

## MISHAP RISK CONTROL FOR ADVANCED AEROSPACE/COMPOSITE MATERIALS

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### ABSTRACT

Although advanced aerospace materials and advanced composites provide outstanding performance, they also present several unique post-mishap environmental, safety, and health concerns. The purpose of this paper is to provide information on some of the unique hazards and concerns associated with these materials when damaged by fire, explosion, or high-energy impact. Additionally, recommended procedures and precautions are addressed as they pertain to all phases of a composite aircraft mishap response, including fire-fighting, investigation, recovery, clean-up, and material disposal. Due to the infinite variability of mishap scenarios, the guidelines are general in nature and not application-specific. The goal of this project is to provide factual and realistic information which can be used to develop consistent and effective procedures and policies to minimize the potential environmental, safety, and health impacts of a composite aircraft mishap response effort.

### DEFINITIONS

Composite: A physical combination of two or more materials.

Examples: Fiberglass (Glass/Epoxy, Glass/Polyester)

Advanced Composite: A Composite Material made with high strength/high stiffness reinforcement (i.e. fibers) in a matrix (i.e. resin).

Examples: Graphite/Epoxy, Kevlar/Epoxy, Quartz/Cyanate Ester,  
Boron/Epoxy

Advanced Aerospace Material: A highly specialized material fulfilling unique aerospace construction, environment or performance requirements.

Examples: Radar Absorbent Material (RAM), Beryllium, Depleted Uranium

Advanced Composites are distinguished from traditional Composites by their increased relative performance, cost, complexity, and mishap hazard potential. It is absolutely essential that a clear distinction be made between Advanced Composites and Advanced Aerospace Materials.

## SCOPE

This report will focus on the hazards and risks associated with exposure to a significant release of damaged *Advanced Composite/Aerospace Material*. Specific emphasis is placed upon carbon/graphite reinforcement and polymer matrix (thermoplastic and thermoset) advanced composites. Other specific advanced aerospace material issues, including beryllium, Radar Absorbent Material (RAM), and depleted uranium, are lightly addressed.

## INTRODUCTION

Advanced composite materials are pressing the envelope of technology by providing design flexibility and superior performance advantages for both military and civilian aerospace vehicles. Distinguished by high-strength, high-stiffness, low weight, and corrosion resistance, these materials are responsible for significant gains in speed, range, payload, agility, efficiency, and low observability. Not only are advanced composites being used on almost every major new aerospace vehicle, including the B-2 Stealth bomber, F-22 Advanced Tactical Fighter, Delta Clipper launch vehicle, and Boeing 777, but they are also used as repairs and modifications on existing systems as well.

Applications have steadily progressed from early minor control surface applications to recent use in secondary and primary structure. However, the inherent diversity of advanced composites/aerospace materials, underscored by the varied chemical mixtures, constituent materials, processing methods, application environments, and mishap scenarios, has limited our understanding of these materials in a mishap event. In the past, a sharply focused emphasis upon performance has been the driver behind technological advancements in materials and applications that have outpaced our ability to fully understand and support them. Society is no longer willing to accept the benefits of technology without careful observation of the human and environmental effects, both on a short- and long-term scale. Tremendous liability, skyrocketing health and disability costs, increased environmental responsibility, and loss potential concerns in this area make risk control absolutely essential.

In their cured or final form, advanced materials/composites are *generally* considered safe, inert, and biologically benign; however, when damaged by fire, explosion, and/or high-energy impact in a mishap, these materials can present environmental, safety, and health hazards that need to be dealt with appropriately. The material hazards are dependent upon the type, amount,

damage extent, and mishap scenario. In all cases, concentrations drive the level of risk.

## BACKGROUND

The relative "infancy" of advanced composite materials combined with the lack of detailed mishap information have contributed to the current level of understanding and often times, misunderstanding, of composite mishaps. Early aircraft fire and crash studies on advanced composites such as the Air Force CORKER program (1975) and HAVE NAME program (JTCG/HN 1 May 81) have incorrectly led to several *fallacies* concerning mishap hazards, including:

- Release of material will cause widespread electrical blackout.
- Dispersed composite material is biologically malignant and should be treated like asbestos.
- Large concentrations of particulates can be carried very long distances downwind in the smoke plume.
- Fractured composites are all deadly razor sharp
- Extreme protection is always required

In fact, these claims have proven to be over-reactive or inaccurate by new research and experience. Although on-going research has often been inconclusive, evidence shows that burned or exploded advanced composites DO cause personnel health and safety problems IF they are not properly protected. Although generally conflicting in nature or narrowly focused, all of the health studies recommend caution and state that unknown health hazards do exist. It should be emphasized that advanced composites are comprised of a complex mixture of materials whose composition, concentration, and toxicity may be unknown, especially in a synergistic mishap environment. For this reason, a high degree of precaution with conservative protection is recommended until the hazard exposures can be characterized for an "optimal" response.

## DISCUSSION

A hazard is defined as "a condition or changing set of circumstances that presents a potential for injury, illness, or property damage." Likewise, it can be described as "the potential or inherent characteristics of an activity, condition, or circumstance which can produce adverse or harmful consequences." In this light, the hazards associated with mishap damaged advanced composites/aerospace materials need to be addressed with a risk control mindset. Essentially, risk control is the process of minimizing

accidental and other extraordinary losses by anticipating and preventing unplanned events. It emphasizes the complexities of exposures and encompasses broad areas of risk, which are indicative of a mishap scene. Additionally, risk control is based on the control of exposures through knowledge and preparation. It is both a pre- and post-loss effort. With this fundamental basis intact, the specific hazards can be addressed and minimized.

Damage to advanced composites materials caused by fire, explosion, and/or high-energy impact in a mishap presents unique environmental, safety, and health hazards. In typical aircraft fires of 1000 to 2000°C, organic matrix materials, or polymers, burn off around 400°C, creating toxic combustion or pyrolysis products and liberating the reinforcement, or fibers. Depending on the fiber, the reinforcement dynamics can vary. Glass or aramid fibers tend to melt under extreme heat, whereas carbon or graphite fibers are oxidized by the heat, thereby altering their size, shape, porosity, and other characteristics. The intense thermal and mechanical forces in a mishap generally cause "explosive" fracture or debonding and degradation of advanced composite structures. While absorbing this energy, the reinforcement, usually stiff and strong, may be broken into particulate fibers, turned to dust, or protruding from the vehicle structure. Because of their stiffness, carbon fibers can readily penetrate the skin. Boron fibers can penetrate bone. Furthermore, the absorbed and adsorbed pyrolysis and combustion products (assumed toxic) on activated, oxidized fibers can be an important injection or inhalation hazard. These types of wounds readily inject the toxins into the body. This phenomenon could be especially critical in mishap scenarios where bloodborne pathogens may be present on damaged debris. In all cases, the type, amount, and extent of damage to advanced composites drive the level of health hazard because concentrations are key.

Coupled with heat, shock, and fragmentation, several different types of damage occur. The effects can range from a simple reduction in strength on one end of the spectrum, to a loss of Low Observable (LO) performance, delamination, debonding, charring, melting, burning, and vaporization at the other extreme. Although advanced composite/aerospace materials represent only one of the many hazards associated with an aerospace mishap (fuel, weapons, metals), they do merit increased awareness because of their hazard potential and persistence. Exposures to the potentially harmful vapors, gases, composite particulates, and airborne fibers generated in a composite mishap need to be controlled because of the symbiotic effect of the dispersion forces and complex chemical mixtures.

Exposure routes for the safety and health hazards of damaged advanced composites/aerospace materials include absorption (contact), inhalation, injection, and ingestion. The toxicology of respirable particulates (3-5 microns) and the disease-producing potential associated with them is a function of: 1) the dose or amount of particulates in the lung; 2) the physical dimensions of deposited particulates; and 3) the particulate durability (lifetime) in the lung. Fire-exposed carbon fibers tend to break into shorter lengths and split into smaller diameters, thereby affecting the aspect ratio. In turn, this increases the probability for respiration and ease of transport. Dry and windy conditions at a mishap site increase dispersion of liberated particulates. Whether inhaled or injected, advanced composites (because of their stiffness) are not easily removed or expelled efficiently. This is especially true for brittle, oxidized fibers. Potential health and environmental effects from damaged advanced composites include dermal and respiratory problems, toxic products, contamination, and, in the case of advanced aerospace materials, radiation. Exposure of unprotected personnel may lead to acute or chronic respiratory and dermal problems. Mechanical injection or cuts are the most common skin hazard, although sensitization (local and systemic) can occur. Off-gassing, toxic products in the smoke plume, smoldering debris, and airborne fire-damaged particulates are the primary respiratory hazards. Examples of combustion products include: Hydrogen cyanide, sulfur and silicon dioxide, formaldehyde, hydrogen fluoride, ammonia, hydrochloric acid, hydrogen sulfide, isocyanates, halogenated compounds and aromatics.

Mishaps involving advanced composites that are electrically conductive (i.e. graphite or carbon fiber) may present electrical shorting or arcing problems if very high concentrations exist (usually at the immediate mishap site only). This may result in electrical equipment degradation or failure, including communication interference, although this is rare. Tests have shown that widespread electrical failure due to environmental release and plume dissipation is highly unlikely, except for the immediate mishap site. Despite the low probability of failure, the risk is always present. Carbon fibers are also influenced by the presence of electrostatic fields, causing them to settle in high voltage areas and reduce the local dielectric properties of free air. This may cause equipment malfunction or failure.

Given the existing and projected increases in advanced composites usage for aerospace applications, realistic policies and procedures that focus on minimizing the safety and health hazards of advanced materials are needed. As the knowledge base grows and the mishaps are characterized, the procedures can be situationally optimized in terms of cost and performance while still maintaining a safe public environment.

Based upon the basic hazards already known to exist, and the fact that there are still unknown risks, personnel safety and health precautions are necessary. Administrative controls, including adequate personal protective equipment (PPE) and worker safety practices need to be immediately implemented because the field environment is not conducive to engineering controls. Risk control biased towards conservative measures is essential.

The major issues currently affecting mishap response for damaged advanced composites are:

1. Fiber dispersion and re-dispersion
  - Including an understanding of the mishap dynamics, effective response procedures and hold-down material (fixant) suitability
2. Synergistic material and combustion effects
  - The combined effects of varied materials and their damage extent
3. Concentrations and compatibility
  - Exposure limits and necessary protection measures, also includes equipment, procedural, and suppression agent compatibility issues
4. Adsorbed and absorbed pyrolysis products
  - The impact and extent of the toxin hazard
5. Site and equipment contamination
  - Including the type and extent of contamination
6. Clean-up and disposal complications (Haz-Mat)
  - Evaluate decontamination methods and determine proper disposal methods and classifications of the waste debris
7. Peripheral Issues (Bloodborne Pathogens)
  - The potential for multiple injections of Hepatitis B and HIV caused by infected remains on damaged advanced composites

These issues are compounded by non-existent or inconsistent material, medical, fire/combustion, environmental, disposal, and operational information. The solution lies in continued research, testing, and the application of experience to provide a knowledge base from which operational guidance may be based.

Because aircraft crashes occur under a diverse assortment of weather and terrain conditions, with widely varying degrees of airframe destruction, a universally applicable set of risk control precautions is not practical. The complex and often times unknown hazards, diverse locations, and infinite variables of a mishap involving advanced composites require conservative protective measures. This includes all phases of a mishap response ranging from first response and firefighting, to investigation, clean-up, recovery, and disposal. A complete "Cradle-to-Grave" mentality must be adopted.

Firefighters (first responders) are considered the primary response group and are subjected to the greatest material hazards; however, they are the best protected in all but the most extreme cases with Self Contained Breathing Apparatus (SCBA) and their bunker or proximity suits. Protection should be worn until the composite fires have been completely extinguished, cooled to a temperature of 300°F (149°C), and no intense smoldering exists. The potential exposure to composite mishap hazards may be more severe for secondary exposure groups, including all of the subsequent response operations, than for initial fire fighting activities because of the duration of exposure and reduced levels of protection. In any case, the hazards exposures are minimal if Personal Protective Equipment (PPE) and proper procedures are used, including:

#### Advanced Composite Mishap Response PPE Guidelines

- A. Burning or Smoldering Composites
  1. Self Contained Breathing Apparatus (SCBA)
  2. Full protective clothing (NFPA 1971/76)
  3. Do NOT use rubber gloves
- B. Broken or Splintered Composites (Post-Fire or Explosion)
  1. Full-face respirator w/dual cartridge filters: High Efficiency Particulate Air(HEPA) and organic dust/mist
  2. Coated, hooded Tyvek disposable suit with booties
  3. Leather work gloves (outer)
  4. Nitrile rubber gloves (inner) [No surgical gloves]
  5. Hard-soled work boots (Steel toe/shank are best)
- C. Peripheral Area Composite Exposure
  1. Long-sleeve work clothing
  2. HEPA filtered respirator
  3. Adequate eye protection (Goggles, or safety glasses)
  4. Leather work gloves (outer)
  5. Nitrile rubber gloves (inner)
  6. Hard-soled work boots (Steel toe/shank are best)

All affected personnel need to know both the hazards and the proper response for mishap risk control. This makes coordination and communication among all groups absolutely essential. Likewise, knowledge and training, accompanied by common sense and good judgment, is key. In order to maximize response effectiveness and minimize hazard exposures, risk control must be exercised using the most current and factual information obtained from all sources, including the military, government, private, industry, academic, and international sectors. This must then be universally applied in operational guidance and constantly updated to reflect revised knowledge.

## MISHAP RISK CONTROL GUIDELINES

The following guidelines are recommended:

1. First Responder(s) [Firefighters] shall conduct an initial survey for:
  - a. Signs of fire damaged composites
  - b. Presence of loose/airborne fibers and particulate
  - c. Prevailing weather conditions/wind direction
  - d. Degree of site exposed to fire/impact/explosions
  - e. Local/proximal equipment/asset damage and hazards
  - f. Exposed personnel
2. Establish control at site.
3. Evacuate areas in the immediate vicinity of the mishap site affected by direct and dense fallout from the fire/explosion generated smoke plume, along with easily mobile and critical equipment. Alter/move aircraft and flight operations exposed to the immediate fallout area. Restrict all unprotected personnel from assembling downwind of the site.
4. Extinguish fire and cool composites to below 300° F (149° C). ONLY fire fighters equipped with self-contained breathing apparatus (SCBA) are authorized in the immediate vicinity of a burning/smoldering mishap site until the fire chief declares the area fire safe. If possible, care should be taken to avoid high-pressure water break-up and dispersal of composite materials.
5. No ground or flight operations are to be permitted within 500 feet above ground level (AGL) of the site and 1,000 feet horizontally.
6. Cordon off the mishap site and establish a single entry/exit point. Only sufficiently protected individuals are authorized in the immediate mishap site and peripheral area (contamination reduction zone). The peripheral area is designated in a coordinated effort by the fire chief and bio-environmental engineer and /or the on-scene commander. As a guide, the peripheral area should be defined as more than 25 feet away from damaged composite parts, although it may vary depending upon environmental conditions (rain, dry, high winds, remote site, etc.).
7. If personnel other than those at the accident site have been directly and significantly exposed to material and smoke hazards, the medical staff will be consulted for evaluation and tracking. Advise the otherwise unthreatened populace in affected or fallout areas of precautions.



8. Access to the crash site to conduct a more thorough survey will be coordinated with the Incident Commander (IC).

a. Identify specific aircraft hazards by inspection and consulting with crew chiefs or weapons system manager, reference documents, contractor, or aircraft specialists. Indicate composites and other hazardous materials to response personnel.

b. Minimize airborne particulates/fibers by avoiding excessive disturbance of the dust by walking, working, or moving materials at the crash site to minimize airborne particulate fibers and dust.

9. Entry/exit from the Entry Control Point (ECP) will be monitored. The following guidelines apply:

a. When exiting the crash site, personnel should use High Efficiency Particulate Air (HEPA) filtered vacuums, if available, to remove advanced composite contaminants from their outer clothing, work gloves boots, headgear, and equipment. If unavailable, efforts must be made to wipe or brush off as much contamination as possible.

b. Clean sites (i.e., tent or trailer) for donning/removal of PPE should be set up as practical.

c. No eating, drinking, or smoking is permitted within the contamination reduction or exclusion zone of the crash site, or as otherwise determined by the on-scene commander. Personnel must be advised to wash hands, forearms, and face prior to eating, drinking or smoking.

d. Wrap and seal contaminated protective clothing and dispose of properly.

e. Personnel should shower (in cool water) prior to going off-duty to preclude injury from loose fibers. Portable showers may need to be provided for this.

f. When practical, remove contaminated outer garments of victims/response personnel at the scene to protect the medical staff. Advise the local medical staff of any ill effects believed to be related to exposure to the advanced composite materials. All contaminated footwear should be

cleaned to limit the spread of debris in the area and inside support vehicle. Symptoms of effects include, but are not limited to:

- (1) Respiratory tract irritation and reduced respiratory capacity
- (2) Eye irritation
- (3) Skin irritation, sensitization, rashes or infections

Material safety data sheet (MSDS) information should be made available to qualified personnel. Security restrictions may require additional control measures during emergencies.

### CONTAINMENT

10. Secure burned/mobile composite fragments and loose ash/particulate residue with:

- a. Plastic
- b. Firefighting agent
- c. Fixant material
- d. Tent

Carefully wrap the coated parts and/or material with plastic sheet/film or place in a plastic bag that is minimum of 0.006 inches (6 mils) thick. Generic garbage bags are generally inadequate unless several are used as plies.

NOTE: Fire fighting equipment should be available during fixant/stripper application, aircraft break-up and recovery.

CAUTION: Fire must be completely out and the composites cooled to below 300° F (149° C).

11. Consult specific aircraft authority and the investigators before applying fixant. Safety concerns may override any delayed application. Two types of fixants are used: one for burned composites and debris, and the other for land surfaces. Fixant is usually not needed for open terrain and improved surfaces (concrete or asphalt) unless high concentrations exist.

- a. Obtain a fixant or "hold-down" solution, such as Polyacrylic acid (PAA) or acrylic floor wax and water. Light oil is not recommended because it may become an aerosol and collect on equipment, hamper material investigations, and present a health hazard. Generic acrylic floor wax, available at a wide variety of stores, should be mixed in a 10:1 water to wax ratio, although this may vary.

b. Apply (preferably spray) a heavy coating of the fixant solution to all burned composite materials and to areas containing scattered/settled composite debris. Completely coat the material until wet to ensure the particulate fiber/dust is immobilized. Allow the coating to dry.

NOTE: Strippability of the fixant coating is required where coatings are applied to debris that must later undergo microscopic analysis by incident investigators. Care must be exercised in the use of the stripping solutions since they can react with some materials and the process of stripping may damage the parts. PAA may be removed by a dilute solution of household ammonia (about 1% by volume of ammonium hydroxide in water) or trisodium phosphate (approximately one 8 ounce cup trisodium phosphate per 2 gallons of water).

12. If deemed necessary, agricultural soil tackifiers may be used to hold materials on sand or soil. Most solutions can be sprayed onto the ground at a rate of 0.5 gal/sq. yd.

13. Improved hard surfaces (i.e. concrete, asphalt) should be vacuumed (with an electrically protected vacuum). The effluent should be collected via plastic or burlap coated trenches or drainage ditches. Sweeping operations should be avoided as they disseminates the particulate debris.

14. Immediately flush/clean fixate-application equipment with a dilute solvent to avoid clogging.

15. Pad all sharp projections from damaged composite parts to prevent accidental injuries.

NOTE: The entire impact or accident site must be diked to prevent run off of AFFF fire fighting agent (to avoid additional clean-up and fines).

16. Fire fighting vehicles and equipment must be decontaminated at the accident site by washing with water or use of vacuums.

#### CLEAN-UP AND DISPOSAL CONCERNS

17. Conduct material disposal according to local, state, federal, and international guidelines. The nearest DoD, government, or private environmental management office should be contacted for relevant disposal procedures for the advanced composite parts/materials which do not require accident investigation evaluation, repair, or are not needed. Ensure the parts are released before disposal is authorized.

18. Place hazardous waste material in containers and disposed of appropriately as hazardous waste. If possible, a HEPA vacuum should be used to clean-up the local area. All crash debris, vacuum bags, coverall, gloves, and any other contaminated materials should be properly disposed and labeled appropriately with the following: "Composite Waste. Do Not Incinerate. Do Not Sell For Scrap. Composite Waste".

19. For open terrain mishap areas, the appropriate soil and surface restoration will be completed.

20. If aircraft were subjected to the smoke and debris of the immediately affected area, the following should be undertaken:

- a. Vacuum the air intakes with an electrically protected vacuum cleaner.
- b. For internally ingested smoke, visually and electronically inspect all compartments for debris and vacuum thoroughly.
- c. Prior to flying, perform electrical checks and engine run-up.

21. For significantly affected structures and equipment:

- a. Thoroughly clean all antenna insulators, exposed transfer bushings, circuit breakers, etc. Inspect air intakes and outlets for signs of smoke or debris and decontaminate, if necessary.

22. Continue to monitor affected personnel, equipment, and mishap site.

## **CONCLUSIONS**

Advanced composites/aerospace materials are the driving force behind the materials enhancements in speed, range, payload, and performance of the worlds most technologically advanced aerospace vehicles. Yet, when damaged by fire, explosion, or high-energy impact, these materials pose unique environmental, safety, and health hazards in all phases of a mishap response. As the usage of these materials steadily increases and the application mediums proliferate, it is absolutely essential to know, understand, and respond appropriately to the hazards they present. The variability in weather, terrain, location, type, amount, and damage extent of mishaps make universal risk control protection and procedures essential. The bottom line is to protect people, property, and the environment with a realistic and optimal mishap response. Knowledge and training are the fundamental cornerstones of employing realistic, although conservative, personal protection and procedures. Risk Control is THE solution.

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# **Sampling and Analytical Methods for Aromatic Amines (MDA Replacements)**

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## **Tools for Monitoring Exposure**

### **Air monitoring**

- **Exposure by inhalation route**

### **Surface monitoring**

- **Dermal exposure**

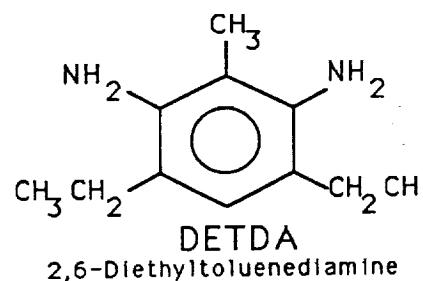
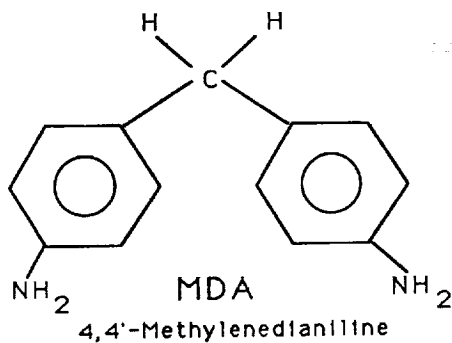
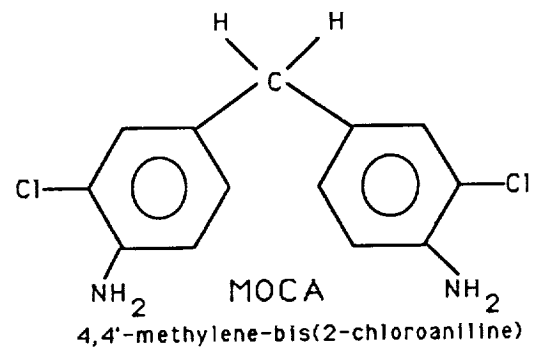
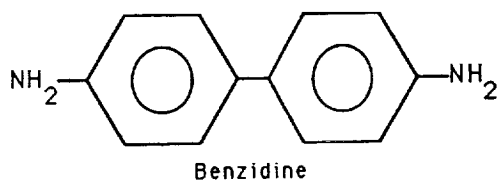
### **Biological monitoring**

- **Exposure by all routes**
  - Inhalation
  - Dermal
  - Ingestion

# Major Urine Metabolites of Aromatic Amines

<b>Benzidine</b>	Hydroxy-, mono- and diacetyl- benzidine (+ N- glucuronides)
<b>MOCA</b>	(+ N-glucuronide)
<b>MDA</b>	mono-acetyl MDA (+ N-glucuronide)
<b>TDA</b>	mono- and diacetyl TDA

## Comparison of Aromatic Amine Structures

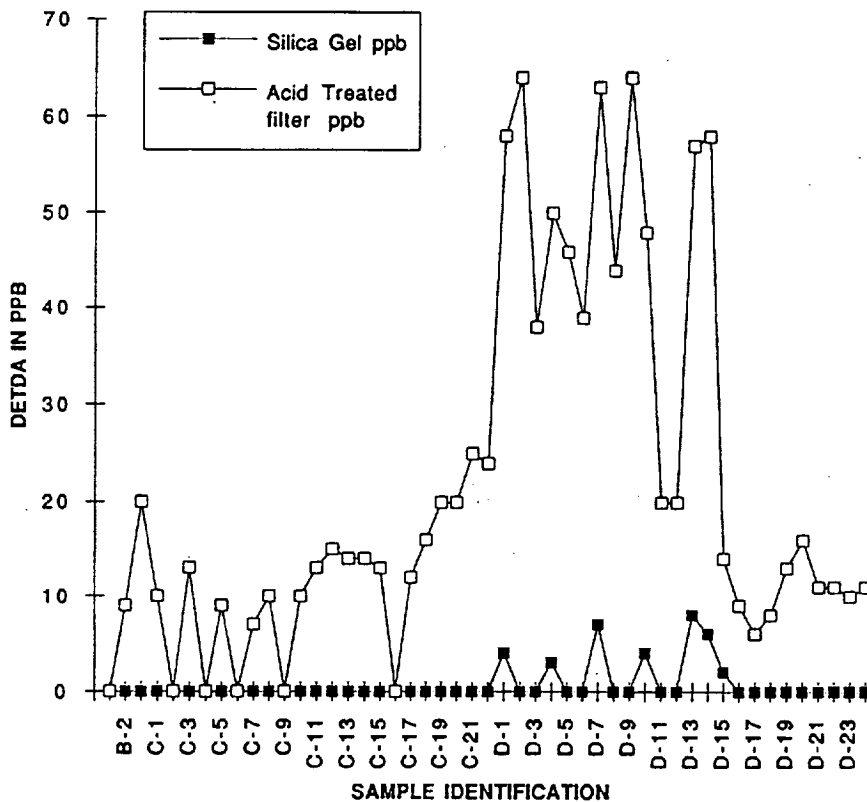




# Air Monitoring

- Indicates level of potential exposure by inhalation
- Does not monitor exposure by other routes
- Currently no proposed airborne limit (TLV or PEL) for DETDA
- Currently no NIOSH analytical method for DETDA (Ethyl Corp. has method)

## Comparison of Silica Gel Sorbent Tubes with Acid-Treated Fiber Filters DETTA in Air (Personal Samples)



# Surface Monitoring Wipe Testing

- Use to identify potential sources of dermal exposure
- Tests the effectiveness of decontamination procedures
- Can be used to test the effectiveness of personal protective gear
- Spot tests are non-specific. All primary amines will respond to some degree
- Lab analysis necessary for identification
- Does not necessarily correlate with actual exposure

# Biological Monitoring

- All routes of exposure are monitored
- Level of physical activity is reflected in the measurement
- Tests the effectiveness of personal protective equipment
- Assumptions are made to set exposure limits

# **Biological Monitoring**

## **Single ring aromatic primary amines**

### **DETDA, TDA, PPD**

#### **Collection**

**End of shift urine**

#### **Handling/storage**

**No preservatives**

**Freeze**

#### **Shipment**

**Overnight delivery**

## **Analysis of Aromatic Amines in Urine**

- **Base hydrolysis- converts metabolites back to parent compound**
- **Solvent extraction- high solvent to urine ratio**
- **Derivatize amine with heptafluorobutyryl chloride**
- **Analyze by GC/MS in the negative chemical ionization mode**

