ABSTRACT

When it comes to complex petroleum-derived materials, test materials used for skin-painting assays need to match what workers are typically exposed to in the workplace, which is no easy task for bitumen fumes. This study had two fundamental goals:

- Collect enough bitumen fumes (from US paving and roofing industries) for a two-year animal skin painting study that match worker exposure
- Perform detailed chemical and biological testing
- Validate fumes to worker exposures

Duplicate the National Institute for Occupational Safety and Health (NIOSH) laboratory protocol using the same source of bitumen fumes and the same analytical balance.

Approach

- Select bitumens
- q 4 Straight Run (Paving) Bitumens (CAS 8052-42-4)
- q PG 64-22 Asphalts
- q Based on prominence of use in US
- q From 4 major Crude Sources
- q No RAP or modifiers in Field Studies
- q From 4 Oxidized (Roofing) Bitumens (CAS 8474-03-4)
- q Type III Bufler
- q From 4 major Crude Sources
-q Based on prominence of use in the US

- Use same bitumen for field exposures and large volume fume collections (~650 grams each)
- Collect worker and mannequin samples from paving and roofing operations to guide large volume fume collection
- Collect ~650 grams of each bitumen fume using the Fraunhofer Institute for Toxicology and Experimental Medicine (ITET) protocol(1-2), guided by worker samples
- Generate fumes from one of the roofing materials using the NIOSH / Silvex protocol
- Prepare skin-painting materials in mineral oil for dosing
- Validate all materials through analytical testing

RESULTS

Field Collection of Worker Bitumen Fume Exposures

Two bitumen fume generation methods were selected to optimize the capture of the most toxicologically relevant components.

Distinctions between paving and roofing fume samples are outlined. Bitumen fumes from the paving sources produced from four different crude sources were quite similar to each other in a number of the tests performed. Bitumen fumes from the roofing sources also were very similar to each other. On the other hand, fumes generated using the NIOSH protocol show results that significantly differ from the corresponding worker exposures.

Analytical Tools & Criteria

- Simulated Distillation
- Flammability
- Fluorescence (4 channel test) and IR
- PAH analysis (US EPA 8270A)
- Fingerprinting by GC/MS (Selected ion comparisons)
- GC/MS and SIMS characterization of complex combustion products generated from bitumen by four different test methods

Figure 2: LARGE-VOLUME Fume Collection Methods

A. Dr. Pohlmann (Fraunhofer ITET) trained our personnel using their protocol, which was then tested.
B. These heated lines were fed into a storage chamber containing the pumps and remaining collection equipment.
C. Fumes were drawn through cooling output into the collection chamber.

C. Analytical fume system (a replication of the NIOSH protocol used for skin-painting studies in the 1980s) was generated and used for fume collection in the laboratory.

D. The lower temperature of the original study produced fumes different from the corresponding worker exposures.

Test Materials Validated:

- How were the Test Materials Validated?
  - How were the Fumes Prepared for dosing?
  - Preparing at 189.5°C (101°C for field)
  - Final post-reactor volume to match IH fume test volume
  - Preparing at 189.5°C (101°C for field)
  - Final post-reactor volume to match IH fume test volume
  - Preparing at 189.5°C (101°C for field)
  - Final post-reactor volume to match IH fume test volume

Figure 3: GC/MS Selected Ion Fingerprinting

How were Asphalt Fume Condensates (AFCs) Validated?

- How were the Test Materials Validated?
  - How were the Fumes Prepared for dosing?
  - Preparing at 189.5°C (101°C for field)
  - Final post-reactor volume to match IH fume test volume
  - Preparing at 189.5°C (101°C for field)
  - Final post-reactor volume to match IH fume test volume
  - Preparing at 189.5°C (101°C for field)
  - Final post-reactor volume to match IH fume test volume

Figure 4: Mutagenicity Index Data (MI)

How were the Fumes Prepared for dosing?

- Preparing at 189.5°C (101°C for field)
- Final post-reactor volume to match IH fume test volume
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- Final post-reactor volume to match IH fume test volume
- Preparing at 189.5°C (101°C for field)
- Final post-reactor volume to match IH fume test volume

SUMMARY

In summary, four paving (straight run) and four roofing (oxidized) bitumens representative of the most commonly used binders in the respective U.S. industries today were collected and validated in this study. Fumes were generated from these bitumens and compared to industrial hygiene measurements of worker exposures. Using the Fraunhofer-ITET method of fume collection, six out of eight of these samples met all of the acceptance criteria for comparability to industrial hygiene exposures. Fumes generated using the Silvex method, however, did not meet these criteria, showing a marked increase in carcinogenic and mutagenic potential by all indicator tests (MI and fluorescence) as compared to the tank samples that much more closely matched worker exposure.

From test materials generated in this study, one roofing fume (TR-A) and its corresponding laboratory generated roofing fume (LR-A) and one paving fume (TP-D) were validated and used in a two-year skin-painting assay. These materials were prepared for skin-painting assays in a mineral oil diluent. All test batches were confirmed as meeting the acceptance criteria in terms of concentration and composition by our laboratory and by an outside testing facility (Fraunhofer ITET).

REFERENCES


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