Occupational Hygiene Survey of Exposure to Diisocyanates and Their Corresponding Diamines in a Variety of Exposure Scenarios

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Introduction

Diisocyanates are widely used in a range of processes, some of which may lead to the generation of the corresponding diamine. Biological monitoring, which is used increasingly to determine whether exposure to diisocyanates has occurred, is based on the measurement of the corresponding diamine in urine. As such there may be issues in determining whether raised diamine urine levels are due to diisocyanate exposure or direct exposure to process-generated diamines. Knowledge of the extent of diamine formation during different processes would be beneficial due to the different health risks associated with these chemicals (sensitisation versus carcinogenicity).

Method

Seven site visits were conducted at sites using diisocyanates in casting, spray painting, foam blowing and floor screeding. Air monitoring and glove analysis (inner cotton liners) were conducted for both the relevant diisocyanate (MDHS25/3) and its corresponding amine (MDHS475). Urine samples were measured for the corresponding amine (Jones et al., 2013) in pre- and post-shift samples over a number of days following the site visit.

Table 1: Summary of companies visited, isocyanates used and applications

<table>
<thead>
<tr>
<th>Company</th>
<th>Isocyanate</th>
<th>Process</th>
<th>Aerosol?</th>
<th>Anaest?</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>MDI</td>
<td>Casting</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>B</td>
<td>MDI</td>
<td>Spraying</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>C</td>
<td>MDI</td>
<td>Spraying</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>D</td>
<td>MDI</td>
<td>Casting</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>E</td>
<td>MDI</td>
<td>Floor blowing</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>F</td>
<td>TDI</td>
<td>Foam blowing</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>G</td>
<td>TDI</td>
<td>Foam blowing</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Results

The results show (Table 1) that no process related diamine generation was associated with casting or floor screeding. Diisocyanate air levels (all using MDI) for these processes were also very low but significant amounts were detected on gloves. Urine levels of MDA were significant for two of the companies (not detected in company A) and were positive in multiple pre- and post-shift samples. Levels of MDA detected were considerably greater than would be expected from the inhalation exposure alone (Figure 1), based on a correlation with the German guidance value (-6 µmol/mol creatinine), based on an exposure limit of 50 µg/m3). This and the fact that no MDA was detected (other than in air or on glove liners, indicates that skin absorption of MDI is likely to be the dominant route of exposure in these cases.

Spray-painting, as expected, generated higher atmospheric levels of diisocyanates than the other processes investigated, with some diamine generation (4 – 29% of the diisocyanate levels). All spray tasks involved use of respiratory protective equipment and, as a result, urine diamine levels were low or not detected. No evidence of substantial skin absorption of MDI or diamine was demonstrated.

Foam-blowing generated lower atmospheric levels of diisocyanates (TDI) than spraying but showed significant diamine generation (16 – 850% of the diisocyanate levels), depending on the process. One process, adding water to diisocyanates to generate CO2 and therefore expand the foam, created the greatest diamine levels. Again, levels of diamine in urine were greater than would be expected from inhalation of TDI alone (Figure 2), based on a volunteer study, but it is difficult to say whether the additional body burden results from dermal absorption of TDI and/or MDI and/or inhaled TDI.

Conclusions

This study has shown that amines can be generated during certain isocyanate applications. In the applications that we have monitored, this occurs in aerosol-generating processes. The proportion of amine to isocyanate can vary from ~0% (MDI spraying) to more than 8x (TDI foam blowing with water addition). In applications where no aerosol is generated, airborne MDI exposure is low and where there is the potential for dermal contact, evidence for dermal absorption of MDI has been demonstrated.

Whilst exposures may be complex, urine sampling can assess overall body burden resulting from tasks. However other data may be required to deconvolute the contributing exposure sources and routes.

Acknowledgement

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References


Figure 1: Correlation between MDI in air (µg/m3, 8h TWA) and MDA in urine (post-shift). Black line shows correlation found in inhalation-only volunteer study (Skarping et al, 1991). Red data point indicates worker who used RPE.

Figure 2: Correlation between TDI in air (µg/m3, 8h TWA) and TDA in urine (post-shift).