaluation.

In lieu of performing acceptance testing in-house, organizations that procure DAAMS tubes from vendors must obtain certification from the manufacturer to demonstrate that acceptance testing has been performed as specified above. Vendor certification will include test results, requirements, acceptance criteria, and test procedure references.

Glass tubes will be visually inspected in order to assure the absence of obvious defects such as loose packing, warped tube ends, or loose sorbent material outside the glass wool plug.

Table 1: Number of Testing Samples to Use for Acceptance of Silver Fluoride (AgF) Conversion Pads and Depot Area Air-Monitoring System (DAAMS) tubes.

Lot or Batch Size	General Inspection (Level I, No. of Tubes)	Rejection[a] Number
2-8	5	1
9-15	5	1
16-25	5	1
26-50	5	1
51-90	5	1
91-150	5	1
151-280	20	2
81-500	20	2
501-1200	32	3

[a]Reject the entire lot if this number of samples is found to be defective.

Table 2: Depot Air-Monitoring System (DAAMS) Tube Pressure Drop Criteria

Type of Tube	Highest Acceptable Pressure Drop [Pounds Per Square Inch (psi)]
DAAMS - 6mm - Chromosorb® 106	7.4
DAAMS - 6mm - Tenax®TA	7.4
Transfer tube 3mm - Chromosorb® 106	2.2
Transfer tube 3mm - Tenax® TA	3.4

6.0 Standards and Quality Control

This section presents procedures for technical personnel to prepare standards and laboratory QC samples for chemical agents in DAAMS analyzed by GC.

6.1 Preparing Standards

Technical personnel prepare initial calibration and QC standards from neat agent or from stock standard solutions and label, document, and handle them in accordance with approved procedures.

Store chemical agent standards in a refrigerator at or below 10°C. Allow solutions to warm up to room temperature before opening for use. Return solutions to the refrigerator as quickly as possible after use. Single component working standards or standards where VX and HD are not mixed may be used for up to 30 days after preparation. Standards where VX and HD are mixed may be used for up to seven days.

Prepare standards by spiking DAAMS tubes with appropriate amounts of the compounds of analytical interest. There must be at least four calibration standards for each analysis. One of the calibration standards must be prepared at or below the Hazard Level (HL). At least one calibration standard must be prepared above the HL.

Prepare calibration curve and QC samples [quality laboratory (QL) and quality plant (QP)] by the following procedure:

1. For a calibration curve, sufficient clean DAAMS tubes are placed on a vacuum manifold with a flow of 400 to 600 mL/minute of air through the tube.
2. Tables 3 through 6 give suggested concentrations for calibration standards used in the analysis of XXXX (four X level of decontamination equivalent to the WPL) samples or Igloo G entry.
3. QL and QP samples are spiked with sufficient agent to produce a concentration equal to or lower than the HL of agent for the anticipated field collection procedure.
4. Tubes are allowed to aspirate air for at least 2-3 minutes after the last agent is spiked.
5. For VX and GA tubes, an AgF conversion pad assembly is placed on the DAAMS tube intake end. The agent solution is spiked onto the AgF pad and aspirated through the DAAMS tubes.

Table 3: Suggested levels for GA, GB, GD, and GF Calibration Standards

Calibration Standard	**Spike Volume (µL)**	**Standard Concentration (µg/mL)**	**Amount on DAAMS Tube (ng)**
1	0.50	0.20	0.10
2	2.5	0.20	0.50
3	5.0	0.20	1.0
4	3.3	1.50	5.0
5	6.6	1.50	10.0
6	10.0	1.50	15.0

Table 4: Suggested levels for VX Calibration Standards

Calibration Standard	**Spike Volume (µL)**	**Standard Concentration (µg/mL)**	**Amount On DAAMS Tube (ng)**
1	0.8	0.05	0.040
2	2.0	0.05	0.10
3	4.0	0.05	0.20
4	6.0	0.05	0.30
5	8.0	0.05	0.40
6	10.0	0.05	0.50

Table 5: Suggested levels for HD Calibration Standards

Calibration Standard	**Spike Volume (µL)**	**Standard Concentration (µg/mL)**	**Amount On DAAMS Tube (ng)**
1	0.50	20.0	10.0
2	1.00	20.0	20.0
3	1.50	20.0	30.0
4	2.00	20.0	40.0
5	4.00	20.0	80.0
6	6.00	20.0	120.0
7	8.00	20.0	160.0
8	10.00	20.0	200.0

Table 6: Suggested levels for HN3 Calibration Standards

Calibration Standard	**Spike Volume (µL)**	**Standard Concentration (µg/mL)**	**Amount On DAAMS Tube (ng)**
1	0.50	10.0	5.0
2	1.00	10.0	10.0
3	1.50	10.0	15.0
4	2.00	10.0	20.0
5	4.00	10.0	40.0
6	6.00	10.0	60.0
7	8.00	10.0	80.0
8	10.00	10.0	100.0

6.2 Preparing Laboratory Quality Control Samples

Technical personnel prepare laboratory QC samples (QL and QP) as follows, using C-106 for the nerve agents (GA, GB, GD, GF, and VX) and Tenax® TA for the blister agents (HD and HN3). The spiking procedure for laboratory QC samples is the same as described in Paragraph 6.1, Preparing Standards.

- Verification Standards - Prepare calibration verification standards, also known as QL standards, independently by spiking unexposed DAAMS tubes with an appropriate amount of standard solution (at or below the HL). Record preparation of verification standards in a laboratory notebook.
- Method Blank (MB) Samples - MB samples consist of unexposed DAAMS tubes that are treated exactly as a sample. One MB per laboratory sample lot is required.
- QP standards - QP standards, which function similarly to method blank spikes (MBS), are prepared in duplicate by spiking unexposed DAAMS tubes with an appropriate amount of standard solution (at or below the HL). The spiked tubes are sent, along with sampling tubes, to the sampling area where air is drawn through, as done for samples. Record preparation of QP samples in a laboratory notebook.

NOTE: QL and QP samples must be prepared from a different stock solution than the stock solution used to prepare analytical standards.

For each QC sample prepared, technical personnel will record the following information in the logbook:

- Spiking solution identification number
- Mass of agent spiked onto tube
- Analyst initials
- Date prepared

Table 7 gives suggested spiking levels for QL and QP samples assuming a four hour sampling time. **NOTE**: HN3 is sampled for two hours.

Table 7: Suggested Spiking Levels for Quality laboratory (QL) and Quality Plant (QP) Samples

Agent in QL or QP Sample	Spike Volume (µL)	Spike Concentration (µg/mL)	Amount on DAAMS Tube (ng)
GA, GB, GD, GF	2.4	1.50	3.6
VX	2.4	0.05	0.12
HD	2.4	20.0	48
HN3	2.4	10.0	24

7.0 Procedure

To analyze chemical agents using GC, the analyst performs the following tasks:

- Handling and preparation of samples for analysis.

- Setting up the instrument.
- Calibrating the instrument.
- Performing sample desorption and analysis.

7.1 Handling and Preparation of Samples for Analysis

Keep samples cold (≤6°C but above freezing) and analyze them within seven days of collection. Do not expose conditioned DAAMS and filters to moisture.

Field samples, QC samples, and calibration standards are prepared for manual analysis by desorbing the contents of the DAAMS sampling tubes onto 3mm transfer tubes packed with the same sorbent (C-106 for the nerve agents and Tenax® TA for the blister agents). Table 8 describes steps to prepare samples for manual analysis.

Table 8: Manual Sample Preparation; Analysis of Chemical Agents GA, GB, GD, GF, VX, HD, and HN3 on DAAMS Tubes by Gas Chromatography

Step	DAAMS Tubes
1	Adjust temperature of DAAMS transfer block to 200°C±10°C
2	Connect DAAMS tubes to 3 mm transfer tubes (packed with Chromosorb 106 for nerve agents or Tenax® TA for blister agents) using a stainless steel reducing union with Teflon® ferrules or O-rings
3	Connect 3 mm transfer tube to vacuum line and adjust airflow to approximately 200 mL/min
4	Insert DAAMS tube end of desorption unit into heated block
5	Desorb and collect the effluent from the DAAMS tube for at least four minutes
6	Remove assembly from heated block and remove 3mm transfer tube from reducing union.
7	Arrange transfer tubes in sequence with DAAMS tubes and enter information into the Chemstation sequence table.

Table 8: Manual Sample Preparation; Analysis of Chemical Agents GA, GB, GD, GF, VX, HD, and HN3 on DAAMS Tubes by Gas Chromatography (Cont'd)

Step	DAAMS Tubes
8	Connect appropriate end of 3 mm transfer tube to helium carrier gas line. Insert into heated inlet port on GC and manually start GC.

7.2 Setting Up the Instrument

To setup the GC, the analyst performs the steps outlined in the instrument operating manual using as a starting point the following conditions:

1. Column: 30 m capillary or equivalent, 0.53 mm inner diameter, various phases and thicknesses
2. Carrier Gas: helium
3. Detector: FPD, FID, or MSD
4. Sample Size: entire sample is desorbed and analyzed

5. Helium flow rate: 20 mL/min
6. Injector temperature: 225°C
7. Oven temperature: 80°C
8. Detector temperature: 250°C
9 Program: Temperature programmed from 80°C to 250°C at 20°C per minute

7.3 Calibrating the Instrument

To calibrate the instrument, the analyst performs the following steps:

1. Gather DAAMS tubes spiked with standard agent solutions as described in Paragraph 6.1.
2. Prepare tubes for manual GC analysis as described in Paragraph 7.1.
3. Connect each 3mm transfer tube to the carrier gas supply and insert the tube into the heated inlet port of the GC. **NOTE**: All desorptions should be done in the back flush direction. Initiate the instrument's analysis program.
4. Perform a data regression of the results to ensure that the calibration curve meets the following criteria:
   - $r^2 \geq 0.99$
   - Once the responses have been entered into the calibration table in the software, recalculate each point of the calibration curve. The percent recovery (%R) for each standard should be (%R) = 100±25%. Note that after reprocessing the calibration curve there may be slight differences in area counts between those in the calibration table and the recalculated calibration curve.
5. If these criteria are not met, re-spike up to three points. If more than three points are required to be re-spiked, analyze a new calibration curve. Do not count systematic errors (i.e., tube not spiked, tube double spiked, tube spiked at the wrong concentration, etc.) as re-spikes.
6. Ensure that the calibration verification (QL) standard %R is 100±15%. If it does not meet this requirement, re-spike two verification (QL) standards and analyze them. If either of these two are outside the requirements, prepare a new curve.
7. Generate a calibration report (See Exhibit A).

7.4 Sample Desorption and Analysis

To desorb and analyze samples and field QC (such as QP samples), the analyst performs the following steps:

1. Ensure that the COC is complete and correct when the samples are received.
2. Spike two QL samples with the appropriate agent. If analyzed immediately after the calibration, the calibration verification sample can replace the first QL.
3. If the sample is a QL or a QP, perform data evaluation of QC samples as follows:
   - Calculate the %R of the sample.
   - Verify the control status of the GC by determining the recovery range for the QC standards and evaluating as follows:
     - If the recoveries for the QC standards are in the following range, the analysis is in control.
       - QL standard: 85 - 115% (±15%)
       - QP standard: 75 - 125% (±25%)
     - If the percent recovery is not within these parameters, analyze one additional QL standard. If result is outside the specified range, perform corrective action such as

bakeout, instrument maintenance, or recalibration. Acceptable instrument performance must be performed by successfully analyzing two sequential QL standards.

- If the recovery of the QP sample is less than 50% analyze the second QP sample as long as it is still within the seven day holding time.
- If the QP sample has a recovery less than 75% but greater than 25% the data may be used if the following conditions are met:
  1. The QL recoveries are met (85 - 115%).
  2. The recovery is sufficient so that the action level can still be supported based on the recovered mass and air volumes.
  3. The low recoveries are documented in the narrative.
  4. Generate a Data Analysis Sheet (See Exhibit B).
- If the ending continuing calibration verification (CCV) fails high for a particular analyte and that analyte is not detected in the sample, the non-detect value may be reported. The high bias must be documented and narrated.

8.0 Data Reduction and Assessment

This section presents the following procedures performed by the analyst to reduce data and assess QC sample results:

- Performing data reduction.
- Assessing quality control data.

8.1 Performing Data Reduction

To reduce data, the analyst or other technical personnel perform the following steps:

1. Record the amount detected on the DAAMS Data Analysis Sheet.
2. Calculate the airborne concentration using the following equation:
3. If the airborne concentration is greater than the HL in mg/m^3, notify the person who requested the analysis.

$$\text{Air Concentration } (mg/m^3) = \frac{\text{Amount x 1,000 L/m3}}{\text{Flow x Time x 1,000,000 ng/mg}}$$

Where:

Amount is the amount of analyte detected (ng)
Flow is the lowest value of the beginning and ending sample collection flowrate (L/min)
Time is the total sample collection time (minutes).

8.2 Assessing Quality Control Data

To assess QC data, technical personnel ensure that the QC samples listed in Table 9 were analyzed and that the results meet the listed criteria to be considered acceptable.

Table 9: Quality Control Criteria

QC Sample	Equation[a]	Criteria	Action
Initial Calibration	Regression	r^2>0.99	Recalibrate instrument
Initial Calibration Verification (QL)	$\%R = \frac{\text{Found}}{\text{Expected}} \times 100$	%R = 85 to 115%	Recalibrate instrument
Calibration Check (QL)	$\%R = \frac{\text{Found}}{\text{Expected}} \times 100$	QL %R = 85 to 115% of expected value and every sample is bracketed by valid CC standards	If the %R is not within these parameters, analyze one additional QL standard. If that result is outside the specified range, perform corrective action such as bakeout, instrument maintenance, or recalibration. Acceptable instrument performance must be performed by successfully analyzing two sequential QL standards. If the ending CCV fails high for a particular analyte and that analyte is not detected in the sample, the non-detect value may be reported. The high bias must be documented and narrated.

Table 9: Quality Control Criteria (Cont'd)

QC Sample	Equation[a]	Criteria	Action
Cleanliness	NA	MB concentrations <0.5 times the hazard level for each analyte	Initiate corrective action
Accuracy	$\%R = \frac{\text{SSR}}{\text{SA}} \times 100$	QP recoveries = 75 to 125%	See Paragraph 7.4.3

Expected - the standard concentration; SA - the spike amount; SSR - the spiked sample result

9.0 References

US Army Dugway Proving Ground (DPG), Utah, Waste Permit, Attachment 1-10, *Central Hazardous Waste Storage Facility (CHWSF) Quality Assurance Program Plan.*

Figure 1 – Method Schematic

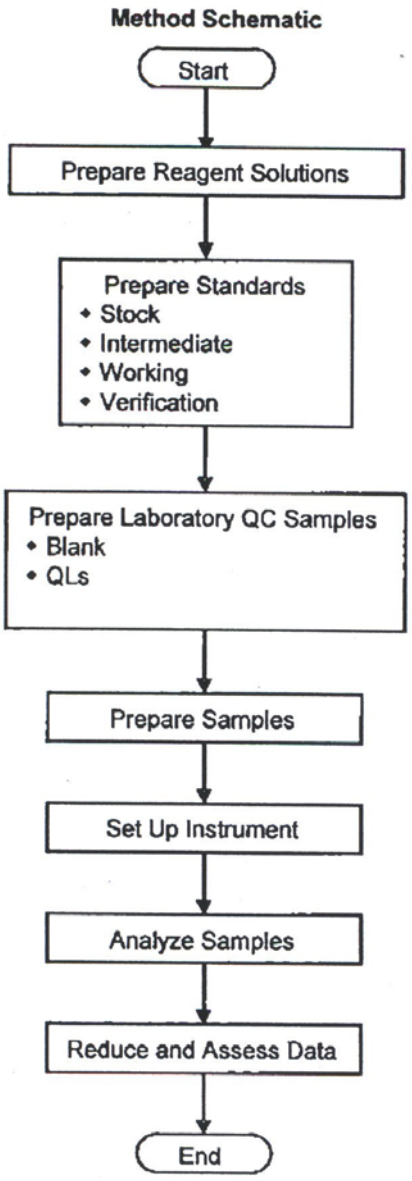


Figure 2

Typical Analytical Sequence

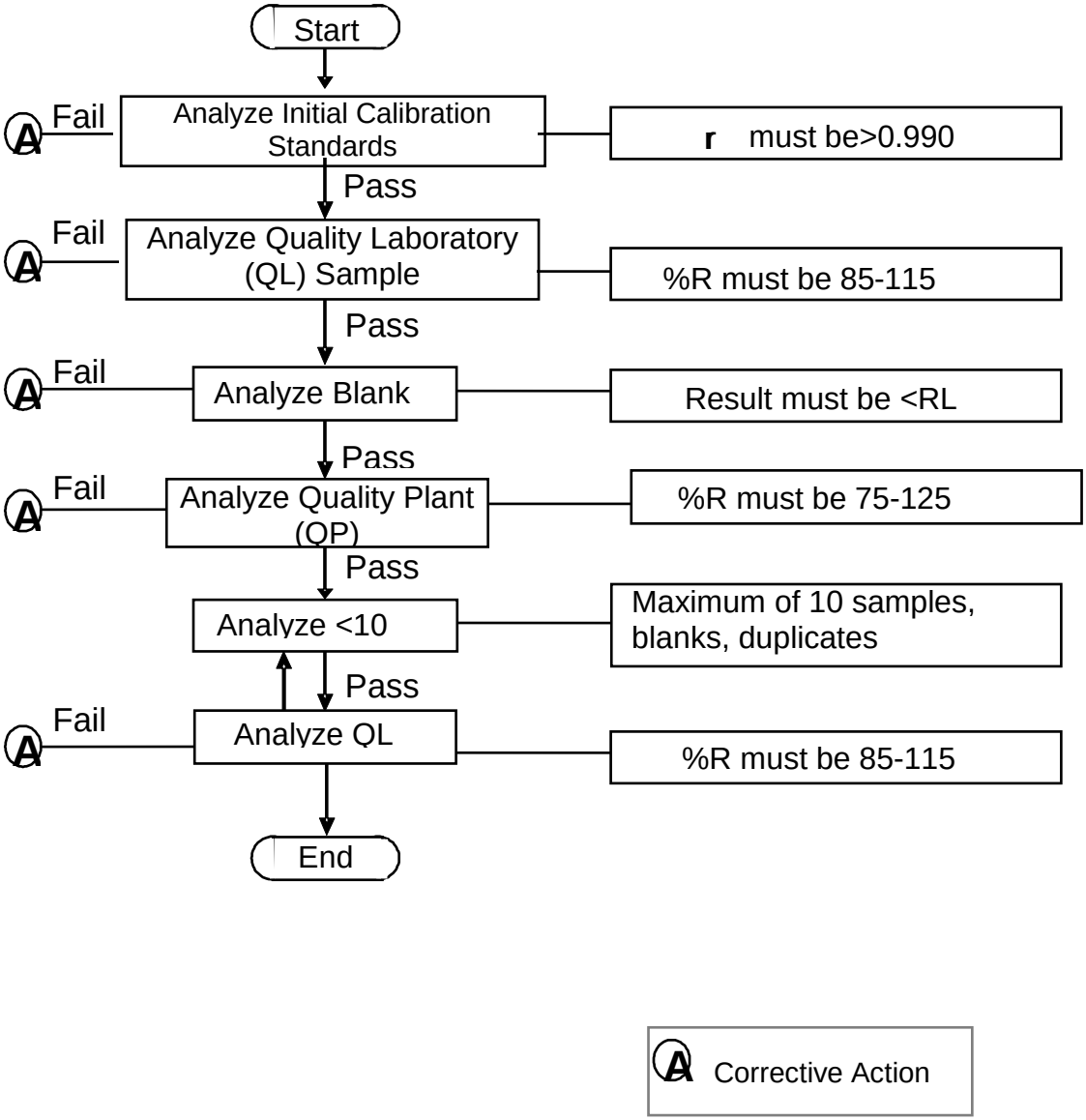
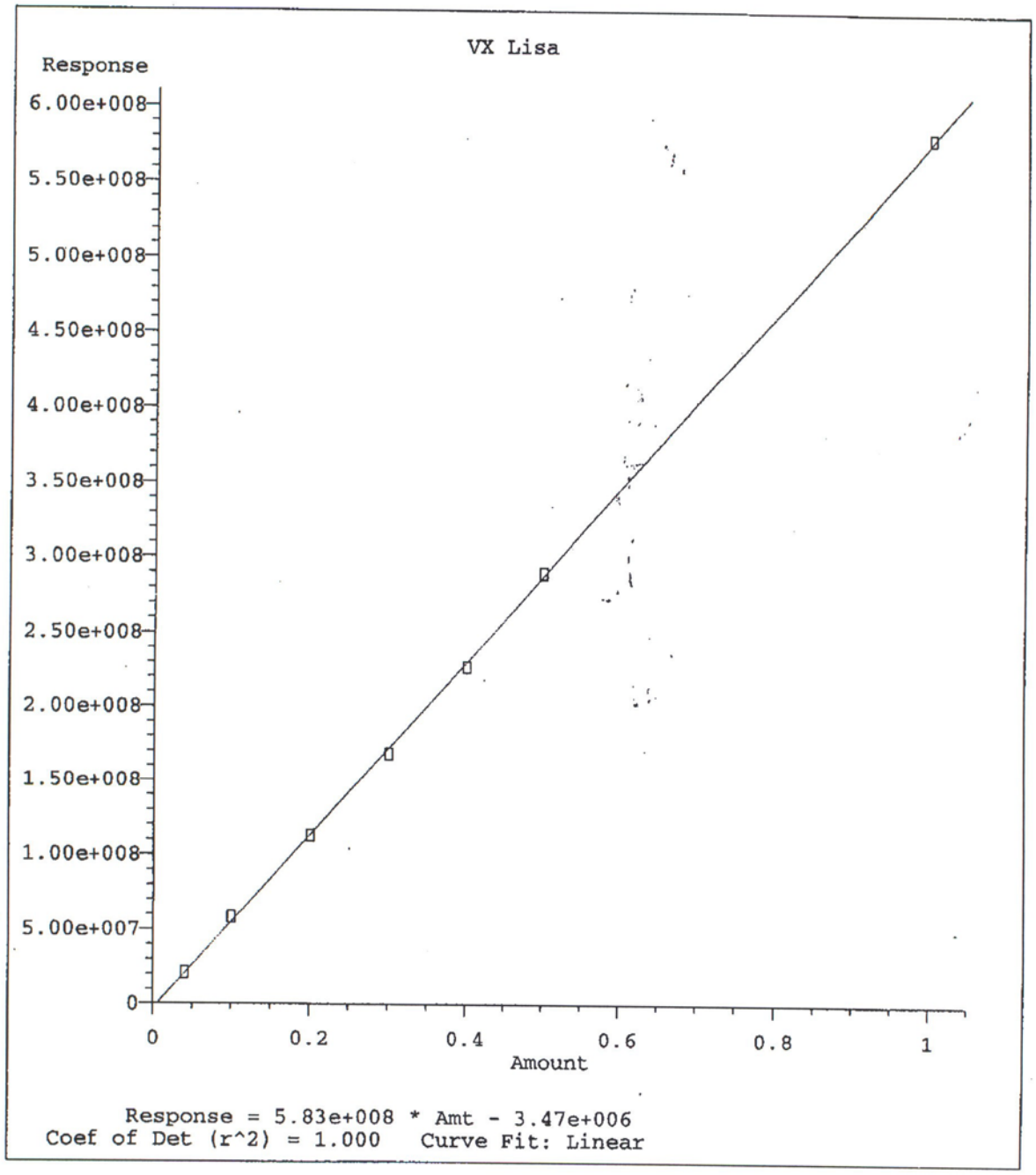


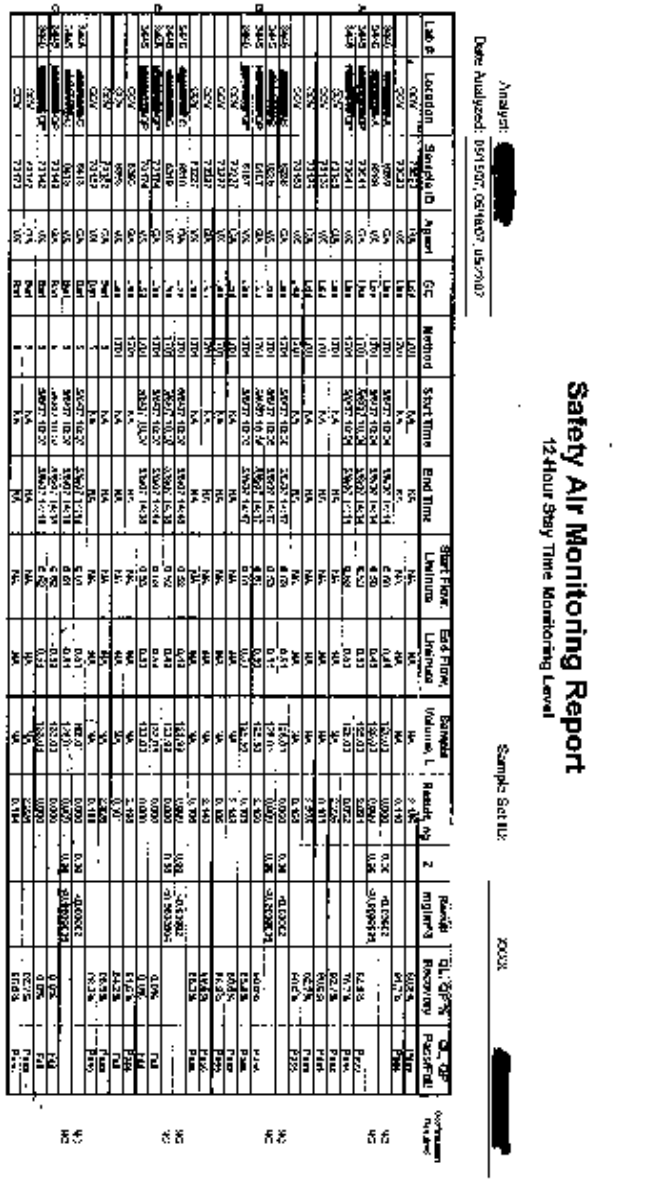
Exhibit A
Depot Area Air-Monitoring System (DAAMS) Calibration Report



Method Name: D:\GC-LISA\METHODS\VXGA_1701_050907.M
Calibration Table Last Updated: Thu May 17 12:53:47 2007

NOTE: VX-o-ethyl-s-(2-diisopropylaminoethyl) methylphosphonthioate

Exhibit B
Depot Area Air-Monitoring System (DAAMS) Data Analysis Sheet



Safety Air Monitoring Report
12-Hour Stay Time Monitoring Level

Analyst: [redacted]
Date Analyzed: 05/15/07, 05/16/07, 05/17/07

Sample Set ID: XXXX

[redacted]