Development of a Skin Exposure Dosimeter for Methylene Diphenyl Diisocyanate (MDI)

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Research Purpose: Skin exposure to isocyanates is suspected to play a role in sensitization. Therefore the use of reliable and sensitive quantitative techniques is essential for skin exposure assessment in occupational settings.

Relevance: Methods used to assess skin exposure to isocyanates have employed removal techniques (tape stripping, wiping) to collect isocyanates deposited on the skin surface. The chemically reactive nature of the different isocyanate species, especially aromatic isocyanates such as MDI, the sampling media used for sample collection, and sampling time after exposure are factors that can lead to substantial underestimation of workplace skin exposures measured using removal techniques. To address these issues, an alternative skin dosimeter based on an interception technique using cotton gloves was developed and field tested in workers producing polyurethane products.

Participants: Human subjects participated in the pilot field testing of the skin dosimeter. Participants in the study were all workers in a polyurethane (PU) production plant who provided written informed consent.

Methods: Cotton gloves were impregnated with the derivatizing agent 1-9-anthracenylmethyl-piperazine (MAP). Experiments included laboratory investigations to asses MDI losses due to reaction with the cotton glove fabric, and optimization of impregnation and loading of the MAP reagent on the fabric. A protocol for field use and sample preparation and analysis in the laboratory was also developed.

The study was approved by Yale University's institutional review board, and all work was performed in accordance with Yale University's rules regarding the ethical conduct of clinical research and protection of human rights.

Analysis: The skin dosimeters were analyzed by a newly developed LC-UV-MS/MS method. The method can quantitate accurately and with high sensitivity 4,4'-MDI, 2,4'-MDI, 2,2'-MDI, MDI trimer, tetramer and pentamer. The limit of detection for 4,4'-MDI was 10 pg/mL. Only 4,4'-MDI results are presented here. 4,4'-MDI represents at least 50% of the total NCO in bulk materials.

Results: A total of 15 pairs of dosimeters were collected from 6 different workers in the plant. From the 15 pairs, 378 samples were processed and analyzed in order to understand temporal (0.25-8 hr duration) and spatial variation (9-18 regions/hand) of isocyanate skin exposure. Samples were quantitated for 4,4'-MDI, 2,4'-MDI, 2,2'-MDI, MDI trimer, tetramer and pentamer.

Full shift values (from consecutive dosimeters) ranged from 5.9 to 200 µg of 4,4'-MDI/worker. Surface area adjusted values ranged from 10.8 – 366 ng MDI/cm2. Highest exposures were found in the dominant hand, in the regions of the palm and thumb, consistent with the performed tasks and material handling. Surface area adjusted MDI values measured with the skin dosimeter are at least 10 fold higher than the corresponding values obtained with removal techniques (wipes and tape strips).

Conclusions: Potential for skin exposures to isocyanates exists in various settings. Removal techniques may underestimate skin exposure to reactive aromatic isocyanates. Interception techniques that rely on reagent impregnated media and mass spectrometry-based quantitation may provide a more accurate assessment of potential skin exposure to isocyanates.

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