Determination of Occupational Exposure to Alkanolamines in Metal-Working Fluids

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Overall exposure to alkanolamines in metal-working fluids (MWFs) in machine shops was studied by determining alkanolamines in air samples and in rinse-off samples from the hands of machinists. Methods for collecting airborne alkanolamines and alkanolamines absorbed to the skin of the hands were developed and tested. The exposure measurements were carried out in nine machine shops. After a 2 h working period the dominant hand of 37 machinists was rinsed with 200 ml of 20% isopropanol for 1 min in a plastic bag. Personal air samples were also collected during the 2 h working period onto acid-treated glass fibre filters. The filter samples were desorbed with methanol and analysed by liquid chromatography with mass spectrometric detection (LC-MS). The rinse-off samples were also analysed for alkanolamines by LC-MS. The median air concentration of monoethanolamine (EA) was 57 µg m⁻³, diethanolamine (DEA) 64 µg m⁻³ and triethanolamine (TEA) 6 µg m⁻³. The workers’ overall exposure to alkanolamines was estimated by calculating the amount in inhaled air and the amount on the skin. The median amount of EA on the skin of the dominant hand was 9-43 times the median amount in inhaled air during 2 h exposure. The corresponding ratio for DEA was 100 and for TEA 170. According to this study the exposure to alkanolamines occurs mainly through the skin. EA was the only alkanolamine with a noticeable inhalation uptake compared to the skin uptake. Total exposure to MWFs may be reduced by reducing skin exposure. The hand rinsing method can be used to assess the efficiency of protective gloves.

Keywords: alkanolamines; dermal exposure; filter sampling; hand rinsing; inhalation; liquid chromatography; mass spectrometry

INTRODUCTION

Skin and respiratory symptoms are very common among machinists using water-miscible metal working fluids (MWFs) (Suuronen et al., 2004). MWFs are used e.g. to cool the work piece, and to protect the work piece from corrosion and to wash away the removed metal swarf. Airborne exposure to MWFs is usually assessed by measuring oil mist concentrations, though nowadays the concentrations are usually well below the occupational exposure limit (OEL) due to changes in the compositions of the fluids (NIOSH, 1998; Simpson et al., 2000). Alkanolamines, such as monoethanolamine (EA), diethanolamine (DEA), triethanolamine (TEA), and methyldiethanolamine (MDEA), act as corrosion inhibitors and pH adjusters and they are often added as borates to the MWF. They may induce asthma even at air concentrations below OELs (Savonius et al., 1994; Pipari et al., 1998). EA, DEA and TEA can cause irritant contact dermatitis due to their alkalinity. They have also been frequently reported to cause allergic contact dermatitis. (Bruzé et al., 1995; Geier et al., 2004). However, none of them has so far been classified in the EU as a substance which can cause sensitization by skin contact. Carcinogenic nitrosamines can be formed from DEA and other secondary alkanolamines. (NIOSH, 1998).

Airborne alkanolamines have been collected in impingers with acidified water (NIOSH, 1994; Serbin and Birkholz, 1995), on silica gel adsorbents (Serbin and Birkholz, 1995; Giachetti, 1998) and on coated XAD-2 chemosorbents (OSHA, 1987, 1988). EA and DEA have been analysed by liquid chromatography (LC) with fluorescence detection.
after derivatization with fluorenlyl methyl chloroformate (Serbin and Birkholz, 1995) or with UV-detection after in situ derivatization with naphthyl isothiocyanate on XAD-2 adsorbents (OSHA, 1987, 1988). In Finland, primary and secondary alkanolamines have been analysed as dansyl chloride derivatives after collection of air samples in diluted sulphuric acid (Henriks-Eckerman and Laijoki, 1985). However, tertiary alkanolamines cannot be derivatized using those derivatization reagents. TEA has been determined by gas chromatography-mass spectrometry (GC-MS) after silylation of the hydroxyl groups (Giachetti, 1998). Before silylation the extracted samples should be evaporated to dryness (Giachetti, 1998). All types of alkanolamines can be determined without derivatization using ion exchange liquid chromatography (IC) by measuring the conductivity of the eluent (NIOSH, 1994). MS detection in combination with IC separation is nowadays used to determine alkanolamines in environmental samples, such as water extracts (Headley et al., 1999; Peru et al., 2004).

Alkanolamines can appear simultaneously both as aerosol and as vapour in the workplace air, and therefore the sampling device should be able to collect both phases efficiently including both free and bound alkanolamines. Acid-treated glass fibre filters are used to collect air samples of semivolatile aromatic diamines by transforming them to the corresponding sulphate salts on the filter (OSHA, 1989a, 1989b). Filters are user friendly collection devices making personal sampling easy, and as sulphate salts of volatile alkanolamines are non-volatile, acid-treated filters should be expected to be an efficient collection device for alkanolamines.

In order to evaluate the overall exposure of machinists to alkanolamines or MWFs, reliable information about quantitative skin exposure data are also needed. As far as we know, there are no biomonitoring methods reported for alkanolamines. A biomonitoring method for N-nitrosodiethanolamine, which can be formed from DEA, has been published (Spiegelhalder et al., 1984). Dermal exposure to MWFs in the UK was assessed by measuring boron adsorbed to oversuits and to white cotton gloves worn underneath the protective gloves by the machinists (Roff et al., 2004). According to that study the main dermal exposure was found to occur through the skin of the hands, but the surrogate skin sampling media were not generally accepted by the workers. It is also possible that the surrogate skin method overestimates the dermal exposure. (van Wendel de Joode et al., 2005). Other quantitative methods for measuring dermal exposure to, for example, MWF have been the fluorescent tracer method and the video-recording method. However, both of these methods are expensive and difficult to apply. (Wassenius et al., 1998; van Wendel de Joode et al., 2005).

The aim of this study was to measure overall exposure, both dermal and airborne, to alkanolamines contained in MWFs. A sampling method was developed utilizing acid-treated glass fibre filters, with which both vapours and aerosols could be collected simultaneously. Work place air concentrations were determined by LC-MS after a slight modification of the method for alkanolamines in water extracts. The same analytical method was used to analyse simultaneously collected rinse-off samples from the dominant hands of the machinists. Assessment of exposure to MWFs by using alkanolamines as markers is discussed.

**MATERIALS AND METHODS**

**Chemicals**

The solvents used in the experiment were methanol (HPLC gradient grade, J.T. Baker), isopropanol (Merck, purity 99%) and acetonitrile (HPLC grade S, Rathburn). The acids used were formic acid (purity 98%, J.T. Baker) and sulphuric acid (purity 95–97%, Merck). EA, DEA, TEA and N,N-diisopropyl aminoethanol (DIPAE) with the purity of all >99% were purchased from Fluka, and MDEA (purity 99%) from Aldrich. Water was purified by a Milli-Q-academic plus Elix S water purification system to 18.2 MΩ cm. Whatman GF/B glass fibre filters (25 mm I.D.) free from organic binders were used to prepare the sampling devices, which were kept in Svinnex® filter holders from Millipore during sampling. A Millex HV type filter (PVDF Durapore, 13 mm I.D., 0.45 μm, Millipore) was used to clean up the filter sample desorption solution before injection.

**Instrumental**

A single quadrupole mass spectrometer (Waters Platform LCZ MS Detector) was used in the electrospray mode monitoring positive ions (ESI+). The cone voltage was 23 V, and the temperature of the ion source was 100°C. The mass spectrometer was connected to a Waters Alliance 2690XE separation module consisting of a quaternary solvent delivery system, a refrigerated, integrated autosampler, a column heater and a variable volume injection system.

The alkanolamines were analysed using a mobile phase of methanol–water (1 + 1) containing 1% formic acid. The flow rate was 0.2 ml min⁻¹. The LC column was a cation exchange column IonPac CS14 (250 × 2.1 mm I.D., Dionex Corp.). The column temperature was held at 30°C and the autosampler temperature was 10°C. The retention times varied between 5 and 8 min depending on the alkanolamine and on the condition of the column.
Laboratory testing of the desorption and retention efficiency of the acid-treated filters

The testing was performed in a chamber with constant temperature (23°C ± 1°C) and relative humidity (RH, 50% ± 3%). Air was pumped through the filter with a Gilian 3500 air sampling pump at an airflow rate of about 2 l min⁻¹ for 2 h. Air sampling was simulated at two different concentration levels with six replicates of each level. With the airflow on, 10 μl of acetonitrile containing a mixture of alkanolamines (5 μg of each) or 50 μl of acetonitrile containing the same alkanolamine mixture (25 μg of each) were injected onto the filter. The following alkanolamines were tested: EA, DEA, TEA and MDEA. A back-up sampler with an acid-treated filter was coupled to each collection device. Retention and desorption efficiency (DE) was calculated as the mean value of 5 or 6 parallel, successfully performed spiking collections. Freshly prepared standards in methanol containing acid-treated filters were used for the calculations. A seventh collection performed with only acetonitrile was used as a blank. The total air volume was about 240 l.

Laboratory testing of the recovery efficiency of the hand rinsing method

Diluted MWF (1.0 and 3.0 ml) (a mineral oil-based semisynthetic MWF-emulsion, 5% in water) was added to each hand of the test subjects (three people) in portions of 0.5 ml during 30 min with six replicates of each dose. Some sample loss occurred throughout the 3 ml dose experiment, and the remaining dose was estimated to be a total of 2.5 ml per hand. The test subjects held their palms upwards for another 30 min after the last addition. The right hand was not in contact with the left hand. After that (a total of 60 min from the beginning of the experiment) the hand was rinsed for 1 min using 200 ml of 20% isopropanol in a plastic bag. The rinsing was repeated with 100 ml to determine the recovery efficiency. Portions of 0.5 ml were also added to test tubes in order to determine the alkanolamine content of the added dose and the precision of the addition. According to our analysis results, the MWF concentrate contained 5.9% of EA and 5.4% of TEA. The pH of the diluted MWF was 9.3, as stated in the material safety data sheet. The storage stability of the rinse-off samples at +4°C was determined by analysing the samples 7 days and 4 weeks after sampling. The risk of adverse skin effects in the subjects was discussed with an experienced toxicologist. The risk was assessed as minor, as the exposure was very small compared to a normal MWF exposure of machinists.

Work-up procedure and quantification

The filter samples were desorbed with methanol (5 ml). The hand rinse-off samples were analysed as such or after dilution. The samples of the MWF were analysed after dilution with methanol. After sampling, a known amount (10 μg) of internal standard (DIPAE) in acetonitrile was added to the sample solutions (5 ml each) and to the standard solutions. Standards containing acid-treated filters were prepared by adding 5–50 μl of a 0.5 mg ml⁻¹ standard solution to the liquid phase. Standards and samples in pure methanol or in 20% isopropanol were acidified with formic acid (50 μl). The sample and standard vials were placed in an ultrasonic bath for 10 min. The solutions from the filter samples were passed through a Millex filter into an autosampler vial. Four different concentrations, 2.5–25 μg per sample, were used for the calibration curve. The injection volume was 5 μl. The 25 μg sample and the corresponding standards were analysed after dilution, as the detector response was linear only up to about 15 μg per sample (3 μg ml⁻¹). The analyte was quantified using the internal standard method by monitoring protonated molecular ions in the single ion monitoring mode. The protonated ions to be used were determined separately for each alkanolamine by scanning mass spectra from m/z 50–300. The limit of detection (LOD) was 0.01 μg ml⁻¹ for EA and MDEA, 0.02 μg ml⁻¹ for DEA and 0.15 μg ml⁻¹ for TEA. These LODs correspond to air concentrations of 0.002–0.03 mg m⁻³ for 15 min sampling or rinse-off amounts of 4–20 μg per hand for undiluted samples. The chromatographic performance of the analytical method has been thoroughly studied by Headley et al. (1999).

Stability of air samples and sample solutions

Spiked filters from the retention efficiency testing were stored at +4°C for 1 day, 4 days and for 4 weeks before desorption. After desorption the sample solutions were analysed within 1–2 days. One sample set was desorbed after 4 days storage of the filters at +4°C and these sample solutions were further stored at +4°C for 4 weeks before analysis. Freshly prepared standards in methanol containing acid-treated filters were used for the calculations.

Field sampling in machine workshops

Exposure measurements were carried out in nine machine work shops during the year 2004. The companies did different types of machining, including making tools, manufacturing of bodies and parts of machines and vehicles. All of the MWFs observed in the companies were water-miscible. About 70% of the MWFs were mineral oil-based, and about 20% were synthetic MWFs. There was one vegetable oil-based MWF, and a MWF of a new type that did not contain alkanolamines at all. Samples of diluted MWFs in use were collected in plastic bottles to be analysed for their alkanolamine content. After 2 h
working period the dominant hand of 37 machinists was rinsed for 1 min using 200 ml of 20% isopropanol in a plastic bag. After that, the machinists washed their hands with soap and warm water, and then samples were collected by using the same rinse-off method. Personal air samples were also collected during the two working hours onto acid-treated glass fibre filters. The measurements took place in the morning between coffee break and lunch. The workers were not informed that their hands were to be washed after about 2 h work in order to avoid influence on their working habits.

The filters for air sampling were prepared by soaking each filter with 0.5 ml of 0.26 N sulphuric acid (OSHA, 1989a, 1989b). The filters were then dried in an oven (100°C, 1 h). One filter per filter holder was used. Air was pumped through the filter with personal sampling pumps calibrated to give an accurate airflow of 1.5–2.1 min⁻¹.

**RESULTS**

**Retention efficiency and breakthrough of acid-treated filters**

The retention efficiency of the acid-treated filters was calculated by comparing the amount found on the first filter to the total amount of both filters in series in the laboratory testing. As no alkanolamines were detected in the back-up filters, the LODs were used to calculate the retention efficiency, which then was found to be >85% for DEA and >97% for EA, TEA and MDEA. The tested total amount of 20 µg (= 4 × 5 µg) per filter corresponded to a total alkanolamine concentration of 0.7 mg m⁻³ (15 min sampling) or 0.08 mg m⁻³ (2 h sampling) in air. The higher amount 100 µg (= 4 × 25 µg) corresponded to a total alkanolamine concentration of 3.3 mg m⁻³ (15 min sampling) or 0.4 mg m⁻³ (2 h sampling) in air. The breakthrough was also tested in two work places, where the air concentrations of alkanolamines were 0.04–0.12 mg m⁻³ (EA, n = 6) and 0.05–0.12 (DEA, n = 3). No detectable amounts were found in the back-up filters after 2 h sampling.

**Recovery efficiency of the hand rinsing method**

The recovery efficiency was about 55% for EA and about 67% for TEA. The detailed results of the recovery experiment are presented in Table 1. The second rinsing increased the recovery efficiency by <10% to about 60% for EA and about 71% for TEA.

**Stability of air samples, sample solutions and rinse-off samples**

Storage of alkanolamines spiked onto acid-treated filter and storage of the filter samples in methanol after desorption was performed to test the stability of alkanolamines after air sampling. The stability was calculated as DE by using freshly prepared standards containing acid-treated filters (Table 2). As can be seen from column B in Table 2, a DE of in general 85% or more is achieved, if the filter samples are desorbed within 4 days after sampling and standards solutions prepared simultaneously. Therefore, field desorption is not needed.

Rinse-off samples in 20% isopropanol were analysed for their EA and TEA concentrations after 7 days and after 4 weeks in the refrigerator after the rinse-off experiment. The decline was 3% (TEA) and 8% (EA), when the concentration was about 8 µg ml⁻¹. The decline was 1% for both alkanolamines when the concentration was about 20 µg ml⁻¹. The declines were within the relative standard deviations of the determinations, meaning that no deterioration took place.

**Work place measurements**

Diluted MWFs in use during the work place measurements were analysed for their main alkanolamine contents (Table 3). In one machine a MWF containing MDEA as alkanolamine additive was used. The concentration was 0.51%. Two

<table>
<thead>
<tr>
<th>Alkanolamine</th>
<th>nᵃ</th>
<th>Applied dose (mg hand⁻¹)</th>
<th>RSDᵇ (%)</th>
<th>Recovery efficiency and standard deviation (%) First rinse-off</th>
<th>Second rinse-offᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA (0.5 ml dose)</td>
<td>4</td>
<td>2.8</td>
<td>6.4</td>
<td>59.1 ± 4.5</td>
<td>5.5 ± 0.90</td>
</tr>
<tr>
<td>EA (3 ml dose)</td>
<td>5</td>
<td>7.5</td>
<td>7.4</td>
<td>51.3 ± 7.8</td>
<td>4.6 ± 1.4</td>
</tr>
<tr>
<td>TEA (0.5 ml dose)</td>
<td>4</td>
<td>2.6</td>
<td>4.9</td>
<td>64.8 ± 11</td>
<td>4.2 ± 0.95</td>
</tr>
<tr>
<td>TEA (3 ml dose)</td>
<td>5</td>
<td>6.8</td>
<td>3.4</td>
<td>69.2 ± 15</td>
<td>4.1 ± 1.3</td>
</tr>
</tbody>
</table>

EA, monoethanolamine; TEA, triethanolamine.

ᵃn is the number of samples analysed to determine the alkanolamine content in the applied dose and the precision of addition. 1–2 samples per dose have been discarded due to wrong handling.

ᵇPrecision of the applied dose expressed as relative standard deviation (RSD).

⁴n = 6.

⁵100 ml was used.
machinists used a MWF with no alkanolamine additives. The main results of the work place measurements are presented in Tables 4 and 5. The following alkanolamines were also identified and quantified in some of the air samples: N,N-dimethylaminoethanol (4–8 μg m⁻³, n = 4), amino-2-propanol (27–47 μg m⁻³, n = 6) and aminoethylpropanediol (3 μg m⁻³). Morpholine was afterwards identified in most samples taken, when bismorpholine containing MWFs were in use. It could not be quantified as a pure standard was not in use and the protonated molecular ion was not monitored during analysis.

The amounts of alkanolamines in the rinse-off samples from the dominant hand corresponded to a retainment of 1–2 ml of diluted MWF during 2 h work. After collection of the rinse-off samples,

Table 2. Stability of air samples and air sample solutions expressed as DE compared to freshly prepared standards containing acidified filters

<table>
<thead>
<tr>
<th>Alkanolamine</th>
<th>Spiked amount (μg)</th>
<th>DE ± standard deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A: 1 day filter storageᵃ</td>
<td>B: 4 days filter storage</td>
</tr>
<tr>
<td>Monoethanolamine</td>
<td>5</td>
<td>106.7 ± 20</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>93.9 ± 6.1</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>5</td>
<td>106.2 ± 18</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>91.9 ± 4.7</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>5</td>
<td>97.1 ± 18</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>85.6 ± 4.4</td>
</tr>
<tr>
<td>Methyl-diethanolamine</td>
<td>5</td>
<td>98.8 ± 17</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>89.3 ± 5.2</td>
</tr>
</tbody>
</table>

ᵃNo air was pumped through the filter.
ᵇSamples were analysed 4 weeks after desorption.

Table 3. Concentrations of alkanolamines in diluted MWFs in use during the exposure measurements

<table>
<thead>
<tr>
<th>Alkanolamines in MWFs</th>
<th>nᵃ</th>
<th>Identified alkanolamine in the MWF</th>
<th>Concentration in diluted MWF (%, w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Median</td>
</tr>
<tr>
<td>Monoethanolamine</td>
<td>10</td>
<td>EA</td>
<td>0.59</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>5</td>
<td>DEA</td>
<td>0.82</td>
</tr>
<tr>
<td>Monoethanolamine and triethanolamine</td>
<td>9</td>
<td>EA, TEA</td>
<td>0.30</td>
</tr>
</tbody>
</table>

ᵃn = Number of MWF samples.

Table 4. Amounts of alkanolamines in rinse-off samples from the dominant hand of machinists

<table>
<thead>
<tr>
<th>Alkanolamines in MWFs</th>
<th>nᵃ</th>
<th>Identified alkanolamine in rinse-off samples</th>
<th>Amount in rinse-off samples (mg/hand)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Median</td>
</tr>
<tr>
<td>Monoethanolamine</td>
<td>10</td>
<td>EA</td>
<td>7.4</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>5</td>
<td>DEA</td>
<td>12</td>
</tr>
<tr>
<td>Monoethanolamine and triethanolamine</td>
<td>19</td>
<td>EA, TEA</td>
<td>1.1</td>
</tr>
</tbody>
</table>

ᵃn = Number of rinse-off samples.

Table 5. Air concentrations of alkanolamines in the workers breathing zone during 2 h work with MWFs

<table>
<thead>
<tr>
<th>Alkanolamines in MWFs</th>
<th>nᵃ</th>
<th>Identified alkanolamine in air samples</th>
<th>Air concentration (μg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Median</td>
</tr>
<tr>
<td>Monoethanolamine</td>
<td>10</td>
<td>EA</td>
<td>54</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>5</td>
<td>DEA</td>
<td>64</td>
</tr>
<tr>
<td>Monoethanolamine and triethanolamine</td>
<td>19</td>
<td>EA, TEA</td>
<td>59</td>
</tr>
</tbody>
</table>

ᵃn = Number of air samples.
the machinists washed their hands with soap and warm water, and then samples were collected by using the same rinse-off method. These samples contained alkanolamine residues well below 1 mg hand⁻¹.

Two exceptions were noticed: a TEA residue of 1.3 mg hand⁻¹ (2% of the content in the ordinary rinse-off sample) and a DEA residue of 1.4 mg hand⁻¹ (4% of the content in the ordinary rinse-off sample).

Estimation of overall exposure to alkanolamines

The workers’ overall exposure to alkanolamines was estimated by using the measurement results of alkanolamines to calculate the amount in inhaled air and the amount on the skin (Table 6). According to this estimation, exposure to EA took place both through the airways as well as through the skin, when the machinists were exposed to both EA and TEA containing MWF at the same time. The exposure to TEA was mainly dermal, as the ratio of median amount on the skin compared to the median amount in inhaled air was 170. When the machinists used only EA or only DEA containing MWFs, the median amount on the skin of the dominant hand was 43 times (EA) or 100 times (DEA) the median amount in inhaled air during 2 h of exposure.

DISCUSSION AND CONCLUSIONS

Impinger methods are usually used when collection of all types of alkanolamines (primary, secondary and tertiary) is needed (NIOSH, 1994). However, an impinger is not a user-friendly collection device. Therefore, we tested if acid-treated glass fibre filters could be used instead. According to our test results the alkanolamines were efficiently captured by the sulphuric acid on the first filter in series at a sampling rate suitable for aerosols (2 l min⁻¹), as no evaporation from the sampling filter to the backup filter took place, neither with pure reference substances nor in the field sampling. The retention efficiency was tested at an RH of 50% with pure reference

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**Table 6. Estimation of the workers’ exposure to alkanolamines in machine work shops during 2 h work with MWFs**

<table>
<thead>
<tr>
<th>Identified alkanolamine in the MWFs</th>
<th>nᵃ</th>
<th>Amountᵇ of alkanolamine in inhaled air (mg)</th>
<th>Amountᶜ of alkanolamine retained on the skin (mg/dominant hand)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Median</td>
<td>Range</td>
</tr>
<tr>
<td>Monoethanolamine</td>
<td>10</td>
<td>0.23</td>
<td>0.03–0.65</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>5</td>
<td>0.19</td>
<td>&lt;0.02–0.44</td>
</tr>
<tr>
<td>Monoethanolamine and Triethanolamine</td>
<td>19</td>
<td>0.21</td>
<td>0.03–1.2</td>
</tr>
</tbody>
</table>

ᵃNumber of personal measurements.
ᵇAn inhalation rate of 30 l min⁻¹ was assumed.
ᶜThe amount in rinse-off samples were corrected for the recovery efficiency of the method (59% for EA and 65% TEA) and for sampling time. The recovery efficiency for TEA was also used for DEA.
influence on the sampling efficiency in this case. Despite some application difficulties during the validation, the repeatability of the rinse-off method was good with standard deviations of 15% or lower for TEA and of 8% or lower for EA (Table 1).

The Finnish 8 h OEL is 2.5 mg m\(^{-3}\) for EA and 2 mg m\(^{-3}\) for DEA. For TEA the Swedish OEL, 5 mg m\(^{-3}\), can be applied. Assuming that the machinists were exposed to the measured alkanolamine concentrations during the whole working day, the OELs were in none of the cases exceeded. The measured maximum air concentration for EA, 345 µg m\(^{-3}\), was 14% of the OEL. Generally, airborne exposure to MWF is assessed by measuring oil mist. Nowadays the measured oil mist concentrations are usually very low, below 0.5 mg m\(^{-3}\) (NIOSH, 1998; Simpson et al., 2000). During oil mist sampling volatile compounds like EA are missed as they break through the filter during sampling (Volkens et al., 1999). By using alkanolamines as markers it is possible to get much more reliable information about airborne exposure to MWF than by measuring only the oil mist. For example, commonly used biocides are built up of formaldehyde and of alkanolamines or amines. According to our measurement results these biocides can be analysed as their corresponding alkanolamines. Also morpholine, the ingredient of the biocide bismorpholine, was afterwards identified in most of the air samples. Whether the biocides are collected on the filters as such or as their corresponding alkanolamines or amines, we do not know yet.

As alkanolamines can cause both irritant and allergic contact dermatoses as well as asthma, the exposure should be kept as low as reasonably achievable. Other exposure routes than inhalation should also be considered. In machine shops, skin exposure was considered important. The main skin exposure was expected to occur through the hands and consequently the dominant hand was chosen as the target of skin exposure measurements. About the same time as our measurements were performed Roff et al. showed by measuring boron in surrogate skins that the main skin exposure route is by the hands, as the deposition rates of the hands were about 20 times that of the body. In order to compare inhalation and skin exposure the measurement results were recalculated as follows: the air concentrations were expressed as amount of inhaled alkanolamine and the amount of alkanolamines in the rinse-off samples were expressed as amount retained on the skin of one hand during 2 h exposure. The amount per cm\(^2\) of skin provides information about skin exposure and the risk to develop allergic or irritant contact dermatitis. The bigger amount is retained on the skin the higher is the risk. According to our comparison (Table 6) the exposure to alkanolamines was mainly dermal. The only alkanolamine with a noticeable inhalation uptake compared to skin exposure was EA. Dermal exposure was quite high probably due to the fact that most machinists did not use proper chemical protective gloves. Permeable leather and textile gloves were commonly used. Many machinists did not use gloves at all or used them only occasionally.

According to results from the testing of the hand rinsing method (Table 1) about 60% of EA and about 70% of TEA could be recovered, if a two step rinsing was applied. This means that theoretically 30% of TEA could have penetrated the stratum corneum. For EA the systematic uptake is probably much smaller than the theoretical 40%, as EA is a fairly volatile compound compared to TEA. However, in order to evaluate more thoroughly the role of systemic uptake during skin exposure, further studies, such as biomonitoring, are needed.

New information about overall exposure to MWFs was obtained by developing simple methods for measuring alkanolamines in air as well as in rinse-off samples from the hands of machinists. These collection methods are easy to perform and well accepted by the machinists. The efficiency of protective gloves may also be assessed by this hand rinsing method. The conclusions of this study were that in machine shops skin exposure to alkanolamines is considerably compared to inhalation exposure. Consequently, the overall exposure may be markedly reduced by reducing skin exposure with correct work habits and by use of nitrile rubber protective gloves or protective gloves coated partly with nitrile rubber as they are impermeable to metalworking fluids and their ingredients.

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REFERENCES


OSHA (1989a) 4,4’-Methylenedianiline. Method No 57.
OSHA (1989b) Benzidine, 3,3′-dichlorobenzidine, 2,4–
toluenediamine, 2,6-toluenediamine. Method No 65.