



Determination of alkylamine permeation through protective gloves using aliphatic amine pads†

Evanly Vo and Stephen P. Berardinelli

National Institute for Occupational Safety and Health, Division of Safety Research,
1095 Willowdale Road, Morgantown, WV, 26505, USA

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A quantitative study of alkylamine permeation through a glove material using Permea-Tec aliphatic amine pads, used for the detection of chemical breakthrough of protective clothing, was performed for triethylamine following a microwave-extraction process and gas chromatographic analysis. Triethylamine exhibited >99% adsorption on the pads at a spiking level of 729 ng (1.0 ml). Triethylamine showed recoveries from 63 to 90% (RSD \leq 5%) over the range 0.2–1.0 ml (146–729 ng) applied to pads. The ASTM F739 standard and direct permeability testing procedures were used to determine breakthrough times for five protective glove materials using triethylamine as a challenge chemical. Breakthrough times for six protective gloves were determined ranging from 40 s to >4 h. The quantitative concentration of triethylamine on the pads following permeation through the gloves was also determined, ranging from 101 to 103 ng cm⁻² (382–386 ng per pad).

Introduction

Respiratory and dermal exposures to chemical agents are known to occur in the workplace.^{1–4} A major occupational health focus has been respiratory monitoring and control, yet damage caused by other routes of exposure is also a major cause of occupational ill-health.^{5,6} Other routes of exposure are mainly through the skin; therefore, workers are required to wear chemically resistant gloves and protective clothing to prevent skin exposure to toxic chemicals in the workplace.

Aliphatic amine pads have been developed to enhance workers' ability to protect themselves from skin exposure to alkylamines. Fresh pads are attached to the hands of a worker before gloving. Permeation of alkylamines through the glove will result in adsorption on the pads, which can be quantified through subsequent analysis. Although the glove-selection process is typically based on manufacturers' chemical permeation data, many factors, such as temperature, pressure and product variation among suppliers, bring into question the reliability of this process. Passive dermal monitoring could be used to evaluate glove performance during 'actual use' conditions and could bridge the gap between laboratory data and 'real world' performance. We report here the validation of an assay using pads attached to the palm, the cuff or the fingers of gloves to determine time to breakthrough and the concentration of triethylamine at timed intervals.

Experimental

Chemicals

Triethylamine was used as a spiked, standard chemical for testing pads. It was also used as a neat challenge chemical for glove permeation testing. Cyclohexane was used as the extraction solvent. Both chemicals (ACS reagent grade) were purchased from Aldrich Chemical (Milwaukee, WI, USA).

Selected gloves and pads

Six different types of gloves were selected for this study: non-sterile vinyl gloves purchased from Baxter Healthcare (Valencia, CA, USA); polymer-coated latex, co-polymer, and powdered nitrile gloves purchased from VWR Scientific Products (West Chester, PA, USA); and disposable vinyl and Sol-Vex gloves purchased from Ansell-Edmont (Coshocton, OH, USA). Permea-Tec aliphatic amine pads were purchased from Colormetric Laboratories (Des Plaines, IL, USA).

Apparatus

An Ames (Waltham, MA, USA), 214-10 micrometer with a pressure foot of 1 cm was used to determine the thickness of each glove. A Miran (Miniature Infrared Analyzer) closed-loop configuration which consists of a metal bellows pump (Model MB-41), a 2.5 cm chemical permeation cell and a Miran was used to determine time to breakthrough for the glove material. A CEM (Matthews, NC, USA) MES-100 microwave extraction (ME) system was used to extract triethylamine in pads. A Perkin-Elmer (Norwalk, CT, USA) gas chromatographic system, which consisted of a PE Nelson Model 1022 Personal Integrator and an AutoSystem gas chromatograph, was used to analyze chemicals.

Evaluation of sorption properties of pads

Spiking pads. New pads were removed from sealed packages and the adhesive areas removed with scissors. Pads were tested to determine if there was any pad-media interference. Known volumes of triethylamine (0.2–1.0 μ l) were added directly to the surface of the pads using a syringe (0.1–1.0 μ l). The pads were then inserted into 300 μ l of extraction solvent in 3 ml Savillex vials and the vials were covered with the vial caps.

The ME process and GC analysis. The ME-GC procedure was run according to the method of Vo *et al.*⁷ as follows. The closed vials were immersed in 25 ml of water in extraction vessels, then, the vessels were placed in the MES-100 system and extracted for 15 min at 100 °C, 70 lb in⁻², and 60% power.

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The extracted solutions were allowed to cool to room temperature for 20 min before opening the vial caps for GC analysis in order to obtain maximum recovery of these chemicals without evaporation loss.

The optimum GC conditions were as follows: column, 3.05 m \times 3.1, 8 mm id, 3% SP-1500 on 80–120-mesh Carboxen B (Supelco, Bellefonte, PA, USA); helium flow rate, 25 ml min⁻¹; oven temperature, 225 °C; column temperature, 215 °C; temperature of the flame ionization detector (FID), 235 °C; data collection time, 0–21 min; main plot time, 13–21 min; and y -maximum, 50 mV. Volumes of 5 μ l of extracted samples of spiked triethylamine in extracted solutions were injected into the GC column using a syringe (0.1–5.0 μ l), up to four times for each sample. The areas of the spiked triethylamine peaks in the resulting gas chromatograms were used for spiked triethylamine determinations.

Efficiency of adsorption during triethylamine spiking. In order to assess whether complete adsorption of triethylamine is determined during spiking on pads, two Savillex vials were used. In the first vial, 1 μ l of triethylamine was added to a pad and the vial was covered with the vial cap. The vial was left at room temperature for 30 min before the pad was inserted in 300 μ l of extraction solvent in the second vial. Then, 300 μ l of the extraction solvent were added directly to the first vial to extract excess triethylamine which did not adsorb on the spiked pad. These vials were then used for the extraction process and GC analysis.

Triethylamine recovery. Standard triethylamine determinations were performed using the same spiked triethylamine procedure, but without using pads. Known volumes of triethylamine (0.2–1.0 μ l) were added directly to 300 μ l of extraction solvent in the vials. These vials were then used for the extraction process, and 5 μ l samples of the extracted solutions were subjected to GC analysis. The areas of the standard peaks in the resulting gas chromatograms were used for standard triethylamine determinations. Triethylamine recovery was calculated as the percentage of spiked triethylamine peak area divided by standard triethylamine peak area.

Glove thickness test

The thickness test was performed at three positions on each glove: the palm, the entire middle finger and the cuff (3 cm from the open end), as these represent the areas of highest contact and glove abrasion, which enhances chemical penetration. Five thickness measurements for each position on the glove were recorded and the mean thickness and variation were calculated. All measurements were made to the nearest ± 0.01 mm.

Glove breakthrough time determination

A modified ASTM F739 method was used to determine breakthrough time.⁸ The IR conditions were as follows: slit, 1.0 mm; wavelength, 9.3 μ m; pathlength, 20.25 m; and minimum detectable concentration, 0.4 ppm. The 2.5 cm permeation cell is divided into a 'challenge side' which contains the chemicals and a 'collection side' which contains the sweep gas. Sections from the palm and the cuff of gloves containing a pad attached to the inner surface of the section were used as a membrane between two halves of the permeation cell with the outer surface toward the challenge side of the permeation cell. The experiment was conducted at room temperature (22 ± 1 °C). A 15 ml volume of challenge chemical was injected into the challenge side of the cell and a timer was immediately started. Permeation of triethylamine through the glove was detected by the change in color of the pads or the analyzer-detected response. Direct permeability testing procedure was also performed on the finger position of gloves. A finger of the

gloves was turned inside out and a pad was attached to the finger. The glove finger was then fastened to a glass cylinder (2×15 cm) by using duct tape at the open end of the glove finger as the attachment area. The glass cylinder served as a fill tube. A 10 ml volume of challenge chemical was injected into the glass cylinder and a timer was immediately started. Permeation of triethylamine through the glove finger was detected by the change in color of the pads. Breakthrough time was recorded and the pads were immediately removed from the glove and inserted into 300 μ l of extraction solvent in the vials for the extraction process.

Quantitative determination of triethylamine

The closed vials of triethylamine were extracted as described above. Volumes of 5 μ l of extracted samples were subjected to GC analysis. The areas of the peaks in the resulting gas chromatograms were used for challenge triethylamine quantification. The quantitative concentration of challenge triethylamine was determined against a known concentration of spiked triethylamine based on its linear equation and the degree of triethylamine recovery.

Results

Resolution

Good resolution of the extraction solvent and triethylamine was achieved by setting the optimum GC conditions as described. None of the blanks (unexposed pads in the extraction solvent) produced chromatograms containing peaks corresponding to triethylamine. The GC retention times for triethylamine and extraction solvent obtained under these conditions are given in Table 1.

Efficiency of adsorption during triethylamine spiking

Excess triethylamine which did not adsorb on the spiked pad in the first vial was low, being <1% (the area peak was <1% of the area peak for the triethylamine found in vial No. 2). Triethylamine exhibited >99% adsorption on the pads at spiking level of 729 ng.

Calibrations of pads

Triethylamine spiked on the pads (0.2–1.0 μ l) could be detected on the chromatograms. The relationship between signals (peak area) on the gas chromatograms and volumes over the range 0.2–1.0 μ l ($n=5$) of triethylamine applied to the pads was analyzed using Microsoft Excel software. A linear correlation for triethylamine was obtained over the range 0.2–1.0 μ l [$r^2=0.9989$, $p<0.001$, with the linear equation $y=197x-32$ (x =volume; y =peak area)]. No such linear correlation for triethylamine was obtained when ≤ 0.1 μ l of triethylamine was added to pads.

Triethylamine recovery

For experiments performed with repeated extraction process and GC measurements, recoveries from 63 to 90% (RSD $\leq 5\%$) were obtained over the range 0.2–1.0 μ l (146–729 ng) of triethylamine applied to the pads (Table 1). No significant improvement in the recovery was observed when ≥ 1.2 μ l of triethylamine was added to pads.

Glove thickness test

Table 2 summarizes the results obtained for the mean thickness of five thickness measurements for each type of glove.

Table 1 Retention time and recovery of triethylamine (bp 88.8 °C) at different volumes applied to pads (mean recovery \pm SD, $n=3$). A 300 μ l volume of extraction solvent (retention time of cyclohexane=3.84 min) was used to extract triethylamine from the pads and 5.0 μ l of the extracted solutions of triethylamine were analyzed by GC

| Volume of triethylamine applied to pad/ μ l | Recovery (%) | Retention time/min |
|---|--------------|--------------------|
| 0.2 | 63 \pm 4.9 | 17.56 |
| 0.4 | 68 \pm 4.5 | |
| 0.6 | 73 \pm 4.0 | |
| 0.8 | 86 \pm 3.3 | |
| 1.0 | 90 \pm 3.1 | |

Glove breakthrough time determination

The data demonstrated breakthrough with any of the gloves tested with the ASTM F739 standard and direct permeability testing procedures, except the Sol-Vex glove (Table 2). Permeation of triethylamine through the gloves was detected by the change in color of the pads (triethylamine causes the pads to change from yellow to blue), but not by the analyzer-detected response.

Quantitative determination of triethylamine

The concentration of challenge triethylamine on the pads following permeation through the gloves was determined, ranging from 101 to 103 ng cm⁻² or 382–386 ng per pad [pad: 2.0 cm \times 1.9 cm; 382–386 ng per pad (0.52–0.53 μ l per pad) of triethylamine based on adsorption of about 0.35–0.36 μ l per pad from its linear equation and its recovery of 68% at 0.4 μ l added].

Precision

The recovery precision was good, with RSD \leq 5% for triethylamine (over the range 0.2–1.0 μ l of triethylamine applied to pads and 5 ml of extracted solutions for GC analysis).

Sensitivity

The gas chromatograms of triethylamine were obtained with 0.2 μ l of triethylamine spiked onto the pads, and 5.0 μ l of extracted solutions of triethylamine applied for GC analysis. These volumes represent 146 ng of triethylamine per pad and 2.43 ng of triethylamine applied for GC analysis.

Discussion

The efficiency of adsorption of triethylamine on the pads was assessed. It was found that triethylamine was nearly completely adsorbed (99–100%) on the pads at a spiking level of 729 ng.

The results obtained with the ME-GC procedure were consistent with a reproducible recovery of triethylamine from pads which had been exposed to this chemical. The recovery was obtained over the range 0.2–1.0 μ l of triethylamine applied

to pads and 5 ml of the extracted solutions subjected to GC analysis. The recovery was also dependent on the extraction process and the volume of triethylamine applied to the pad.

No such linear correlation for triethylamine was obtained when \leq 0.1 μ l of triethylamine was added to pads. An excellent linear correlation ($r^2=0.9989$ and $p<0.001$) was obtained for triethylamine over the range 0.2–1.0 μ l added to pads and 5 μ l of the extracted solutions used for GC analysis. The color change on the pad occurs on adsorption of about 0.35–0.36 μ l per pad from its linear equation and its recovery of about 68%, and that this corresponds to volumes about 0.52–0.53 μ l per pad (382–386 ng per pad) or 101–103 ng cm⁻², which is within this linear response range. These values are below the recommended exposure limit (REL) for triethylamine [ACGIH (American Conference of Government Industrial Hygienists) threshold limit value (TLV) of 3 ppm (12 mg m⁻³) as a ceiling concentration, as its REL].

It was also shown that the GC system is sensitive enough to detect the presence of triethylamine in extraction solvent. Low-nanogram amounts of triethylamine (2.43 ng) can be detected and they are clearly resolved under the GC conditions described.

The results indicated that differences in material density and thickness yielded different breakthrough times. The results of the permeation experiments, as shown in Table 2, demonstrated that within a given material type of the gloves tested, thickness had a primary effect on the breakthrough time of the challenge chemical. Differences in glove materials yielded different breakthrough times (Table 2). For nitrile rubber materials, slow permeation by triethylamine was observed (\geq 70 min), while rapid permeation by triethylamine for natural latex rubber, polymerized alkenes or vinyl materials was observed.

Table 2 also shows that there were significant differences in breakthrough times between the ASTM F739 standard and direct testing methods for these gloves where the thicknesses were almost similar. It is probable that the pressure which was generated by the pump within the closed-loop system caused triethylamine to permeate more quickly than actual breakthrough times.

Permeation of triethylamine through the gloves was detected by the change in color of the pads before the IR analyzer detector responded. It is possible that triethylamine with a low vapor pressure gave the impression of longer than actual breakthrough times.

Since both thickness and density measurements represented an average of the swatch surface area, they did not indicate small regions of ‘thin’ areas where permeation occurred more rapidly. The instrumentation used in this experiment is sensitive enough to detect concentrations in the pads caused by permeation in these thinner areas of the material. Hence, although we cannot accurately measure material variations, we can still observe the effects of these variations through their contribution to the permeation-rate variations.

Quantitative data were obtained for triethylamine permeation through various glove materials. The results indicate that

Table 2 Results of the glove permeation tests ($n=3$) for triethylamine

| Type of glove | Material of glove | Style or Model No. | Thickness ^a (palm and cuff)/mm | Breakthrough time ^b (palm and cuff) | Thickness ^a (finger)/mm | Breakthrough detection time ^c (finger) | Mass of triethylamine found/ng per pad |
|----------------------|----------------------|--------------------|---|--|------------------------------------|---|--|
| Non-sterile vinyl | Vinyl (non-sterile) | Triflex | 0.15 \pm 0.01 | 78 \pm 5 s | 0.11 \pm 0.01 | 62 \pm 3 s | 384 \pm 3 (103 ng cm ⁻²) |
| Polymer-coated latex | Natural latex rubber | Boxed Ambi | 0.15 \pm 0.01 | 40 \pm 3 s | 0.15 \pm 0.01 | 42 \pm 4 s | 386 \pm 4 (103 ng cm ⁻²) |
| Copolymer | Polymerized alkenes | Boxed Ambi | 0.12 \pm 0.01 | 40 \pm 4 s | 0.16 \pm 0.01 | 68 \pm 5 s | 383 \pm 5 (102 ng cm ⁻²) |
| Disposable vinyl | Vinyl | Dura-Touch | 0.18 \pm 0.01 | 115 \pm 7 s | 0.18 \pm 0.01 | 140 \pm 6 s | 385 \pm 4 (102 ng cm ⁻²) |
| Powdered nitrile | Nitrile | Boxed Ambi | 0.11 \pm 0.01 | 70 \pm 2 min | 0.12 \pm 0.01 | 77 \pm 1 min | 382 \pm 4 (101 ng cm ⁻²) |
| Sol-Vex | Nitrile butyl rubber | 37-175 | 0.36 \pm 0.01 | >4 h | 0.38 \pm 0.01 | >4 h | nd ^d |

^aMean thickness \pm SD ($n=5$). ^bBreakthrough time detected by the change in color of aliphatic amine pads (the ASTM F739 testing procedure). ^cBreakthrough time detected by the change in color of aliphatic amine pads (the direct testing procedure). ^dNot detected at 4 h.

pads exposed to triethylamine can be successfully analyzed under the conditions for the extraction process and GC analysis described ($101\text{--}103\text{ ng cm}^{-2}$). This procedure offers potential for developing permeation breakthrough indicators for the entire series of alkylamine compounds which may be encountered in workplace exposure situations. A companion study under actual workplace conditions will be conducted in order to determine the validity of laboratory findings under dynamic conditions found during workplace exposures.

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