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# A Quantitative Study of Aromatic Amine Permeation Through Protective Gloves Using Amine Adsorptive Pads

A quantitative study of aromatic amine permeation through a glove material using Permea-Tec aromatic amine pads, used for the detection of chemical breakthrough of protective clothing, was performed for aniline following the microwave extraction process and gas chromatographic analysis. Aniline exhibited >99% adsorption on the pads at a spiking level of 1.94 mg (1.9  $\mu$ L). Aniline showed recoveries from 65 to 89% (RSD  $\leq$ 5.6%) over the range 1.1–1.9  $\mu$ L (1.12–1.94 mg) of aniline applied to pads. The modified ASTM F739 and direct permeability testing procedures were used to determine breakthrough times for five protective glove materials using aniline as a challenge chemical. Breakthrough times for six protective gloves were determined, ranging from 182 sec to 82 min. The quantitative concentration of aniline on the pads following permeation through the gloves also was determined, ranging from 0.53 to 0.55 mg/cm<sup>2</sup> (1.79–1.88 mg/pad).

**Keywords:** aromatic amine pads, breakthrough time, health and safety, protective gloves, quantitative methods, skin chemical exposure

**R**espiratory and dermal exposures to chemical agents are known to be present in the workplace.<sup>(1–3)</sup> A major occupational health focus has been respiratory monitoring and control, yet damage caused by other routes of exposures is also a major cause of occupational ill-health.<sup>(4,5)</sup> Other routes of exposures 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.

Aromatic amine pads have been developed to enhance workers' ability to protect themselves from skin exposure to aromatic amines. Fresh pads are attached to the hands of a worker before gloving. Permeation of aromatic amines 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. The authors 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 aniline at timed intervals.

## MATERIALS AND METHODS

### Chemicals

Aniline 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, Wis.).

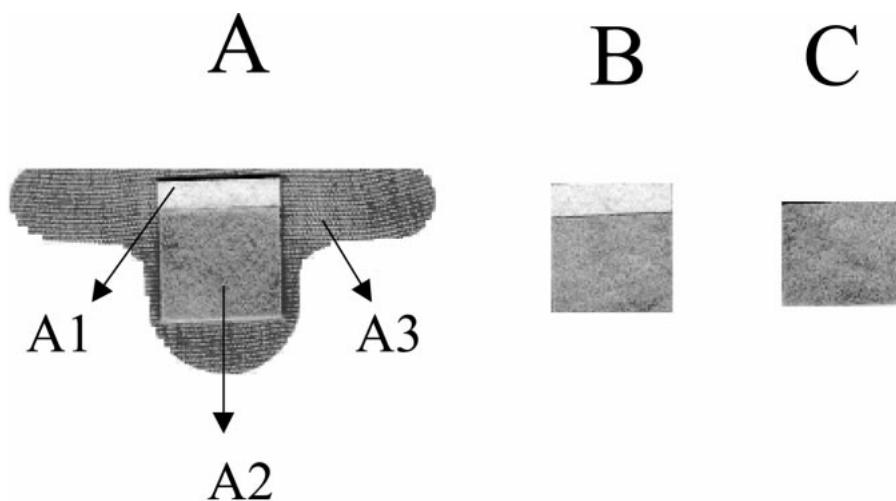


FIGURE 1. Aromatic amine pads. Pad A: an aromatic amine pad with the white area containing the color activator (A1), the yellow area (A2), and the adhesive area (A3). Pad B: an aromatic amine pad without the adhesive area. Pad C: only the yellow area of the pad is shown.

### Selected Gloves, Pads, Chemical Permeation Cells, and Savillex Vials

Six types of gloves were selected for this study: nonsterile vinyl gloves (style: Triflex) purchased from Baxter Healthcare (Valencia, Calif.); polymer-coated latex (style: Boxed Ambi), copolymer (style: Boxed Ambi), and powdered nitrile gloves (style: Dura-Touch) purchased from VWR Scientific Products (West Chester, Pa.); disposable vinyl (style: Boxed Ambi) and Sol-Vex gloves (model 37-175) purchased from Ansell-Edmont (Coshocton, Ohio). Permea-Tec aromatic amine pads were purchased from Colormetric Laboratories (Des Plaines, Ill.). Chemical permeation cells (2.5 cm in diameter) were purchased from AMK Glass Co. (Vineland, N.J.). Savillex vials (3-mL vials, part number 221253, and 7-mL vials, part number 221252) were purchased from CEM (Matthews, N.C.).

### Apparatus

An Ames (Waltham, Mass.), 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 consisting of a metal bellows pump (Model MB-41, Metal Bellows Corp., Sharon, Mass.), a 2.5-cm chemical permeation cell, and a Miran (Foxboro Co., Norwalk, Conn.) was used to determine time to breakthrough for the glove material. A CEM MES-100 microwave-extraction (ME) system was used to extract aniline in pads. A Perkin-Elmer (Norwalk, Conn.) gas chromatographic system, consisting of a PE Nelson Model 1022 Personal Integrator and an AutoSystem gas chromatograph (GC), was used to analyze chemicals.

### Evaluation of Sorption Properties of Pads

#### Spiking Pads

New pads (Figure 1, Pad A) were removed from sealed packages and the adhesive areas removed (Figure 1, Pad B) with scissors. Pads were tested to determine whether there was any pad-media interference. The aromatic amine sensor of this pad involved a two-stage reaction to activate the detection system. The white area of the pad (Figure 1, Pad A) contains the color activator; therefore, to prepare this pad, 200  $\mu$ L of distilled water was slowly applied to the white border strip using a 200- $\mu$ L Pipetman, and

the reaction was allowed to proceed at room temperature for 5 min. Known volumes of aniline (1.1–1.9  $\mu$ L) were added directly to the surface of the yellow area of the pads (Figure 1, Pad C). The pads were then inserted into 300  $\mu$ L of extraction solvent in 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.<sup>(6)</sup> as follows. The vials were immersed into 25 mL of tap water in extraction vessels; then, these vessels were placed in the MES-100 system and extracted for 10 min at 100°C, 70 psi, and 60% power. The extracted solutions were allowed to cool to room temperature for 20 min before the vial caps were opened for GC analysis 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 i.d., 3% SP-1500 on 80–120-mesh CarboPack B (Supelco, Bellefonte, Pa.); helium flow rate, 25 mL/min; oven temperature, 230°C; column temperature, 235°C; temperature of the flame ionization detector (FID), 235°C; data collection time, 0–16 min; main plot time, 11–16 min; and y-maximum, 40 mV. The 8- $\mu$ L extracted samples of spiked aniline in extracted solutions were injected into the GC column (n=4). The areas of the spiked aniline peaks in the resulting gas chromatograms were used for spiked aniline determinations.

#### Efficiency of Adsorption During Aniline Spiking

To assess whether complete adsorption of aniline occurs during spiking on aromatic amine pads, two Savillex vials were used (two vials were used only to perform the efficiency tests, whereas one vial was used to test each pad in the spiked, standard, and challenge aniline determinations). Two hundred microliters of distilled water were slowly applied to the white border strip of an amine pad and the reaction was allowed to proceed at room temperature for 5 min. The yellow part of the pad was then inserted into the first vial and 1.9  $\mu$ L of aniline was added directly to the surface of the yellow area 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  $\mu$ L of extraction solvent in the second vial. Then, 300  $\mu$ L of the extraction solvent was added directly to the first

vial to extract excess aniline that did not adsorb on the spiked pad. These vials were then used for the extraction process and GC analysis.

### Aniline Recovery

Standard chemical determinations were performed using the same spiked chemical procedure, but without using pads. Known volumes of aniline were added directly to 300  $\mu$ L of extraction solvent in the vials. These vials were then used for the extraction process, and 8  $\mu$ L samples of the extracted solutions were injected into the GC. The areas of the standard peaks in the resulting gas chromatograms were used for standard aniline determinations. Aniline recovery was calculated as the percentage of spiked aniline peak area divided by standard aniline 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 enhance rapid chemical permeation. 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  $\pm 0.01$  mm.

### Glove Breakthrough Time Determination

A modified ASTM F739 method as described by Berardinelli et al.<sup>(7)</sup> was used to determine breakthrough time. The Miran conditions were as follows: slit, 1.0 mm; wavelength, 9.4 mm; pathlength, 20.25 m; minimum detectable concentration, 0.2 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 (house air in the closed loop) and a glove membrane (sections from the palm and the cuff of gloves were used as a membrane between two halves of the permeation cell with the outer surface toward the challenge side of the permeation cell). A yellow part of a pad (Figure 1, Pad C) was attached to the half inner surface of the glove section and covered with parafilm, then clear plastic tape, so the pad was in direct contact with the glove surface and easily removed from the glove. The other half of the glove section was opened for chemicals to reach the analyzer detector. This system was operated in the closed-loop mode, and the experiment was conducted at room temperature ( $22 \pm 1^\circ\text{C}$ ). Fifteen milliliters of a challenge chemical (aniline) were injected into the challenge side of the cell using a 30-mL glass syringe, and a timer and a metal circulation pump were immediately started. Permeation of aniline through the glove was detected by the analyzer-detected response or the change in color of the pads (aniline causes the pads to change from yellow to red, which could be seen from either side of the pad because the adhesive area of the pads was removed).

Breakthrough times for the finger position of gloves also were determined as follows. A finger of the gloves was turned inside out and a yellow part of a pad was then attached to the finger and covered with parafilm, then clear plastic tape. The glove finger was then fastened to a glass cylinder (2  $\times$  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. Ten milliliters of a challenge chemical were injected into the glass cylinder and a timer was started immediately. Permeation of aniline through the glove finger was detected by the change in color of the pads. This procedure was designated "the direct permeability testing procedure." Breakthrough time was recorded, and the pads were immediately

**TABLE I. Retention Times, Peak Areas, and Recoveries of Aniline (bp 184 °C) at Different Volumes Applied to Pads\***

Volume of Aniline Applied to Pad ( $\mu$ L)	Recovery (%)	Peak Areas ( $\times 10,000$ )	Retention Time (min)
1.1	65 $\pm$ 5.6	0.3	12.54
1.3	69 $\pm$ 5.3	21.7	
1.5	76 $\pm$ 4.2	47.0	
1.7	81 $\pm$ 3.5	70.3	
1.9	89 $\pm$ 3.9	69.2	
2.1	90 $\pm$ 4.0	122.0	

\*Note: Three hundred microliters of extraction solvent (retention time of cyclohexane, 3.59 min) were used to extract aniline from the pads and 8.0  $\mu$ L of the extracted solutions were analyzed by GC.

removed from the glove and inserted into 300  $\mu$ L of extraction solvent in the vials for the extraction process.

### Quantitative Determination of Aniline

The closed vials of aniline were extracted as previously described. The 8- $\mu$ L extracted samples were injected into the GC. The areas of the peaks in the resulting gas chromatograms were used for challenge aniline quantification.

The quantitative concentration of a challenge chemical was determined against a known concentration of a spiked chemical based on its linear equation and the degree of chemical recovery, according to the method of Vo et al.<sup>(8)</sup>

## RESULTS

### Resolution

Good resolution of the extraction solvent and aniline 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 aniline. The GC retention times for aniline and extraction solvent obtained under these conditions are given in Table I.

### Efficiency of Adsorption During Aniline Spiking

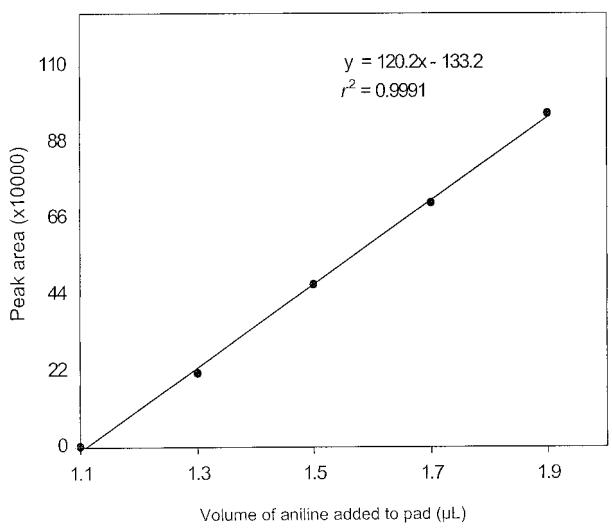
Excess aniline that did not adsorb on the spiked pad in the first vial was low, being  $<1\%$  of the area peak for the aniline found in vial No. 2 (with a low vapor pressure, unabsorbed aniline trapped on the surface of the vial as vapor was insignificant). Aniline exhibited  $>99\%$  adsorption on the pads at a spiking level of 1.94 mg.

### Calibrations of Pads

The relationship between signals (peak area) on the gas chromatograms and volumes over the range 1.1–1.9  $\mu$ L ( $n = 5$ ) of aniline applied to pads (Table I) was analyzed using Microsoft<sup>TM</sup> Excel<sup>TM</sup> software. Figure 2 shows a linear correlation for aniline over the range 1.1–1.9  $\mu$ L ( $r^2 = 0.9991$  and  $p < 0.001$ ).

### Aniline Recovery

For experiments performed with multiple extraction process and GC measurements, recoveries from 65 to 89% ( $\text{RSD} \leq 5.6\%$ ) were obtained (Table I) over the range 1.1–1.9  $\mu$ L (1.12–1.94 mg) of aniline applied to the pads. No significant improvement in the



**FIGURE 2.** A calibration plot of peak area against volume of aniline added to pads (the source of the data in Table I) following the extraction process. Eight microliters of the extracted solution was applied to GC analysis. The best straight-line fit from linear analysis of the data also is shown. The best linear correlation for aniline was obtained over the range 1.1–1.9  $\mu\text{L}$  ( $n = 5$ ).

recovery was observed when  $\geq 2.1 \mu\text{L}$  of aniline was added to pads (Table I).

#### Glove Thickness Test

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

#### Glove Breakthrough Time Determination

The data demonstrated breakthrough with any of the gloves tested with the modified ASTM F739 and direct permeability testing procedures (Table II). Permeation of aniline through the gloves was detected by either the analyzer-detected response or the change in color of the pads; however, the change in color of the pads was slow to develop, so the pads were removed from the glove immediately when the change in color of the pads turned

to light orange or based on the analyzer-detected response. Slower permeation by aniline was observed for nitrile butyl rubber (Sol-Vex gloves) and natural latex rubber (polycoated latex gloves) materials, whereas rapid permeation by aniline for polyvinyl chloride (PVC, vinyl gloves), nitrile (powdered nitrile gloves), and polymerized alkenes ( $\geq$  a carbon–carbon double bond in monomer) materials was observed (Table II). The nitrile and nitrile butyl rubber glove materials swelled at the permeation time.

#### Quantitative Determination of Aniline

The concentration of challenge aniline on the pads following permeation through the gloves was determined, ranging from 0.53 to 0.55 mg/cm<sup>2</sup> or 1.79–1.88 mg/pad (pad:  $2.0 \times 1.7 \text{ cm}$ ; 1.79–1.88 mg/pad [1.75–1.84  $\mu\text{L}$ /pad] of aniline based on its linear equation from Figure 2 [at 1.21–1.27  $\mu\text{L}$ /pad] and its recovery of 69% at 1.3  $\mu\text{L}$  added).

#### Precision

The extraction-GC process was analyzed for aniline at a variety of volumes. The recovery precision was good, with RSD  $\leq 5.6\%$  (over the range 1.1–1.9  $\mu\text{L}$  of aniline applied to pads and 8.0  $\mu\text{L}$  of extracted solutions for GC analysis).

## DISCUSSION

The efficiency of adsorption of aniline on the pads was assessed. It was shown that aniline was nearly completely adsorbed (99–100%) on the pads at spiking level of 1.94 mg.

The results obtained with the ME-GC procedure were consistent for reproducible recovery of aniline from pads that had been exposed to this amine. The recovery was obtained over the range 1.1–1.9  $\mu\text{L}$  of aniline applied to pads and 8.0  $\mu\text{L}$  of the extracted solutions for GC analysis. Recovery depended on the volume of aniline applied to the pad (Table I).

Excellent linear correlations ( $p < 0.001$ ) were obtained for aniline over the range 1.1–1.9  $\mu\text{L}$  to pads and 8.0  $\mu\text{L}$  of the extracted solutions for GC analysis.

The results indicated that differences in thickness and glove materials yielded different breakthrough times. The results of the permeation experiments, as shown in Table II, demonstrated that within a given material type of the gloves tested, thickness had a

**TABLE II.** Results of Glove Permeation Tests ( $n = 3$ ) for Aniline

Type of Glove	Material of Glove	Style or Model No.	Thickness <sup>A</sup> (palm & cuff) (mm)	Breakthrough Time <sup>B</sup> (palm & cuff)	Thickness <sup>A</sup> (finger) (mm)	Breakthrough Detection Time <sup>C</sup> (finger)	Mass of Aniline Found (mg/pad)
Nonsterile vinyl	PVC	Triflex	0.15 $\pm$ 0.01	250 $\pm$ 6 sec	0.11 $\pm$ 0.01	380 $\pm$ 4 sec	1.79 $\pm$ 0.09 (0.53 mg/cm <sup>2</sup> )
Polycoated latex	natural latex rubber	Boxed Ambi	0.14 $\pm$ 0.01	500 $\pm$ 5 sec	0.15 $\pm$ 0.01	640 $\pm$ 5 sec	1.81 $\pm$ 0.05 (0.53 mg/cm <sup>2</sup> )
Copolymer	polymerized alkenes	Boxed Ambi	0.10 $\pm$ 0.01	190 $\pm$ 7 sec	0.16 $\pm$ 0.01	380 $\pm$ 8 sec	1.85 $\pm$ 0.08 (0.54 mg/cm <sup>2</sup> )
Disposable vinyl	PVC	Dura-Touch	0.18 $\pm$ 0.01	510 $\pm$ 5 sec	0.18 $\pm$ 0.01	690 $\pm$ 6 sec	1.83 $\pm$ 0.07 (0.54 mg/cm <sup>2</sup> )
Powdered nitrile	nitrile	Boxed Ambi	0.10 $\pm$ 0.01	182 $\pm$ 6 sec (swelled)	0.12 $\pm$ 0.01	400 $\pm$ 5 sec (swelled)	1.88 $\pm$ 0.09 (0.55 mg/cm <sup>2</sup> )
Sol-Vex	nitrile butyl rubber	37-175	0.36 $\pm$ 0.01	51 $\pm$ 1 min (swelled)	0.38 $\pm$ 0.01	82 $\pm$ 1 min (swelled)	1.87 $\pm$ 0.06 (0.55 mg/cm <sup>2</sup> )

<sup>A</sup>Mean thickness  $\pm$  SD ( $n=5$ )

<sup>B</sup>Breakthrough time detected by the analyzer-detected response or by the change in color of indicator pads (the ASTM F739 testing procedure)

<sup>C</sup>Breakthrough time detected by the change in color of indicator pads (the direct permeability testing procedure)

primary effect on the breakthrough time of the challenge chemical. Differences in glove materials yielded different breakthrough times (Table II). For vinyl, nitrile, or polymerized alkenes materials, rapid permeation by aniline was observed, whereas slower permeation by aniline for natural latex rubber or nitrile butyl rubber materials was observed.

Table II also shows that there were significant differences in breakthrough times between the modified ASTM F739 and direct testing methods for these gloves when the thicknesses were similar. It is probable that the pressure generated by the pump within the closed-loop system in the modified ASTM F739 method caused aniline to permeate more quickly than actual breakthrough times in the direct testing method.

Permeation of aniline through the gloves was detected by either the change in color of the pads or the analyzer-detected response. It was found that the aromatic amine pad itself needed 4 to 5 min to develop a color characteristic in the detection system.

Since thickness 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 concentration in the pads caused by permeation in these thinner areas of the material. Thus, although material variations could not be accurately measured, the effects of these variations could still be observed through their contribution to the permeation variations.

## CONCLUSION

Quantitative data were obtained for aniline permeation through various glove materials. The results indicate that pads exposed to the aniline studied can be successfully analyzed under the conditions for the extraction process and GC analysis described. This procedure offers potential for developing permeation breakthrough indicators for the entire series of aromatic amine compounds that may be encountered in workplace exposure situations. A companion study under actual workplace conditions will be conducted to determine the validity of laboratory findings under the dynamic conditions found during workplace exposures.

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