

# Permeation of a straight oil metalworking fluid through disposable nitrile, chloroprene, vinyl, and latex gloves

Wenhai Xu\*, Shane S. Que Hee

*Department of Environmental Health Sciences and UCLA Center for Occupational and Environmental Health,  
UCLA School of Public Health, 650 Charles Young Jr. Drive South, Los Angeles, CA 90095-1772, USA*

Received 27 September 2006; received in revised form 12 January 2007; accepted 24 January 2007

Available online 31 January 2007

## Abstract

The aim was to investigate the permeation of a straight oil metalworking fluid (MWF) through four types of glove materials using the gravimetric method and the modified American Society for Testing and Materials (ASTM) F739-99a method with perfluorohexane and hexane as collection solvents. The residual masses on the collection side were determined after solvent evaporation for both MWF and blank (air) challenges. With perfluorohexane, the permeated MWF through gloves after 8 h was around the lower quantifiable limit for nitrile,  $0.7 \pm 0.2 \text{ mg/cm}^2$  for vinyl,  $10.0 \pm 1.2 \text{ mg/cm}^2$  for chloroprene, and  $33.0 \pm 0.7 \text{ mg/cm}^2$  for latex. Hexane increased the amounts and rates of MWF permeating all gloves 39–73 times, except for vinyl where extractable mass was so high that the residues for MWF challenges and for hexane blanks were indistinguishable. Hexane as a collection solvent also extracted more glove components than did perfluorohexane, and back-permeated gloves in much larger amounts. Perfluorohexane allows better estimates of the real permeation rates and breakthrough times than does hexane. Recommendations based on breakthrough times and permeation rates with hexane collection are thus too conservative, although the relative ranking of these four types of gloves was the same with either collection solvent.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Permeation; Perfluorohexane; Disposable gloves; Metalworking fluids; Gravimetry; Solvent effect

## 1. Introduction

Metalworking fluids (MWFs) improve machining performance and prolong cutting tool life through lubricating, cooling, and removing debris from the workpiece and the tool. One of the four major types of MWFs is the straight oil type [1]. Straight oil MWFs are essentially 100% refined distillate (mineral oil) of petroleum or vegetable oils with some added components such as bactericides and extreme pressure additives. The latter are often chlorinated paraffins, organosulfur-, or organophosphorus-compounds. Straight oil MWFs are used directly without dilution with water [1–3].

The National Occupational Exposure Survey in 1981–82 by the National Institute for Occupational Safety and Health (NIOSH) of the United States estimated 1.2 million workers were potentially exposed to MWFs, and the industrial use of MWFs has continued to increase [1,2,4,5]. Exposures to

MWF are associated with respiratory disorders [1,4,6,7], and historically with various cancers [1,4]. Available data are still inadequate to conclude whether efforts to eliminate carcinogenic components have lowered cancer risk because of the long latency period [1,8,9]. Many exposed workers (14–67%) develop irritant or allergic contact dermatitis [1]. Other cutaneous disorders include folliculitis, oil acne, oil keratosis, squamous cell carcinoma, pigment changes, oil granuloma, nail disorders, paronychia, photosensitivity reactions, and mechanical cuts from metal shavings [1].

The major routes of MWF exposure to workers are inhalation and skin contact. Skin contact can occur during the preparation or draining of fluids, handling of workpieces, changing and setting of tools, and during maintenance and cleaning operations. During machining, fluids may splash if there are no splashguards or if the latter are inadequate. Under such circumstances, gloves should be worn to protect the skin and to lower skin absorption [1,4].

Based on limited data, NIOSH recommended nitrile gloves for workers handling MWFs [1,10,11]. The permeation of MWFs is difficult to quantify, because they are complex mixtures

\* Corresponding author.

E-mail address: [xuwenhai@ucla.edu](mailto:xuwenhai@ucla.edu) (W. Xu).

[2,12] and our research team has shown that MWF composition in the collection solvent can change relative to the original challenge [10,13]. The permeation of a straight oil MWF Deolene D4 through a disposable and a chemically protective nitrile glove has previously been studied using chromatographic and gravimetric methods [10]. The collection medium was hexane instead of water or air, because hexane immediately and adequately removed the permeated non-polar and non-volatile challenge from the inner surface of the gloves, and avoided underestimation of exposure to the challenge MWF through the glove. The steady state permeation rate of D4 through the disposable glove was  $3.5 \pm 2.2 \mu\text{g}/\text{cm}^2/\text{min}$ , and the detection breakthrough time was  $0.7 \pm 0.3 \text{ h}$ . The normalized breakthrough time was  $<0.7 \text{ h}$ . It was recommended that the disposable nitrile glove could be worn for about 30 min for incidental contact with straight oil MWFs. Disposable gloves were tested because disposable gloves provide better dexterity and user comfort than the thicker chemically protective gloves, and they are usually preferred by workers [14,15].

One permeation guide [16] for the thicker chemically protective gloves classifies nitrile to perform excellently against hexane with breakthrough over 360 min; neoprene (another name for chloroprene) had its breakthrough at 40 min and higher steady state permeation rate; natural rubber (similar to latex) and vinyl were degraded by hexane, and their permeation behavior was not tested. Perfluorohexane is more non-polar than hexane, and it may be a better collection solvent than hexane for disposable nitrile, latex, chloroprene, and vinyl gloves challenged by non-polar compounds like the straight oil MWF.

In the present study, the permeation of a complex metalworking fluid through disposable nitrile, latex, chloroprene, and vinyl gloves was investigated using both perfluorohexane and hexane as the collection solvents. The effects of collection solvent on the permeation through each glove and the effects on the relative ranking of the performance of different gloves were determined.

## 2. Experimental

### 2.1. Materials

The straight oil type MWF Deolene D4 was purchased from W. S. Dodge Oil (Maywood, CA). The MSDS listed only mineral

oil (CAS# 64741-97-5) of “variable amount”. This mineral oil contained hydrocarbons predominantly in the C15 through C30 range with relatively few normal paraffins [17]. The boiling point of D4 was  $>190 \text{ }^\circ\text{C}$ .

Optima grade hexane was from Fisher Scientific (Pittsburgh, PA). Perfluorohexane was from Apollo Scientific (Bredbury, Cheshire, UK).

The trade names, manufacturers, and structural information of the four disposable gloves (one each of nitrile, latex, chloroprene, and vinyl, purchased from Fisher Scientific, Pittsburgh, PA) are listed in Table 1.

### 2.2. Permeation procedure

The permeation procedure was based on a modified American Society for Testing and Materials (ASTM) F739-99a permeation method [10,18–20]. Out-of-the-box gloves were conditioned for 24 h in a desiccator, where the relative humidity was maintained at  $55 \pm 1\%$  by saturated aqueous sodium dichromate as recommended by the ASTM method. Circular pieces of 42.5 mm diameter were cut from the palm area of six gloves of each type. Right before permeation, the thickness of gloves was measured by a calibrated Marathon Electronic Digital Micrometer Model CO 030025 (0–25 mm, 0.001 mm resolution) (Fisher Scientific). Six random readings for each cut glove piece were made. At the same time, a Mettler analytical balance AE260 DeltaRange (Mettler, Hightstown, NJ) was used to weigh the gloves.

Each piece was then held between the two Teflon gaskets and the Pyrex chambers of an I-PTC-600 ASTM-type permeation cell (Pesce Lab, Kennett Square, PA) by a uniform torque, with the outer surface of the glove facing the challenge chamber. The test area of the glove between the two chambers had a diameter of 25.4 mm. For each type of glove, three replicates were tested for permeation of D4 using perfluorohexane or hexane as the collection solvent. A 10 mL volume of D4 was pipeted into the challenge chamber, and 10 mL of perfluorohexane or hexane was pipeted into the collection chamber. Three perfluorohexane or hexane blank tests with 10 mL perfluorohexane or hexane in the collection chamber, and only air in the challenge chamber, were also performed. The total challenge and control gloves were 48 pieces.

Table 1  
Disposable gloves used in this study

Glove type	Descriptive brand name	Manufacturer (address)	Monomer	Thickness $\pm$ standard deviation ( $\mu\text{m}$ )
Nitrile	Kimberly-Clark safeskin blue nitrile exam gloves (nitrile powder-free latex-free)	Kimberly-Clark (Roswell, GA)	Acrylonitrile/butadiene	$118 \pm 5$
Latex	Kimberly-Clark safeskin satin plus powder-free latex exam gloves	Kimberly-Clark (Roswell, GA)	<i>cis</i> -Isoprene	$134 \pm 8$
Chloroprene	SemperCare CRX by sempermed chloroprene examination gloves (latex-free powder-free beaded)	Sempermed (Clearwater, FL)	Chloroprene	$157 \pm 5$
Vinyl	OAK laboratory handies standard weight vinyl gloves (nonallergenic latex-free powder-free recyclable single use)	Oak (Stow, OH)	Vinyl chloride	$175 \pm 24$

The permeation cells were immersed six at a time in a Fisher Shaking Water Bath model 127 at  $35.0 \pm 0.5^\circ\text{C}$ . The cells were agitated for 8 h at an average horizontal shaking speed of  $70 \pm 5$  cycles/min, with traveling distance of 10.24 cm/cycle.

After permeation testing, the collection solvent and the challenge D4 were weighed. The permeation cells were disassembled, and the outer surfaces of glove pieces were blotted dry with Kimwipes. The glove pieces were re-conditioned in the desiccator for 24 h before weighing and thickness measurements.

### 2.3. Determination of permeated mass

To determine the amount of permeated D4, the final collection solution of each 8-h test or blank run was evaporated in pre-weighed 5-mL V-vials placed in a Temp-Blok Module Heater model H2025-1 (Lab-Line Instruments, Melrose Park, IL) at  $35 \pm 3^\circ\text{C}$  under a nitrogen flow of  $500 \pm 50$  mL/min. The mass ( $m$ ) of permeated D4 was determined from weighing after 40 min of solvent evaporation.

The time-weighted permeation rate ( $P_a$ ) was calculated using equation

$$P_a = \left( \frac{m/A}{t} \right)$$

where  $m$  is the permeated mass corrected for blank extractable mass,  $A$  is the exposed permeation area of the glove, and  $t$  is the duration of the permeation tests.

All gravimetric experiments were done in triplicate.

### 2.4. Statistics

The independent *Student's t*-testing was performed when the variances were equal. *Welch's t*-test was used instead when the variances were significantly different. The normality assumption of these tests may be questionable. Thus, the non-parametric *Wilcoxon* test, which assumed no normality of data, was also used. The difference in a comparison of two groups was considered significant if  $p \leq 0.05$ .

## 3. Results and discussion

### 3.1. Glove physical changes

#### 3.1.1. Thickness

The thicknesses of glove materials before permeation are listed in Table 1. The gloves from thin to thick were nitrile, latex, chloroprene, and vinyl. The thickness of vinyl was the most variable, with coefficient of variation (CV) of about 14%. The CVs of the other gloves were less than 10%.

In the blank tests, chloroprene, nitrile, vinyl, and latex did not swell significantly after exposure to perfluorohexane alone ( $p > 0.05$ ). Chloroprene, nitrile, and latex did not swell significantly after exposure to hexane alone either. Vinyl shrank about 16% ( $29 \pm 21 \mu\text{m}$ ) ( $p < 0.001$ ), and it became rigid.

The thicknesses of nitrile and vinyl after exposure to D4 did not change significantly for perfluorohexane collection.

Chloroprene swelled about 8.8% ( $13 \pm 5 \mu\text{m}$ ) ( $p < 0.001$ ). Latex swelled about 28% ( $37 \pm 7 \mu\text{m}$ ) ( $p < 0.001$ ).

The thicknesses of nitrile after exposure to D4 did not change significantly with hexane collection. Chloroprene swelled about 9.0% ( $15 \pm 4 \mu\text{m}$ ) ( $p < 0.001$ ). Latex swelled about 32% ( $43 \pm 11 \mu\text{m}$ ) ( $p < 0.001$ ). Vinyl shrank about 17% ( $30 \pm 14 \mu\text{m}$ ) ( $p < 0.001$ ). Thus, hexane rather than D4 was responsible for the shrinkage of vinyl.

#### 3.1.2. Weight

For the blank experiments with perfluorohexane collection, the weights of vinyl decreased 0.7% ( $2.1 \pm 0.1$  mg). The weight changes of other gloves were less than 0.3% or 0.5 mg.

For blank experiments with hexane collection, the weight change of nitrile was not significant ( $p > 0.05$ ). Chloroprene decreased 0.7% ( $1.8 \pm 0.3$  mg). Latex decreased 0.4% ( $0.7 \pm 0.3$  mg). Vinyl decreased 17% ( $56.3 \pm 9.5$  mg). These changes were statistically significant at  $p \leq 0.05$ .

For D4 permeation with perfluorohexane collection, the weight of nitrile increased 0.4% ( $0.7 \pm 0.1$  mg). Chloroprene increased 12% ( $31.6 \pm 5.0$  mg). Latex increased 59% ( $110 \pm 20$  mg). Vinyl decreased 1.9% ( $5.5 \pm 0.7$  mg). These changes were statistically significant at  $p \leq 0.05$ .

For D4 permeation with hexane collection, the weight of nitrile increased 1.7% ( $2.9 \pm 1.1$  mg). Chloroprene increased 12% ( $36.2 \pm 3.2$  mg). Latex increased 72% ( $136.9 \pm 9.6$  mg). Vinyl decreased 15% ( $47.5 \pm 8.8$  mg). These changes were statistically significant at  $p \leq 0.05$ .

#### 3.1.3. Effects of D4 and collection solvents on glove thickness and weight change

The thickness and weight changes of chloroprene and latex gloves were mostly due to D4 rather than the collection solvent. In the blank tests, the thickness and weight changes for these two gloves were not significant or less than 2.0%. For either glove, the thickness changes for hexane collection and for perfluorohexane collection were comparable. So were their weight changes.

In contrast, the presence of challenge D4 did not affect the thickness of vinyl. The thickness changes for vinyl gloves with hexane collection (16% for blanks and 17% for D4 challenges) were mostly due to hexane. So were the weight changes with hexane collection (17% for blanks and 15% for D4 challenges). With perfluorohexane as the collection solvent, the thickness changes were not significant and the weight decrease was 2%.

The thickness and weight changes for nitrile gloves were minimal.

The above results coincided with challenging these four gloves with D4. Without collection solvents, only latex and chloroprene increased their thickness and weight significantly [21].

### 3.2. Back permeation of collection solvent through the glove

For blank experiments with hexane and perfluorohexane collections, the weights of collection solvents in the collection

chamber after 8 h of experiments were either not significantly different ( $p > 0.05$ ), or the difference was less than 0.1 g. The mass of back-permeated collection solvents through the four types of gloves was thus minimal when the challenge chambers were empty. For D4 permeation testing with perfluorohexane as the collection solvent, the weights of collection solutions were not significantly different from each other. The weights of D4 in the challenge chambers at the end of the experiments for the four types of gloves did not differ either.

For D4 permeation with hexane as the collection solvent, the weights of hexane collection for nitrile and vinyl were not significantly different ( $p > 0.05$ ). The weights of the challenge D4 for these two gloves did not differ. The weights of collection hexane for chloroprene were  $1.3 \pm 0.2$  g less than that for nitrile and vinyl. After permeation testing with D4, latex, and hexane, the liquid level on the challenge D4 side was much higher than that on the collecting hexane side. The weights of challenge D4 for chloroprene were  $1.4 \pm 0.1$  g more than that for nitrile and vinyl. The weights of hexane for latex were  $3.5 \pm 0.1$  g less than that for nitrile and vinyl. The weights of D4 for latex were  $3.6 \pm 0.1$  g more than that for nitrile and vinyl. The masses of permeated D4 through chloroprene and latex were determined in the next section ( $0.444 \pm 0.015$  and  $1.300 \pm 0.047$  g D4 permeated chloroprene and latex with hexane collection, respectively). From that,  $1.8 \pm 0.2$  g hexane back permeated through chloroprene, and  $4.9 \pm 0.2$  g of hexane back-permeated through latex, assuming evaporation was negligible. These data indicate substantial hexane back permeation through chloroprene and latex.

### 3.3. Permeation of D4

The weights of residues after evaporating collection solutions after the 8-h permeation experiments are summarized in Table 2.

Table 2  
The raw data for mass of residue from evaporated collection solutions after 8 h of D4 permeation and for the method blanks

Glove	Collection solvent	Challenge	Residues (mg)		Statistical significance for comparing challenge and blank
			Original masses in triplicate	Mean $\pm$ standard deviation	
Chloroprene	Hexane	D4	426.0, 467.4, 445.3	$446.2 \pm 20.7$	a,c
		Blank	2.8, 1.9, 1.7	$2.1 \pm 0.6$	
	Perfluorohexane	D4	12.2, 8.8, 11.2	$10.7 \pm 1.7$	a,c
		Blank	0.5, 0.3, 0.2	$0.3 \pm 0.2$	
Latex	Hexane	D4	1344.2, 1335.1, 1226.0	$1301.8 \pm 65.8$	a,c
		Blank	1.1, 2.7, 1.6	$1.8 \pm 0.8$	
	Perfluorohexane	D4	32.5, 33.6, 34.3	$33.5 \pm 0.9$	b,c
		Blank	0.5, 0.3, 0.0	$0.3 \pm 0.3$	
Nitrile	Hexane	D4	8.2, 2.3, 10.9	$7.1 \pm 4.4$	c
		Blank	0.3, 0.6, 0.4	$0.4 \pm 0.2$	
	Perfluorohexane	D4	0.4, 0.1, 0.1	$0.2 \pm 0.2$	
		Blank	0.3, 0.0, 0.1	$0.1 \pm 0.2$	
Vinyl	Hexane	D4	39.6, 48.9, 54.1	$47.5 \pm 7.3$	
		Blank	41.0, 51.2, 50.5	$47.6 \pm 5.7$	
	Perfluorohexane	D4	2.2, 2.2, 2.7	$2.4 \pm 0.3$	b,c
		Blank	1.6, 1.7, 1.7	$1.7 \pm 0.1$	

<sup>a</sup> The  $p$ -value  $\leq 0.05$ , calculated with *Welch's t*-test for unequal variance.

<sup>b</sup> The  $p$ -value  $\leq 0.05$ , calculated with *Student t*-test for equal variance.

<sup>c</sup> The  $p$ -value  $\leq 0.05$ , calculated with the non-parametric *Wilcoxon* test.

There are residue data listed for 48 pieces of cut glove, 12 for each glove type.

Evaporation of 10 mL perfluorohexane and 10 mL hexane produced no detectable residue. The evaporation process to measure permeated D4 in hexane collection has been validated elsewhere, and the recovery was  $99.6 \pm 3.1\%$  [10]. The recovery for perfluorohexane collection was  $96.7 \pm 0.4\%$ .

#### 3.3.1. Glove extractables by hexane and perfluorohexane

As a subset and rearrangement of the data from Table 2, Table 3 summarizes the mass of extractables from glove materials. These data were from the blank experiments where the challenge chambers were left empty. The statistical significance column in Table 3 is for the hypothesis that the amounts of extractables are the same for hexane collection and perfluorohexane collection. It was calculated from not only the *Student's t*- and *Welch's t*-tests, but also the non-parametric *Wilcoxon* test, since the masses were near detection limit or below the lower quantifiable limit except for vinyl where the lower quantifiable limit of 1 mg was exceeded. The results showed that hexane extracted more than perfluorohexane did from latex, chloroprene, and vinyl glove ( $p \leq 0.05$ ). For example, the amount of vinyl glove extractable by hexane was about 28 times that by perfluorohexane. The larger loss of glove extractables by hexane compromised glove performance. The difference for nitrile glove was not significant ( $p = 0.06$ ).

The relative amounts of extractables for these gloves are presented in Fig. 1. For both hexane and perfluorohexane collection, vinyl gloves had the most extractables. For hexane collection, the mass of nitrile extractables was significantly less than that for the other gloves. Vinyl glove extractables were significantly higher than those of the other three gloves. The extractables for latex and chloroprene were not significantly different. For

Table 3  
The mass of extractables from disposable gloves

Glove	Collection solvent	Mean $\pm$ standard deviation (mg)	Statistical significance for comparing hexane and perfluorohexane collection
Chloroprene	Hexane	2.1 $\pm$ 0.6	b,c
	Perfluorohexane	0.3 $\pm$ 0.2	
Latex	Hexane	1.8 $\pm$ 0.8	b,c
	Perfluorohexane	0.3 $\pm$ 0.3	
Nitrile	Hexane	0.4 $\pm$ 0.2	
	Perfluorohexane	0.1 $\pm$ 0.2	
Vinyl	Hexane	47.6 $\pm$ 5.7	a,c
	Perfluorohexane	1.7 $\pm$ 0.1	

<sup>a</sup> The  $p$ -value  $\leq 0.05$ , calculated with *Welch's t*-test for unequal variance.

<sup>b</sup> The  $p$ -value  $\leq 0.05$ , calculated with *Student t*-test for equal variance.

<sup>c</sup> The  $p$ -value  $\leq 0.05$ , calculated with the non-parametric *Wilcoxon* test.

perfluorohexane collection, the amount of vinyl glove extractables was significantly higher than that of the other three gloves. The extractables of the other three gloves were not significantly different.

Gas chromatography–mass spectrometry (GC–MS) analysis indicated the major components of the vinyl extractables by both hexane and perfluorohexane were plasticizer phthalates, the health effects of which have caused concern [22,23]. Other investigators have also identified extractables of gloves [24–27].

### 3.3.2. The amount of permeated D4

The statistical significances in Table 2 were for the hypothesis that the residue mass of collection solutions for D4 challenge and that for blank experiments were the same (zero or negligible D4 permeated gloves). The significance from *t*-tests and that from the *Wilcoxon* test agreed except for that for nitrile/hexane, where the  $p$ -value was 0.12 from the *Welch's t*-test and it was 0.04 from the *Wilcoxon* test. The *Wilcoxon* test was more robust than the *t*-tests here, and confirmed statistically that D4 did permeate nitrile when hexane was the collection solvent. Table 2 also shows statistically that except for nitrile/perfluorohexane and vinyl/hexane, significant amounts of D4 permeated gloves ( $p \leq 0.05$ ).

Table 4 lists the permeated D4 mass for 8 h and 8-h time-weighted permeation rate. The statistical significance column in Table 3 was for the hypothesis that the permeated amounts of D4, and equivalently the time-weighted permeation rates, were the same for hexane collection and for perfluorohexane collection. The hypothesis was tested using the *Student's t*-, *Welch's t*-, and the *Wilcoxon* tests. The hypothesis was rejected for chloroprene, latex, and nitrile gloves, where hexane collection resulted in more D4 permeation. This corresponded to the more extractables by hexane for chloroprene and latex gloves. The tests failed to detect the difference for vinyl between hexane collection and perfluorohexane collection. This was probably due to the large amount of extractables by hexane that overwhelm the amount of D4 permeated.

The amounts of permeated D4 after correcting for method blank are presented in Fig. 2. With hexane collection, the amount of D4 permeated in the following decreasing order: latex > chloroprene > vinyl = nitrile. The  $p$ -value from the *Student's t*-test for the three consecutive comparisons were <0.001, <0.001, and 0.17. The 8-h time-weighted permeation rate for nitrile was about 1/63 of that for chloroprene, and about 1/184 of that for latex. The failure to show significant difference between vinyl and nitrile may be due to the large amount of vinyl extractables.

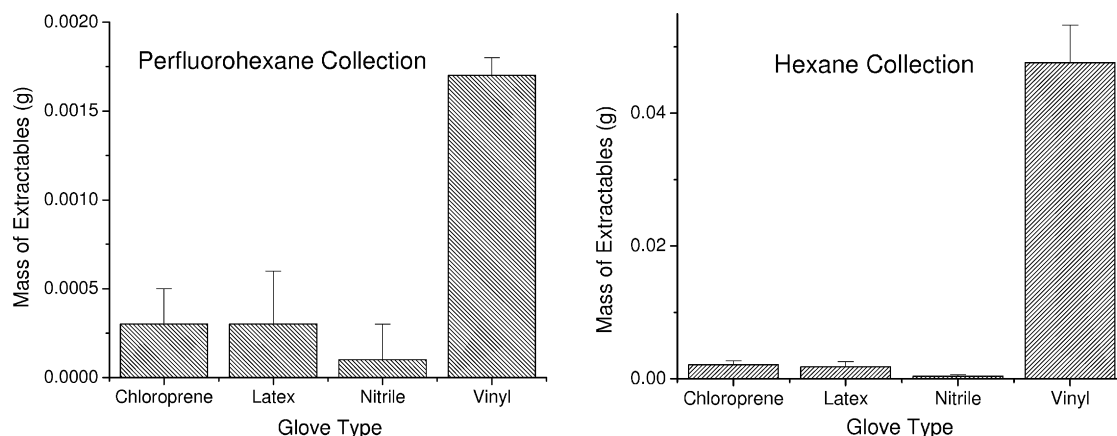


Fig. 1. The masses of extractables from chloroprene, latex, nitrile, and vinyl disposable gloves by perfluorohexane and hexane. Note the scale for hexane collection is about 20 times larger.

Table 4  
The mass of permeated D4 for 8 h and the 8-h time-weighted permeation rate

Glove	Collection solvent	Permeated mass $\pm$ standard deviation (mg)	8-h time-weighted permeation rate $\pm$ standard deviation ( $\mu\text{g}/\text{cm}^2/\text{min}$ )	Statistical significance for comparing hexane and perfluorohexane collection
Chloroprene	Hexane	444 $\pm$ 15	182.4 $\pm$ 6.0	b,c
	Perfluorohexane	10.0 $\pm$ 1.2	4.1 $\pm$ 0.5	
Latex	Hexane	1300 $\pm$ 47	534 $\pm$ 19	b,c
	Perfluorohexane	33.0 $\pm$ 0.7	13.6 $\pm$ 0.3	
Nitrile	Hexane	7.0 $\pm$ 3.1	2.9 $\pm$ 1.3	b,c
	Perfluorohexane	0.1 $\pm$ 0.2 <sup>a</sup>	0.04 $\pm$ 0.08	
Vinyl	Hexane	0.0 $\pm$ 6.6 <sup>a</sup>	0.0 $\pm$ 2.7	
	Perfluorohexane	0.7 $\pm$ 0.2	0.3 $\pm$ 0.1	

<sup>a</sup> The amount of residue for D4 challenge and that for the blank experiments are not significantly different. The original data are shown in Table 2.

<sup>b</sup> The  $p$ -value  $\leq$  0.05, calculated with *Welch's t*-test for unequal variance.

<sup>c</sup> The  $p$ -value  $\leq$  0.05, calculated with the non-parametric *Wilcoxon* test.

With perfluorohexane collection, the amount of D4 permeated in the following decreasing order: latex > chloroprene > vinyl > nitrile. The  $p$ -value from *Student's t*-test for the three consecutive comparisons were <0.001, <0.001, and 0.02. The 8-h time-weighted permeation rate for vinyl was about 1/14 of that for chloroprene, about 1/45 of that for latex, and about 8 times that for nitrile.

With both hexane and perfluorohexane collections for 8 h, the amount of D4 permeating through latex, and the time weighted permeation rate, is the largest. Chloroprene is the second. The permeation rates and amounts permeating nitrile and vinyl are the smallest.

The results based on hexane collection overestimated the actual exposure through glove materials, and provided more conservative protection data. The results based on perfluorohexane probably better reflect the real exposure situation. The choice of the organic collection solvents did not alter the ranking of glove performance. In the case of the straight oil metalworking fluid Deolene D4, the best glove was nitrile, the second vinyl, the third chloroprene, and the worst latex. Recommendations based on the 8-h time-weighted permeation rates with hexane collection overestimated the real exposure by 44, 39, and 73 times for chloroprene, latex, and nitrile, respectively. The vinyl

extractables dominated the residue mass, especially in the case of hexane collection.

It was shown previously that the 8-h time-weighted permeation rate was about 20% less than the steady state permeation rate for D4 permeating disposable nitrile with hexane collection [10]. Combining with the chromatographic method and assuming that chromatographic responses are proportional to the injected MWF, one will be able to determine the lag time, breakthrough time, steady state permeation rate, and diffusion coefficient of MWF permeating glove materials. However, the much simplified gravimetric procedure used in the present paper was sufficient to meet the needs of recommending and ranking gloves and estimating worker exposure. The method is best used for moderately- or non-volatile complex mixtures.

#### 4. Conclusions

The present paper is the first to study and report the permeation of a straight oil MWF through four types of disposable glove materials using the gravimetric method. Nitrile gloves were the best for this type of MWF. Hexane as a collection solvent increased the amounts and rates of D4 permeating all gloves, except for vinyl glove, for which the large amount of

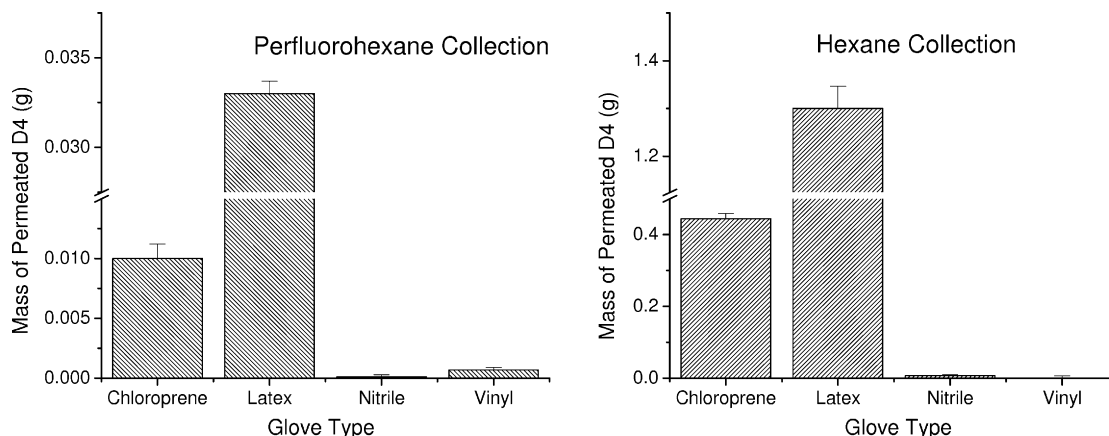


Fig. 2. The masses of permeated D4 through chloroprene, latex, nitrile, and vinyl disposable gloves using perfluorohexane and hexane as the collection solvents. Note the scale for hexane collection is about 40 times larger.

extractables for hexane blank tests made the comparison not significant. Hexane extracted much more glove components than did perfluorohexane, back-permeated gloves more, and increased the permeation of challenge agents. Recommendations based on permeation tests using hexane collection would be too conservative. The results using perfluorohexane collection should be more accurate. The ranking of performance of these four types of gloves for this non-volatile, non-polar MWF are the same with either collection solvent. As many non-volatile and non-polar toxic compounds are used in industry, and limited types of gloves are commercially available to choose for workers, this ranking of glove performance using organic collection solvents is an important and inexpensive screening technique.

### Acknowledgements

This project was funded by UCLA Center for Occupational and Environmental Health (COEH), NIOSH SCERC pilot project 405950, ASPH/NIOSH S1891-21/21, and NIOSH OH03754. We thank Professor Weng Kee Wong and Professor Bob Phalen for valuable discussions.

### References

- [1] NIOSH, Criteria for a Recommended standard: occupational exposure to metalworking fluids, DHHS (NIOSH), Publication no. 98-102, Cincinnati, Ohio, 1998.
- [2] J.P. Byers (Ed.), *Metalworking Fluids*, Marcel Dekker, New York, 1994.
- [3] R. Glaser, J. Pretty, K. Brown, J. Arnold, R.A. Lunsford, S.H. Park, Analytical method research for metalworking fluids at the National Institute for Occupational Safety and Health (NIOSH), *Gefahrst Reinhalt L 63* (2003) 237–240.
- [4] HSE, *Working Safely With Metalworking Fluids: A Guide For Employees*, HSE Books, 2002.
- [5] Independent Lubricant Manufacturers Association, ILMA Report on the Volume of Lubricants Manufactured in the United States and Canada by Independent Lubricant Manufacturers, *Lubricants World* 10 (2000) 10–15.
- [6] A.T. Simpson, M. Stear, J.A. Groves, M. Piney, S.D. Bradley, S. Stagg, B. Crook, Occupational exposure to metalworking fluid mist and sump fluid contaminants, *Ann. Occup. Hyg.* 47 (2003) 17–30.
- [7] M. Stear, Metalworking fluids—clearing away the mist? *Ann. Occup. Hyg.* 49 (2005) 279–281.
- [8] P. Apostoli, M. Crippa, M.E. Fracasso, D. Cottica, L. Alessio, Increases in polycyclic aromatic hydrocarbon content and mutagenicity in a cutting fluid as a consequence of its use, *Int. Arch. Occup. Environ. Health* 64 (1993) 473–477.
- [9] C.R. Mackerer, L.C. Griffis, J.S.J. Grabowski, F.A. Reitman, Petroleum mineral oil refining and evaluation of cancer hazard, *Appl. Occup. Environ. Hyg.* 18 (2003) 890–901.
- [10] W. Xu, S.S. Que Hee, Permeation of a straight oil metalworking fluid through a disposable and a chemically protective nitrile glove, *J. Hazard. Mater.* 137 (2006) 709–715.
- [11] K. Forsberg, K.G. Olsson, B. Carlmark, Testing of candidate glove materials against metal cutting fluids, in: R.L. Barker, G.C. Coletta (Eds.), *Performance of Protective Clothing*, ASTM STP, 900, American Society for Testing and Materials, Philadelphia, 1986, pp. 59–66.
- [12] J.E. Anderson, B.R. Kim, S.A. Mueller, T.V. Lofton, Composition and analysis of mineral oils and other organic compounds in metalworking and hydraulic fluids, *Crit. Rev. Env. Sci. Technol.* 33 (2003) 73–109.
- [13] W. Xu, S.S. Que Hee, Gas chromatography–mass spectrometry analysis of di-*n*-octyl disulfide in a straight oil metalworking fluid: application of differential permeation and Box-Cox transformation, *J. Chromatogr. A* 1101 (2006) 25–31.
- [14] D.H. Anna (Ed.), *Chemical Protective Clothing*, second ed., American Industrial Hygiene Association, Fairfax, VA, 2003.
- [15] A. Boman, T. Estlander, J.E. Wahlberg, H.I. Maibach (Eds.), *Protective Gloves for Occupational Use*, second ed., CPC Press, Boca Raton, 2005.
- [16] Ansell, Ansell, *Chemical Resistance Guide: Permeation and Degradation Data*, seventh ed., Coshocton, 2003.
- [17] American Chemical Society, Property of registered chemicals in SciFinder Scholar 2006, accessed September 26, 2006.
- [18] R.N. Phalen, S.S. Que Hee, Permeation of captan through disposable nitrile glove, *J. Hazard. Mater.* 100 (2003) 95–107.
- [19] Y.W. Lin, S.S. Que Hee, Permeation of a malathion formulation through butyl gloves, *J. Hazard. Mater.* 60 (1998) 143–158.
- [20] ASTM, Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Continuous Contact, ASTM Method F739-99a, in *Annual Book of ASTM Standards*, West Conshohocken, PA, 2004, pp. 1299–1309.
- [21] W. Xu, S.S. Que Hee, Swelling of Four Glove Materials Challenged by Six Metalworking Fluids, *Arch. Environ. Contam. Toxicol.* (2007) submitted for publication.
- [22] J.A. Tickner, T. Schettler, T. Guidotti, M. McCally, M. Rossi, Health risks posed by use of di-2-ethylhexyl phthalate (DEHP) in PVC medical devices: a critical review, *Am. J. Ind. Med.* 39 (2001) 100–111.
- [23] G. Latini, Potential hazards of exposure to di-(2-ethylhexyl)-phthalate in babies: a review, *Biol. Neonate* 78 (2000) 269–276.
- [24] M. Mutsuga, Y. Kawamura, C. Wakui, T. Maitani, Identification of migrants from nitrile-butadiene rubber gloves, *Shokuhin Eiseigaku Zasshi* 44 (2003) 103–109.
- [25] M. Mutsuga, C. Wakui, Y. Kawamura, T. Maitani, Isolation and identification of some unknown substances in disposable nitrile-butadiene rubber gloves used for food handling, *Food Addit. Contam.* 19 (2002) 1097–1103.
- [26] C. Wakui, Y. Kawamura, T. Maitani, Migrants from disposable gloves and residual acrylonitrile, *Shokuhin Eiseigaku Zasshi* 42 (2001) 322–328.
- [27] Y. Kawamura, M. Mutsuga, C. Wakui, T. Maitani, Identification of unknown substances in polyvinyl chloride gloves containing non-phthalate plasticizers, *Shokuhin Eiseigaku Zasshi* 43 (2002) 215–220.