

# Permeation of a straight oil metalworking fluid through a disposable and a chemically protective nitrile glove

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## Abstract

The aim of the present study was to quantify the permeation parameters of a complex water-insoluble straight oil metalworking fluid (MWF) of low volatility through nitrile gloves. The permeation through a chemically protective and a disposable glove was investigated using the American Society for Testing and Materials (ASTM) F739-99a method with hexane as the collection medium. Analysis of collection side samples involved gas chromatography–mass spectrometry (GC–MS) and gravimetry. The detection breakthrough time for the chemically protective glove was >10 h. For the disposable glove, the detection breakthrough time was  $0.7 \pm 0.3$  h, the lag time was  $1.6 \pm 0.1$  h, the diffusion coefficient was  $(3.7 \pm 0.3) \times 10^{-9}$  cm<sup>2</sup>/min, and the steady state permeation rate was  $3.5 \pm 2.2$  μg/cm<sup>2</sup>/min. The disposable nitrile glove can be worn for about 30 min for incidental contact with straight oil MWFs without known carcinogens. The chemically protective nitrile glove should be worn otherwise. The chromatogram for the permeate differed from that of the original MWF, resulting from the faster permeation of lower molecular weight congeners. The combination of chromatography and gravimetry allowed quantifying the permeation parameters of complex water-insoluble non-volatile mixtures.

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## 1. Introduction

Metalworking fluids (MWFs), also called cutting fluids or cutting oils, improve machining performance and prolong cutting tool life through lubricating, cooling, and removing debris from the workpiece and the tool. The four major types of MWFs are straight oil, soluble oil, semisynthetic, and synthetic [1]. Straight oil MWFs are essentially 100% refined distillate of petroleum (mineral oil) or vegetable oils with some added components such as bactericides and extreme pressure additives. The latter are often chlorinated paraffins, organosulfur-, or organophosphorus-compounds. Soluble oil, semisynthetic, and synthetic MWF concentrates have up to 80%, 5–30%, and 0% oil content, respectively, with the remainder being water and other additives such as surfactants, fungicides, bactericides, and corrosion inhibitors. The latter three MWF concentrates are diluted

with water before use. Water cools faster, while oils provide better lubrication [1–3].

The National Occupational Exposure Survey in 1981–1982 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 [1,3,4]. MWF exposure causes skin disorders (skin irritation, rash, oil acne), which are the most frequently reported health problems [1], and respiratory disorders (coughing, chest tightness, and asthma) [1,4,5]. Moreover, there are concerns about the carcinogenicity of MWFs [1]. The major routes of MWF exposure 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 [1,4]. Because the compositions of MWFs are proprietary, many components may not be listed in the material safety data sheet (MSDS). For example, di-*n*-octyl disulfide (DOD)

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was not listed in the MSDS, but about 0.4% (w/w) of this compound was found in the MWF studied in the present study [6]. The permeation properties of chemical mixtures through gloves must be determined by testing—not inferred from the permeation characteristics of the individual constituents [1].

NIOSH's recommendation of nitrile gloves for workers handling MWFs was based on a single paper, which was and is the only prior investigation on MWF permeation published in the peer-reviewed literature in English [1,7]. The MWFs tested were a straight oil MWF (Esso Somentor 33 made of kerosene) and an emulsifiable MWF (a Blasocut Blaser product). The chemically resistant glove materials evaluated were one natural rubber, one neoprene, and three types of nitriles, of thickness 0.32–0.66 mm. The collection medium was nitrogen (open loop), water or isopropanol (closed loop). The two-chamber permeation test cell had 5 mL-water rinses applied every 30 min to collect permeates. The analytical methods were ultraviolet spectrophotometry for water collection, and gas chromatography–flame ionization detection (GC–FID) for nitrogen collection. For the emulsifiable MWF, no permeation rate data were reported; the detection breakthrough times ( $t_{db}$ ) were 120–150 min for natural rubber, and over 150 min for neoprene and nitrile. For the straight oil MWF, only one permeation rate was reported, 2.6 mg/cm<sup>2</sup>/min for neoprene; the  $t_{db}$  were 112 min for neoprene, over 300 min, over 150 min, and over 120 min for the three nitrile types. Forsberg et al. concluded that nitrile was better than neoprene and natural rubber. Limited experimental procedures and results were reported. For example, it was not specified for which data the open or closed loop system was used.

It is difficult to quantify MWF exposure because MWFs are complex mixtures [1,3]. Mineral oils, important components of MWFs except the synthetic type, have not been successfully resolved even with modern chromatographic techniques [8,9]. Three general approaches have been used to characterize exposure to mineral oils or MWFs with mineral oils. The first is to select a marker compound. Roff et al. [10] monitored C<sub>10</sub>H<sub>22</sub> with high-performance liquid chromatography (detector not specified) as a marker of MWF contamination on Tyvek coveralls. This method was unable to determine MWF composition and MWF amount. A second approach is a gravimetric method often used for aerosol sampling. NIOSH method 5524 determines MWF aerosol concentration by the weight of the fraction extracted by a ternary (dichloromethane:methanol:toluene) or binary (methanol:water) solvent blend from an air filter sample [11]. The third approach is used in International Organization for Standardization (ISO) method 9377-2:2000 to determine hydrocarbon mixtures in water. The water sample was extracted with hexane or heptane. Polar substances were removed by Florisil clean-up. The extract was then concentrated by evaporation before analysis by GC–FID. The total peak area between *n*-decane (C<sub>10</sub>H<sub>22</sub>, boiling point 174 °C) and *n*-tetracontane (C<sub>40</sub>H<sub>82</sub>, boiling point 525 °C) was measured as the parameter for all hydrocarbons. The hydrocarbon amount was quantified by the external standards method. However, a representative external standard was not possible because of the complexity of the analyte composition. The response factors of all components were assumed to be equal.

In the present study, a novel procedure of combining the second and the third approaches was used. The amount of permeated MWF was measured directly by weighing the residue of the permeation collection solution after evaporation of the volatile hexane collection medium. The composition of permeated MWF at different permeation times was examined with GC–MS.

## 2. Materials and methods

### 2.1. Chemicals, gases and gloves

A straight oil type MWF, Deolene D-4 (referred to hereafter as 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. The boiling point of D4 was >190 °C. Optima grade hexane from Fisher Scientific (Pittsburgh, PA) was used as solvent for all solutions and as the permeation cell collection medium. Sodium dichromate was also from Fisher Scientific. Helium (99.9999%) as GC–MS carrier gas and nitrogen (99.9999%) for evaporation of hexane were obtained from Air Liquide (Long Beach, CA).

Kimberly-Clark SafeSkin nitrile powder-free exam gloves (Kimberly-Clark No. N330) were from Fisher Scientific. The chemically protective unsupported/unlined nitrile glove was Sol-Vex (catalog number 37–145, Ansell, Coshocton, OH). These two gloves have reliable quality and have been tested extensively by our research group [12–16,18].

### 2.2. Permeation procedure

The detailed procedure is provided elsewhere [12,16], and is based on the standard ASTM F739-99a permeation method [17].

In summary, out-of-the box gloves were conditioned 24 h at 55 ± 1% relative humidity in a desiccator containing saturated aqueous sodium dichromate. Circular glove pieces of 42.5 mm diameter were cut from the glove palms. 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. The test area of the glove between the two chambers had a diameter of 25.4 mm. A volume of 10-mL hexane was added as the collection medium; 10 mL of D4 was pipeted into the challenge chamber. Method blanks with the challenge chamber empty were also performed. Three permeation cells were immersed in a Fisher Shaking Water Bath model 127 at 35.0 ± 0.5 °C. The cells were agitated at an average horizontal shaking speed of 8.4 ± 0.5 cm/s to ensure no concentration gradients in both sides. For SafeSkin, 100 µL samples were withdrawn from the collection side after 0.0, 0.25, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 h, and deposited into 2-mL vials (screwcaps were Teflon-lined). For Sol-Vex, the permeation was stopped after 10 h. The aliquots were stored at –20 °C before they were thawed and a volume of 1 µL injected for GC–MS analysis. After permeation testing, three surface wipes with Kimwipes removed residual D4 on the challenge

side of the glove. The glove pieces were re-conditioned in the desiccator for 24 h before their weight and thickness were re-measured.

### 2.3. Glove physical changes

A Marathon Electronic Digital Micrometer Model CO 030025 (0–25 mm, 0.001 mm resolution) was purchased from Fisher Scientific to measure the thickness of gloves ( $l$ ) before and after permeation testing. Six readings on different spots were measured for each piece of cut glove. A Mettler analytical balance AE260 DeltaRange (Mettler, Hightstown, NJ) was used for weighing the gloves before and after permeation. Changes in glove thickness and weight were calculated relative to those before permeation testing and to method blank gloves. Student's  $t$ -testing determined whether these changes were statistically significant using  $p \leq 0.05$  as the criterion.

### 2.4. GC–MS analysis

GC–MS analyses were performed with an Agilent 6890N Network Gas Chromatograph (Agilent Technologies, Wilmington, DE) connected to an Agilent 5973 Network Mass Selective Detector (MSD) (Agilent Technologies). The column was an HP 5-MS 30 m  $\times$  0.25 mm i.d. (0.25  $\mu$ m film) fused silica capillary column (Agilent Technologies, part number 19091s-433). The flow of helium carrier was  $1.00 \pm 0.05$  mL/min. The temperature of the injector was 260 °C and that of the transfer line was 280 °C. The MSD was a quadrupole with an electron multiplier detector operated over the mass to charge ratio ( $m/z$ ) range 50–550 for total ion current (TIC) scan mode analyses. The selected ion monitoring (SIM) mode with  $m/z$  55 (the most abundant ion of D4) was performed on collection side solutions for Sol-Vex, as well as 0.25-h and 0.5-h permeation collections for SafeSkin to achieve highest sensitivity. A 1- $\mu$ L aliquot was injected. The 70 eV ion source and the quadrupole were held at 230 and 150 °C, respectively. The solvent delay was 3.5 min. The column was initially at 100 °C for 10 min, heated at 5 °C/min to 150 °C, maintained at 150 °C for another 10 min, heated at 5 °C/min to 230 °C, kept at 230 °C for 10 min, and then heated at 5 °C/min to 300 °C. The total run time was 70 min.

### 2.5. Calculation of permeation properties from GC–MS chromatogram parameters

The  $t_{db}$  was obtained from the GC–MS chromatograms when permeated D4 was first detected. The lag time ( $t_l$ ) [17] was determined by plots of GC–MS chromatographic parameters for the collection solution in the steady-state period versus permeation time, after correcting the chromatographic parameters for hexane loss due to collection side evaporation and prior sampling, and for fraction analyzed. Three types of GC–MS chromatographic parameters were used, the total area (the summary parameter for all permeated D4 components minus glove extractables), the maximum abundance of the first broad peak with retention time (RT) of about 20 min, and the maximum abundance of the second broad peak with RT of approximately

40 min. The diffusion coefficient ( $D$ ) was calculated with Eq. (1), valid when the thickness of glove  $l$  does not change [18].

$$D = \frac{l^2}{6t_l} \quad (1)$$

The three  $t_l$  values and their calculated  $D$  values were then compared by Student's  $t$ -testing.

### 2.6. Determination of permeated mass

To determine the amount of permeated D4, the final collection solution (at time  $t_F$ ) of each test run (including method blanks) 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  $35 \pm 3$  °C under a nitrogen flow of  $500 \pm 50$  mL/min. The mass ( $m$ ) of permeated D4 was determined from the weighing after 40 min of solvent evaporation and corrected for prior sampling during permeation experiments. Three 9 mL-hexane solutions containing 10 mg of D4 were also evaporated to measure D4 recovery. The residues of the D4 hexane solutions after evaporation were also analyzed by GC–MS after reconstitution in hexane, and the chromatograms were compared with that of the original D4 at the same concentration to detect possible changes of D4 composition resulting from evaporation.

The time-average permeation rate ( $P_a$ ) was calculated using Eq. (2).

$$P_a = \frac{m/A}{t_F} \quad (2)$$

where  $A$  is the exposed permeation area of the glove.

The steady state permeation rate ( $P_s$ ) was calculated using Eq. (3),

$$P_s = \frac{m/A}{t_F - t_l} \quad (3)$$

All gravimetric experiments were done at least in triplicate.

## 3. Results

### 3.1. Glove physical changes

The colors of the blue SafeSkin and the green Sol-Vex gloves did not change after permeation testing. The disposable SafeSkin glove had a thickness of  $0.113 \pm 0.005$  mm, and the Sol-Vex glove had a thickness of  $0.285 \pm 0.011$  mm before permeation. For both gloves, either no significant change or less than 4% change in thickness or weight occurred relative both to before permeation testing and to method blank gloves. Thus Eq. (1) can be used to calculate  $D$ .

### 3.2. Permeation of D4 through Sol-Vex

The SIM chromatograms for the 10-h collection solution and the method blank for Sol-Vex (Fig. 1A and B, respectively) had no obvious difference. Therefore no detectable D4 permeated. Except for the Sol-Vex extractable at RT 20.3 min (Fig. 1A),

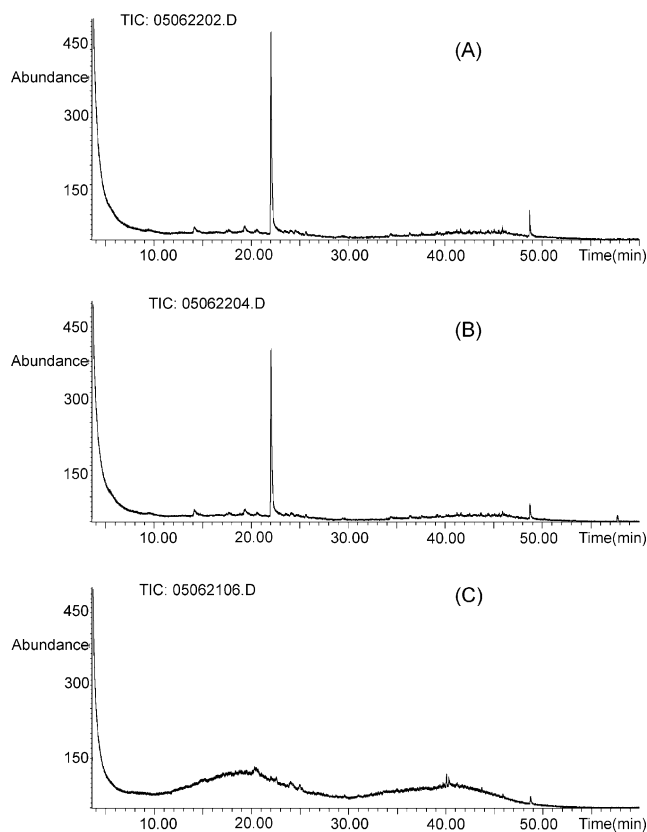


Fig. 1. SIM/GC-MS chromatograms ( $m/z$  55): (A) 10 h permeation collection for Sol-Vex; (B) method blank for Sol-Vex; (C) 17 ng D4.

the SIM chromatographic responses for 10-h collection solution were less than that for 17 ng D4 (Fig. 1C). Thus less than  $34 \mu\text{g}$  D4/ $\text{cm}^2$  accumulated in the 10-h collection, equivalent to a  $P_a$  of less than  $0.056 \mu\text{g}/\text{cm}^2/\text{min}$ . The 10-h permeation collection solution for Sol-Vex was also evaporated, but less than quantifiable residue still resulted. The  $0.25 \mu\text{g}/\text{cm}^2$  ASTM threshold for the normalized breakthrough time ( $t_{\text{nb}}$ ) [17] was still less than the SIM detection limit.

### 3.3. GC-MS of original D4 and SafeSkin permeation collection

Fig. 2A shows the TIC chromatogram of a 1.3 g/L D4 solution, which eluted from 5 to 55 min. The mass spectra at 10, 20, 30, 40 and 50 min all had  $m/z$  55 (base), 69, 81, 95, 109, 123, 137, 151 and 165 as their major ions, affirming they were similar compounds. The shape of the chromatogram was influenced by both the composition of D4 and the temperature program. With increasing temperature from 10 to 20 min, the elution of D4 components from the GC column accelerated, and the GC-MS response increased and peaked at around 20 min. During the following isothermal period, the elution of D4 decreased. From the start of the second temperature ramp, the GC-MS response increased again, peaked at around 40 min, and dropped after 40 min before the end of the ramp at 46 min. Two broad peaks of similar elution time span and maximum abundance resulted.

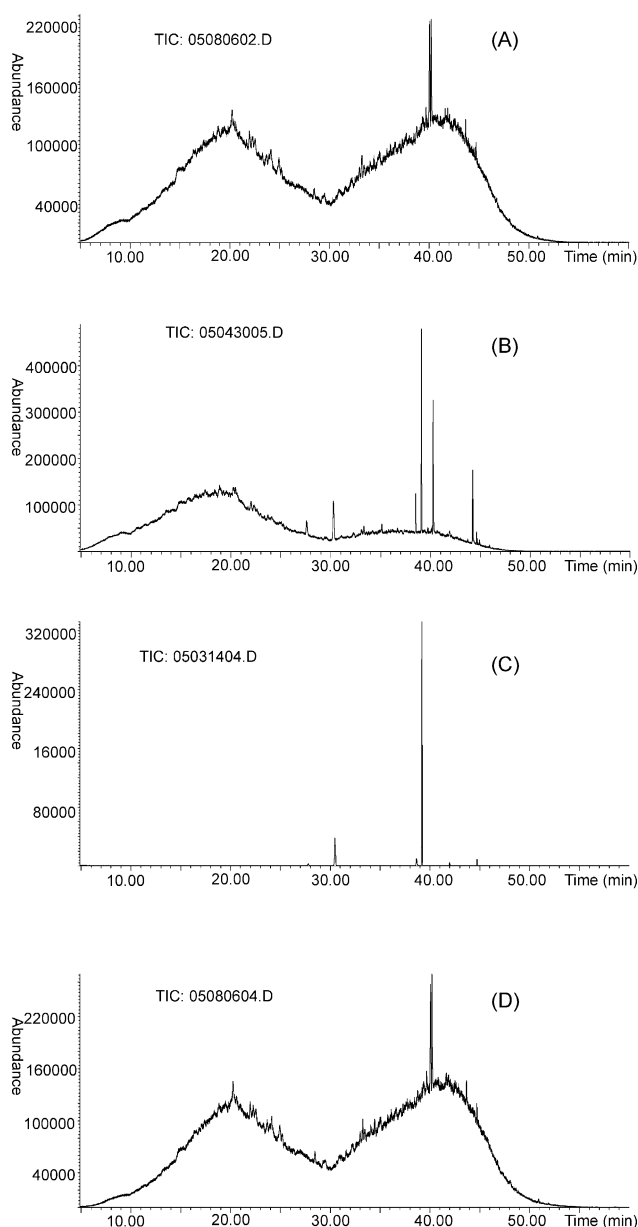


Fig. 2. TIC/GC-MS chromatograms: (A) 1.3  $\mu\text{g}$  original D4; (B) 8-h hexane collection of D4 permeation through SafeSkin; (C) method blank for SafeSkin permeation; (D) 1.3  $\mu\text{g}$  residue of D4 hexane solution after 40 min of evaporation.

Fig. 2B shows the TIC chromatogram of a 8-h permeation collection sample for a SafeSkin glove. Most sharp peaks on top of the two broad peaks in Fig. 2B (RTs 27.8, 30.5, 38.7, 39.2, 42.0, and 44.7 min) were nitrile glove additives extracted by hexane [19], as shown in Fig. 2C for the method blank. The sharp peak of RT 40.3 min was also present in Fig. 2A, but not in Fig. 2C. This peak was determined to be the extreme pressure additive di-*n*-octyl disulfide (DOD) [6]. The peak of RT 44.3 min was not present in either Fig. 2A or C, suggesting that it was an interaction product of D4 and SafeSkin or a nonpolar additive of SafeSkin solubilized by D4.

The chromatogram in Fig. 2B also has two broad peaks of similar time span for the same temperature program, but

the maximum abundance of the second peak was about one third that of the first broad peak. Enrichment of the lower molecular weight components in the first broad peak occurred relative to the high molecular weight components in the second broad peak. The composition of permeated D4 was thus different from the original D4, and the original D4 could not be used as the standard for quantification of permeated D4.

### 3.4. SafeSkin permeation properties characterized by chromatograms

D4 was not detected in 15- and 30-min samples by TIC/GC–MS, but was first detected at 1 h in four of six tests, and at 1.5 h in the rest. The detection limit of TIC/GC–MS for D4 was  $84 \mu\text{g}/\text{cm}^2$ . Thus the permeated D4 at 30 min was less than  $84 \mu\text{g}/\text{cm}^2$ . D4 was first detected by SIM/GC–MS in four of six 30-min samples, and detected in all 1-h samples. The  $t_{\text{db}}$  through SafeSkin was thus  $0.7 \pm 0.3$  h for SIM/GC–MS, 0.5 h shorter than the  $t_{\text{db}}$  for the less sensitive TIC/GC–MS. At  $t_{\text{db}}$  for SIM/GC–MS, the permeated D4 was between 34 and  $84 \mu\text{g}/\text{cm}^2$ , still larger than the  $0.25 \mu\text{g}/\text{cm}^2$  ASTM threshold.

A plot of total area (corrected for hexane volume change because of sampling and hexane evaporation) in the TIC/GC–MS chromatograms versus permeation time for six permeation tests is shown in Fig. 3A. Plots of corrected maximum abundances of the first and second broad peaks versus permeation time are shown in Fig. 3B. The y-axis for Fig. 3A and B is in arbitrary units based on the units of the GC–MS chromatogram, as these chromatographic parameters could not be translated into mass units without the appropriate standard. Fig. 3B shows that between 2 and 8 h, both first and second peak maxima were in steady state, with correlation coefficient  $r$  of 0.9924 and 0.9927, respectively, and both  $p < 0.0001$ . Fig. 3A also shows steady state between 2 and 8 h, with  $r = 0.9922$  and  $p < 0.0001$ . The extrapolation of the steady state region between 2 and 8 h therefore provided valid  $t_1$  values for each permeation analysis type.

The maximum of the first peak (Fig. 2B) had the shortest  $t_1$  of  $1.3 \pm 0.2$  h and the largest  $D$  of  $(4.5 \pm 0.6) \times 10^{-9} \text{ cm}^2/\text{min}$ . The maximum of the second peak had a  $t_1$  of  $2.0 \pm 0.2$  h and a  $D$  of  $(3.0 \pm 0.3) \times 10^{-9} \text{ cm}^2/\text{min}$ . The  $t_1$  of  $1.6 \pm 0.1$  h and  $D$  of  $(3.7 \pm 0.3) \times 10^{-9} \text{ cm}^2/\text{min}$  calculated from the total area analysis were intermediate. The three  $t_1$  and  $D$  differences are presented in Table 1, where all were statistically significant from zero with  $p < 0.01$ .

Table 1

Differences of lag times and diffusion coefficients of D4 through SafeSkin using three different GC–MS chromatographic parameters as surrogates of permeated mass

	Value using first peak maximum – value using total area	Value using total area – value using second peak maximum	Value using first peak maximum – value using second peak maximum
Lag time difference (h)	$-0.3 \pm 0.1$ ( $p = 0.0006$ )	$-0.4 \pm 0.2$ ( $p = 0.0075$ )	$-0.6 \pm 0.2$ ( $p = 0.0003$ )
Diffusion coefficient difference ( $\text{cm}^2/\text{min}$ )	$(7.8 \pm 3.7) \times 10^{-10}$ ( $p = 0.0034$ )	$(6.7 \pm 3.4) \times 10^{-10}$ ( $p = 0.0053$ )	$(1.4 \pm 0.5) \times 10^{-9}$ ( $p = 0.0007$ )

Note:  $p$ -values reflect difference from zero using Student's  $t$ -testing.

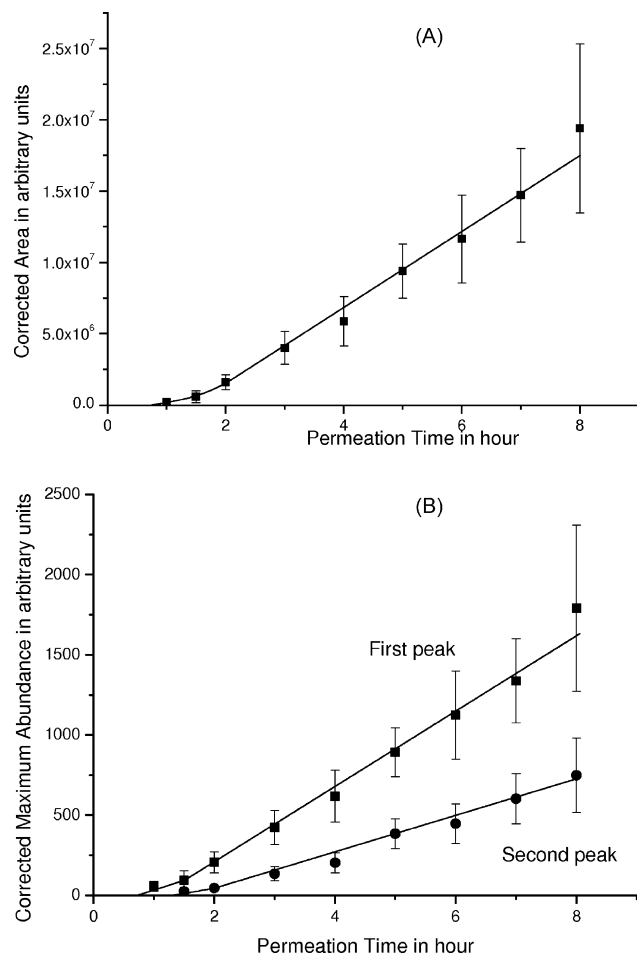


Fig. 3. GC–MS chromatographic parameters of permeated D4 through SafeSkin for six permeation tests versus permeation time: (A) the total area; (B) the maximum abundances of the first and second broad peak.

### 3.5. Permeation rate by gravimetry

No detectable residue resulted from the evaporation of 9 mL hexane. The 40 min period of evaporation provided  $99.6 \pm 3.1\%$  recovery as measured with 9-mL hexane solutions containing 10 mg D4. The chromatogram of the residue reconstituted in hexane (Fig. 2D) was very similar to original D4 (Fig. 2A). Thus the evaporation process did not change D4 composition appreciably. This is not surprising because the stated boiling point of D4 is greater than  $190^\circ\text{C}$ .

For three sets of permeation tests, permeated D4 mass  $m$  was determined to be  $6.7 \pm 4.4$  mg for the 8 h SafeSkin permeation collection after correction for method blanks. Using



$t_1$  for the total area analysis of 1.6 h,  $P_s$  was calculated to be  $3.5 \pm 2.2 \mu\text{g}/\text{cm}^2/\text{min}$  from Eq. (3). In contrast,  $P_a$  was  $2.8 \pm 1.8 \mu\text{g}/\text{cm}^2/\text{min}$ , about 20% lower. This performance was “very good” according to Ansell grading criteria [20].

#### 4. Discussion

In Fig. 2B for the collection side of the permeation cell, the first broad peak represents the more volatile (higher vapor pressure) lower molecular weight congeners that elute earlier and have shorter RTs than the higher molecular weight congeners of the second peak. The maximum of the first broad peak has larger  $D$  and shorter  $t_1$  in the permeation cell than the maximum of the second broad peak (Table 1 and Fig. 3B). The differential permeation shown in Fig. 2B relative to Fig. 2A can be explained by molecular weight and polarity differences. At the same temperature, the mean molecular speeds of the lower molecular weight congeners are faster than those of higher molecular weight congeners. Thus the lower molecular weight congeners will have larger  $D$  and shorter  $t_1$ , other factors being equal. Moreover, congeners with smaller molecular weights are also more polar than larger congeners, and polar molecules have larger  $D$  and shorter  $t_1$  for nitrile [18,20].

The differential permeation of D4 components that causes the differences in the chromatograms of the collection side relative to original D4 (Fig. 2A and B) posed an analytical problem that required a matching external standard for GC–MS quantification. The problem was circumvented by weighing the residue directly after hexane evaporation. The accumulation of permeates in the collection medium was characterized by the chromatograms of collection solution sampled at specific times. The steady state was then demonstrated to be attained between 2 and 8 h (Fig. 3), and this allowed  $t_1$  and  $D$  to be found.  $P_s$  was calculated from Eq. (3) using the total area data because the total area is related to total mass of permeated D4. Thus, the present study used the combination of gravimetry and chromatography representing a unique resolution to the problem of complex mixture quantification that does not necessitate knowing all the components of a mixture beforehand.

An alternative approach was to stop permeation testing at various specific times, and obtain the mass of permeated D4 at each time point by hexane evaporation. There are major limitations to this approach. Firstly, no compositional details of permeated D4 are provided. Secondly, at early collection times gravimetry has inadequate sensitivity to measure the small amount of permeated D4. Thirdly, many more permeation tests are required, while the combined approach allows the essential parameters to be calculated from one permeation experiment. Such an approach can be used for other complex mixtures (like MWFs and petroleum fractions) where elucidation of all the components would be an insuperable analytical challenge. One of the problems of this combined gravimetry/chromatography approach was that the arbitrary  $t_{nb}$  (when  $0.25 \mu\text{g}/\text{cm}^2$  D4 permeated for a closed-loop system [17]) could not be determined for both glove types. A more sensitive determinative analytical technique is necessary for this purpose.

The only MWF permeation rate provided by Forsberg et al. [7] for a chemically protective neoprene glove,  $2.6 \text{ mg}/\text{cm}^2/\text{min}$ , was about 750 times greater than the  $P_s$  for the disposable SafeSkin glove in the present study. This shows that a disposable nitrile glove provides better protection than a chemically protective neoprene glove can. The amount of permeated D4 through SafeSkin at 0.5 h was less than  $84 \mu\text{g}/\text{cm}^2$ . The performance of SafeSkin was “very good” according to Ansell criteria [20]. Although workers may prefer disposable gloves over chemically protective gloves because of better dexterity and user comfort, disposable gloves should only be worn when dealing with less toxic straight oil MWFs. The mineral oils in D4 were intensively hydrogenated to remove carcinogenic components, and this type of mineral oil generally is not carcinogenic [21]. No toxicological studies on either D4 or the component DOD (0.4%, w/w) [6] have been reported. Thus disposable nitrile gloves may be tentatively used for incidental contact (such as splash or spill) when no highly toxic or carcinogenic components are known to be present. The disposable gloves should be replaced at every half hour. If known potential carcinogens are present in straight oil MWFs, chemically protective nitrile gloves must be worn instead.

Based on the Forsberg et al. study, NIOSH estimated the approximate service life of chemically protective nitrile gloves to be about 4 h. The present study showed Sol-Vex protected up to 10 h against D4. The straight oil MWF used by Forsberg et al. was made of hydrocarbons with carbon numbers from 9 to 16 and the stated boiling point greater than  $149^\circ\text{C}$  [22], while D4 was made of hydrocarbons with carbon numbers from 15 to 30 and the stated boiling point greater than  $190^\circ\text{C}$ . Thus NIOSH’s shorter service life estimate is consistent with our results, because our study also showed that the fraction of smaller molecular weight does permeate faster than the higher molecular weight congeners.

#### 5. Conclusions

This is the first paper to quantify the permeation parameters of a complex water-insoluble MWF of low volatility through gloves with a combined chromatographic and gravimetric technique. Less than  $34 \mu\text{g}$  D4/ $\text{cm}^2$  permeated Sol-Vex in 10 h, leading to a time weighted permeation rate  $P_a$  of less than  $56 \text{ ng}/\text{cm}^2/\text{min}$ . Because the detection breakthrough time  $t_{db}$  was  $>10$  h, Sol-Vex is safe to wear for 10 h even for a carcinogenic straight oil MWF. For SafeSkin, the  $t_{db}$  was  $0.7 \pm 0.3$  h. The lag time  $t_1$  and diffusion coefficient  $D$  from the total area calculation for SafeSkin were between those from the maxima of the low molecular weight broad peak and the high molecular weight broad peak. The steady state permeation rate  $P_s$  was  $3.5 \pm 2.2 \mu\text{g}/\text{cm}^2/\text{min}$  between 2 and 8 h. The performance of SafeSkin was “very good” according to Ansell criteria, and the glove can be used for incidental contact with straight oil MWFs without known carcinogens. However, the SafeSkin  $t_{nb}$  was less than 30 min. Therefore it is recommended that workers wear Sol-Vex for straight oil MWFs that are suspected of carcinogenicity as the most conservative protective action.

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