

Biomarkers of oligomeric 1,6-hexamethylene diisocyanate exposure in the automotive refinishing industry

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Background: Spray-painters in automotive refinishing industries are exposed to the oligomeric trimer of 1,6-hexamethylene diisocyanate (HDI) monomer, HDI isocyanurate, a sensitizing agent that poses a significant risk for acute and chronic health effects. Biomonitoring of HDI exposures has been mostly limited to quantification of 1,6-diaminohexane (HDA), the hydrolysis product of HDI monomer, in urine or plasma. Since biomarkers of HDI monomer exposure are not appropriate biomarkers of oligomeric HDI exposures, the magnitude and distinct characteristics of HDI monomer and oligomer exposures, and their relationships to their biomarkers, needs to be determined in exposed workers.

Approach: We hypothesized that trisaminohexyl isocyanurate (TAHI), a hydrolysis product of HDI isocyanurate, is quantifiable in urine or plasma, and is associated with HDI isocyanurate exposures. Towards this goal, sample extraction and analytical methods were developed to measure TAHI levels in urine and plasma from 47 spray-painters whose HDI monomer and HDI isocyanurate exposures, and HDA biomarker levels, were previously characterized. Samples were acid hydrolyzed, extracted with dichloromethane, and derivatized with acetic anhydride for analysis of TAHI by nano-UPLC-ESI-MS/MS.

Results: TAHI biomarker levels were associated with HDI isocyanurate inhalation exposure and task duration in both linear regression and mixed model analyses ($p < 0.05$) and were also correlated with HDI monomer exposures. As expected, HDA levels were observed to be unsuitable biomarkers of HDI isocyanurate exposure.

Conclusions: Based on results obtained in this study, painting in downdraft booths, wearing nitrile or neoprene gloves, and wearing full-face air purifying, PAPR, or supplied-air respirators offers the greatest combination of respiratory and skin protection to reduce hazardous HDI exposures (and biomarkers of exposure) in automotive spray-painters. The method developed for TAHI quantification from in urine and plasma is a notable advancement in the arena of HDI exposure assessment and will advance future investigations into oligomeric isocyanate exposures, and associated biomarkers and health outcomes.