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Development of a Spectrochemical Modification (SM) Technique to Detect Permeation of Chemical Warfare Agent Simulants Through Protective Clothing Materials

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Health and Safety Research Division

DEVELOPMENT OF A SPECTROCHEMICAL MODIFICATION (SM)
TECHNIQUE TO DETECT PERMEATION OF CHEMICAL WARFARE
AGENT SIMULANTS THROUGH PROTECTIVE CLOTHING MATERIALS

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DEVELOPMENT OF A SPECTROCHEMICAL MODIFICATION (SM) TECHNIQUE TO DETECT PERMEATION OF CHEMICAL WARFARE AGENT SIMULANTS THROUGH PROTECTIVE CLOTHING MATERIALS

T. Vo-Dinh
T. Pal

ABSTRACT

This study involves the development of a new and simple analytical procedure based on a spectrochemical modification (SM) technique to monitor chemical warfare agent simulants. The SM technique is applied to evaluate permeation of these compounds through protective clothing materials.

1. INTRODUCTION

The Chemical Stockpile Emergency Preparedness Program (CSEPP) has been established by the Department of the Army's Office of the Program Manager for Chemical Demilitarization to carry out Congressional mandates of 1986 and 1988. The first mandate, the Department of Defense Authorization Act of 1986 (PL 99-145), directed and authorized the Secretary of Defense to destroy the United States stockpile of lethal unitary chemical munitions and agents by September 30, 1994; the Act was amended in 1988 (PL 100-456) to permit operations testing of commercial scale incinerator design and to allow for unitary munitions disposal completion by April, 1997. The inventory of material to be destroyed includes the organophosphate nerve agents GA, GB, and VX as well as the vesicant (blister) agents H, HD, HT (various formulations of sulfur mustard) and Lewisite (an organic arsenical) (see Carnes and Watson, 1989, for details of agent chemistry and toxicity).

There is great concern regarding skin exposure to these chemical warfare agents for personnel involved in handling and disposing of these species as well as those civilian emergency personnel who may need to respond to an unplanned agent release. The chemical, physical and toxicological properties of GB, VX and sulfur mustard, the subject agents of this report, have been described in Carnes (1989), Carnes and Watson (1989), Watson et al. (1989a,b), and Rogers et al. (1990). The degree of protection provided civilian emergency workers in a chemical agent environment is a current unknown due to the untested status of readily available protective clothing. In this project, a simple and rapid method was developed to evaluate the efficacy of protective materials against chemical warfare agent analogues. The new method is based on the detection of spectrochemical modification (SM) (e.g., luminescence quenching) of an indicator compound (IC) in the presence of chemical compounds of interest. To our knowledge, this is the first time that such

an SM technique has been reported for the detection of chemical warfare agent simulants. Several examples of measurement of the permeation rates and breakthrough times for specific chemical agent simulants (dimethyl methyl phosphonate, dibutyl sulfide, diisopropyl methyl phosphonate, and malathion) illustrate the efficacy and potential usefulness of the SM technique developed in this study.

2. EXPERIMENTAL

2.1 INSTRUMENTATION

The luminescence measurements were made with two Perkin-Elmer spectrofluorimeters (Model 43A and Model 650, Perkin-Elmer, Norwalk, Conn.). The excitation light sources were a continuous-wave (CW) 150-W xenon arc lamp and a pulsed 6-W xenon lamp for the Model 43A and Model 650, respectively. The detector was an R777 photomultiplier (Hamamatsu Company, Middlesex, NJ) that has a spectral response from 185 to 850 nm. A spectral bandwidth of 10 nm was used for the excitation and emission monochromators.

2.2 MATERIALS

The protective clothing materials tested were obtained from commercially available sources. Whatman No. 42 filter paper was used as the sorbent medium substrate for chemical agent simulants permeating through the protective clothing material. Warfare agent simulants were purchased at their highest purity available and used without further purification. The four compounds investigated were: dibutyl sulfide (DBS [Aldrich]), a sulfur mustard agent simulant; diisopropyl methyl phosphonate (DIMP [Alpha Products]), GB agent simulant; dimethylmethyl phosphonate (DMMP [Johnson Matthey Electronics]), VX agent simulant; and malathion (MAL [INC]), a commercial insecticide and generic nerve agent simulant.

2.3 PROCEDURE

The employment of the SM technique involves detecting the degree of fluorescence quenching of an indicator compound (IC) (e.g., phenanthrene) in the presence of specific chemical agent simulants or compounds of interest. In this study, the SM technique is used to monitor permeation of several chemical agent simulants through a variety of protective clothing materials by analyzing the surface of a cellulose substrate (e.g., a filter paper patch) treated with a solution of phenanthrene indicator (10^{-2}M).

A disc of the protective material is positioned over the open end of a glass cell containing approximately 1 mL of chemical agent simulant. A 2.0-cm diameter disc of filter paper treated with the IC compound is centered over the area of permeation

in contact with the protective clothing material. The exposure setup is mounted in a clamp to ensure a seal between the clothing material and the glass cell (Figure 1). To initiate a permeation measurement, the glass cell is inverted so that the chemical agent challenges the surface of the protective clothing sample (Figure 1A). After the desired exposure time, the filter paper disc is removed and analyzed directly by measuring the extent of quenching of the IC luminescence (Figure 1B) in order to determine the presence and quantify the amount of chemical agent simulant. No chemical extraction is necessary for the analysis.

To prepare exposed filter paper samples for SM measurements, the discs are mounted on a sample holder previously designed for surface emission measurements (Vo-Dinh, 1984). Once the paper is positioned in the sample holder, it is then spotted with 2.5 μL of the IC solution (e.g., phenanthrene) in a solution of ethanol. After a drying period of 3 min under an infrared heating lamp, the sample is transferred to the spectrofluorometer sample compartment for SM measurement. A number of substrate samples may be spotted simultaneously.

3. RESULTS AND DISCUSSION

3.1 LUMINESCENCE QUENCHING OF THE INDICATOR COMPOUND

This experimental sampling protocol is based on previous works characterizing the permeation of petroleum products through protective clothing materials. Luminescence techniques for detecting polycyclic aromatic compounds (PAC) contained in the petroleum products proved useful (Vo-Dinh and White 1987; White and Vo-Dinh 1988). However, since the chemical warfare agent simulants of interest do not contain PAC and are not strongly fluorescing and/or phosphorescing, we have developed a novel and sensitive spectroscopic method for the study of permeation and breakthrough time using spectroscopic modification of an indicator compound. This work involves the detection of the quenching effect on the luminescence of IC phenanthrene. We conducted extensive measurements using a wide variety of compounds (e.g., pyrene, naphthalene, anthracene, emodin, indole, fluorescein and diphenylamine) and found that phenanthrene is a unique compound that can be used for detecting the presence of chemical warfare agent simulants. Measurements of luminescence quenching of phenanthrene used as the IC have yielded excellent results for detecting chemical agents adsorbed on exposed filter paper substrates. Figure 1 shows the fluorescence signal of phenanthrene on filter paper with and without malathion. Phenanthrene is a three-benzene ring polyaromatic hydrocarbon that has the longest absorption at approximately 345-355 nm. The excitation at 352 nm used in this investigation was therefore absorbed directly by phenanthrene, which exhibits fluorescence emission in the 380-470 nm range. Excitation at higher energies can be selected to coincide with strong absorption bands of phenanthrene:

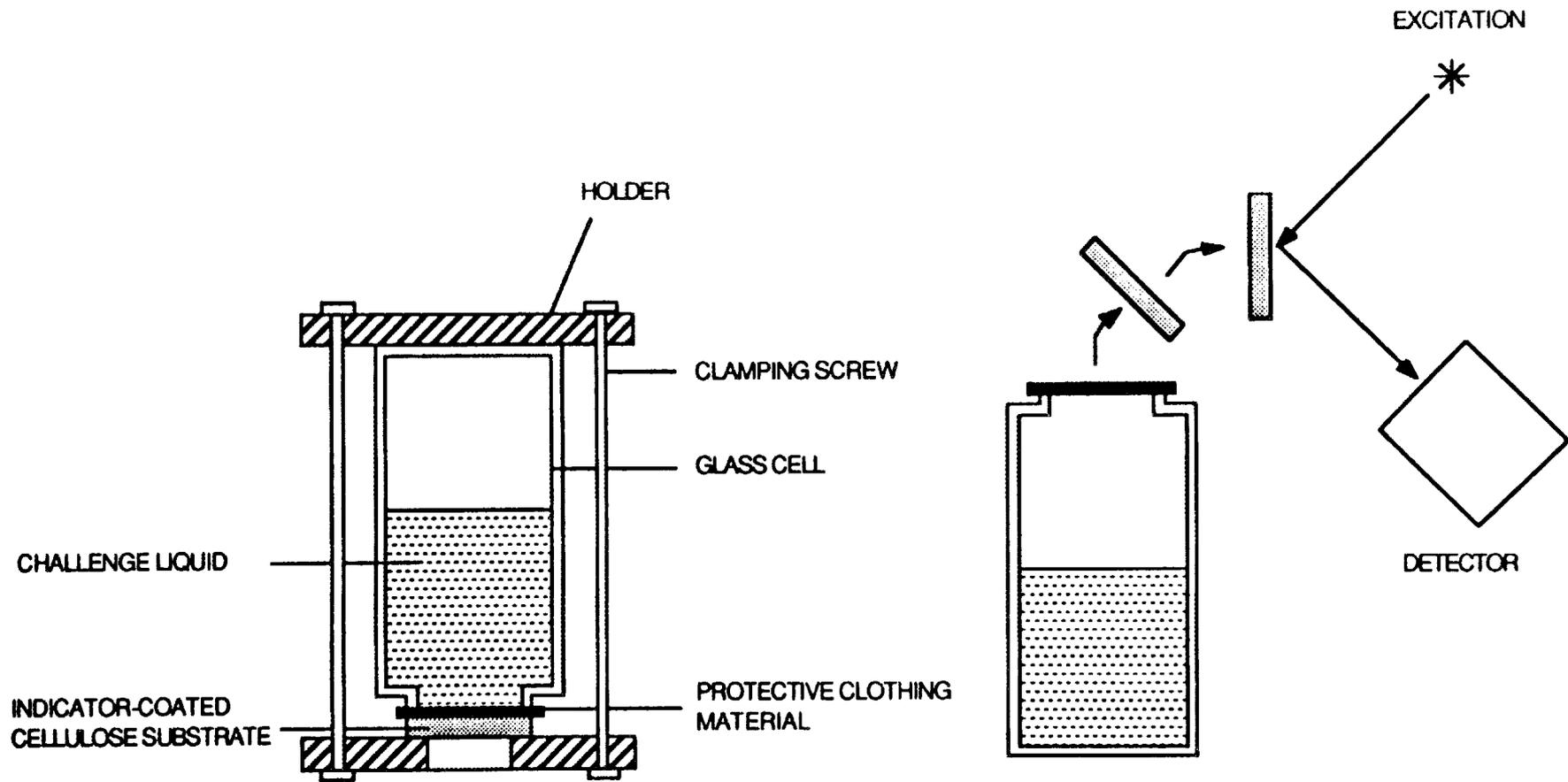


Figure 1. Schematic diagram of the permeation cell and monitoring procedure

(A) EXPOSURE

(B) DETECTION

S_2 singlet state at $34,200\text{ cm}^{-1}$ (292 nm) with $\epsilon=14800$, S_3 state at $39,900\text{ cm}^{-1}$ (250 nm) with $\epsilon=67,000$, and S_4 state at $47,300\text{ cm}^{-1}$ (211 nm) with $\epsilon=35,500$ (Birks, 1970). Figure 2 shows that the fluorescence intensity of phenanthrene on the filter paper is quenched after phenanthrene (10^{-2}M) comes in contact with malathion (10^{-2}M) that has permeated through a protective material. The decrease of the intensity of phenanthrene caused by the quenching process was clearly observed. The spectral profile of phenanthrene fluorescence following quenching by malathion (Figure 2, solid curve) remained similar to that of unquenched phenanthrene (Figure 2, dashed curve). Both spectra consist of a principal series of four vibronic bands of diminishing intensities, equally spaced at energy intervals of approximately 1400 cm^{-1} , which correspond to the frequency of the dominant C-C vibrational modes. The similarity of the fluorescence spectra in Figure 2 indicates that malathion induced quenching but did not alter the chemical structure of phenanthrene, which would have made visible energy changes in the excited singlet state (e.g., spectral shift of the O-O band). Furthermore, intensity distribution of the two spectra in Figure 2 also indicated that interaction with malathion did not induce significant changes in the relative positions (i.e., Stokes shift) of the energy potentials of the ground and excited state.

Figure 3 illustrates the fluorescence spectra of phenanthrene (10^{-2}M) following interaction with DBS, DIMP and DMMP. The fluorescence spectrum of phenanthrene (10^{-2}M) alone under similar conditions is shown previously in Figure 1. The results indicate that the SM technique can be used to indicate the interaction of DBS, DIMP and DMMP with phenanthrene by detecting the fluorescence quenching effect.

3.2 QUANTITATIVE ANALYSIS

Figure 4 shows the quantitative calibration curve relating the quenching effect of phenanthrene fluorescence to the concentration of chemical agent simulants. In this series of experiments, the concentration of the indicator compound (phenanthrene) was kept constant ($2.3 \times 10^{-2}\text{M}$) and the amount of the analyte (DMMP) was varied over 5 orders of magnitude (spot sample from 0.1 ng to $10\text{ }\mu\text{g}$). The results shown in Figure 4 indicate that there is a direct relationship between the extent of fluorescence quenching and the amount of DMMP added to the sample spot of phenanthrene. There is to be an inverse relationship between the fluorescent intensity of the indicator compound and the logarithm of the concentration of the analyte compound (i.e., DMMP). The results displayed in Figure 4 demonstrate that the SM technique developed in this study can provide a practical and efficient tool to quantitatively detect the amount of analyte. Figure 5 shows another example of quantitative analysis employing the quenching effect of the indicator compound (phenanthrene) by another analyte, malathion.

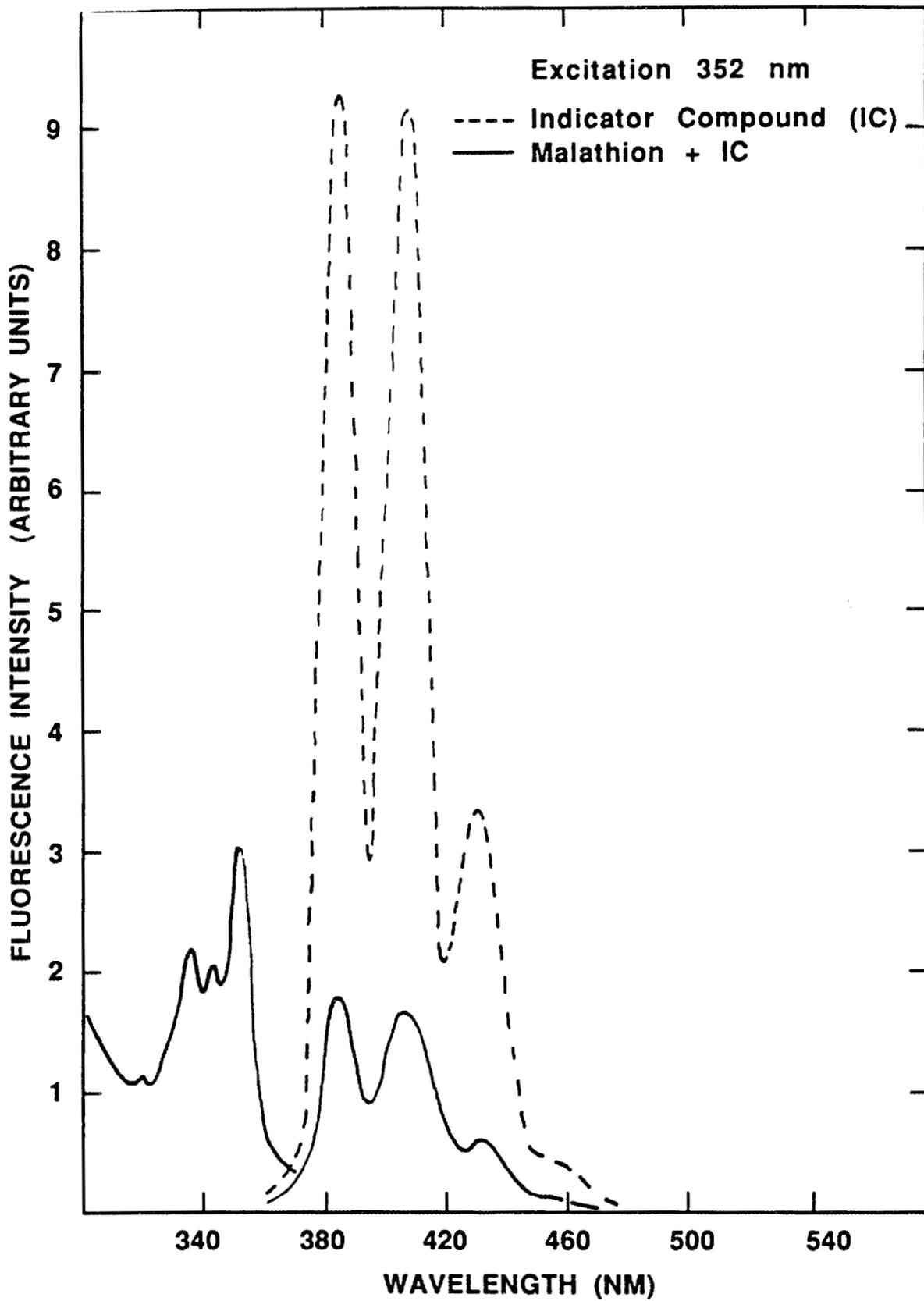


Figure 2. Fluorescence quenching of phenanthrene by malathion

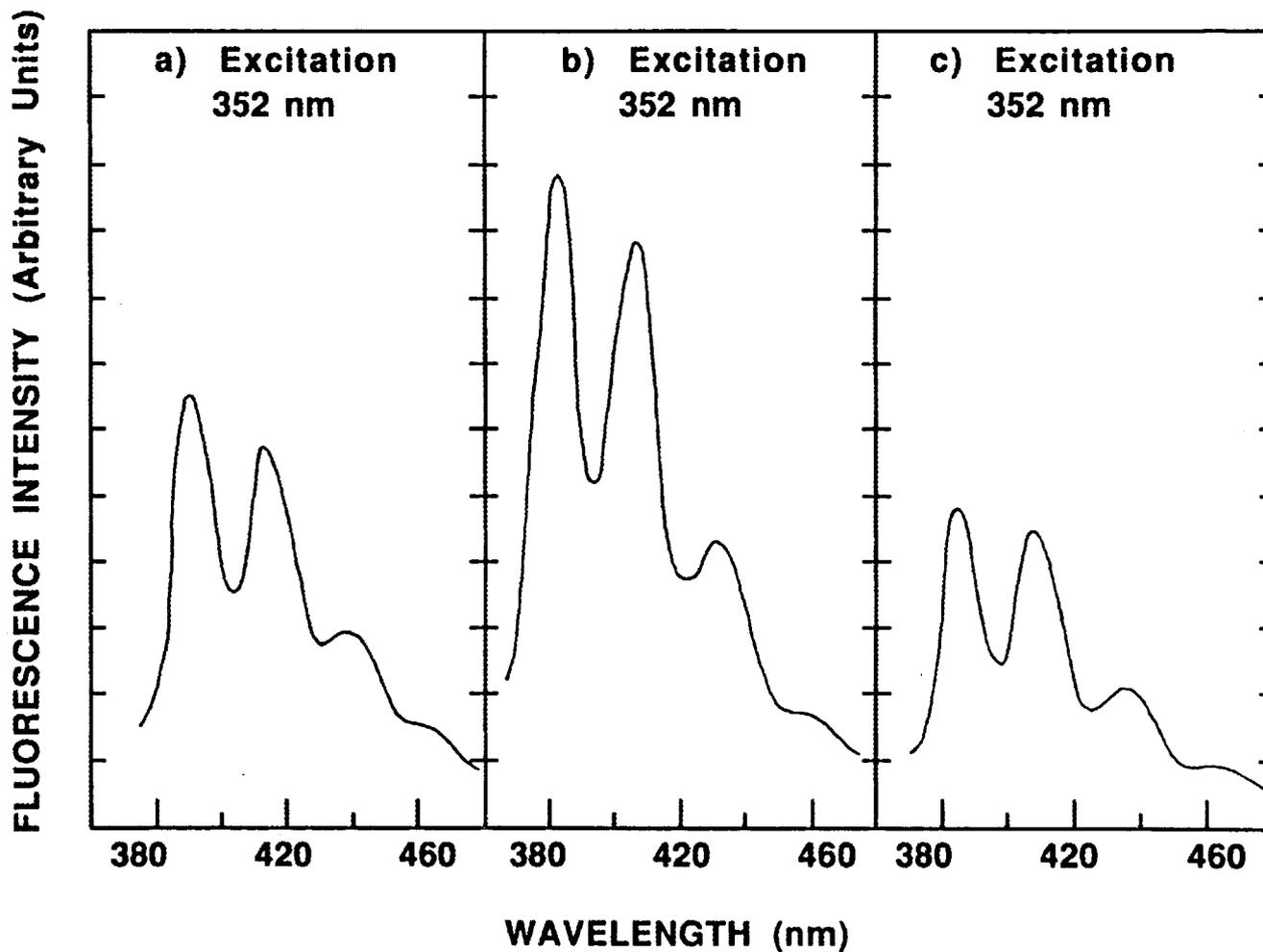


Figure 3. The SM technique applied to DIMP, DMMP, and DBS chemical warfare agent simulants

a) Dimethyl Methyl Phosphonate (10^{-2} M) on Paper Substrate

b) Diisopropyl Methyl Phosphonate (10^{-2} M) on Paper Substrate

c) Dibutyl sulfide (10^{-2} M) on Paper Substrate

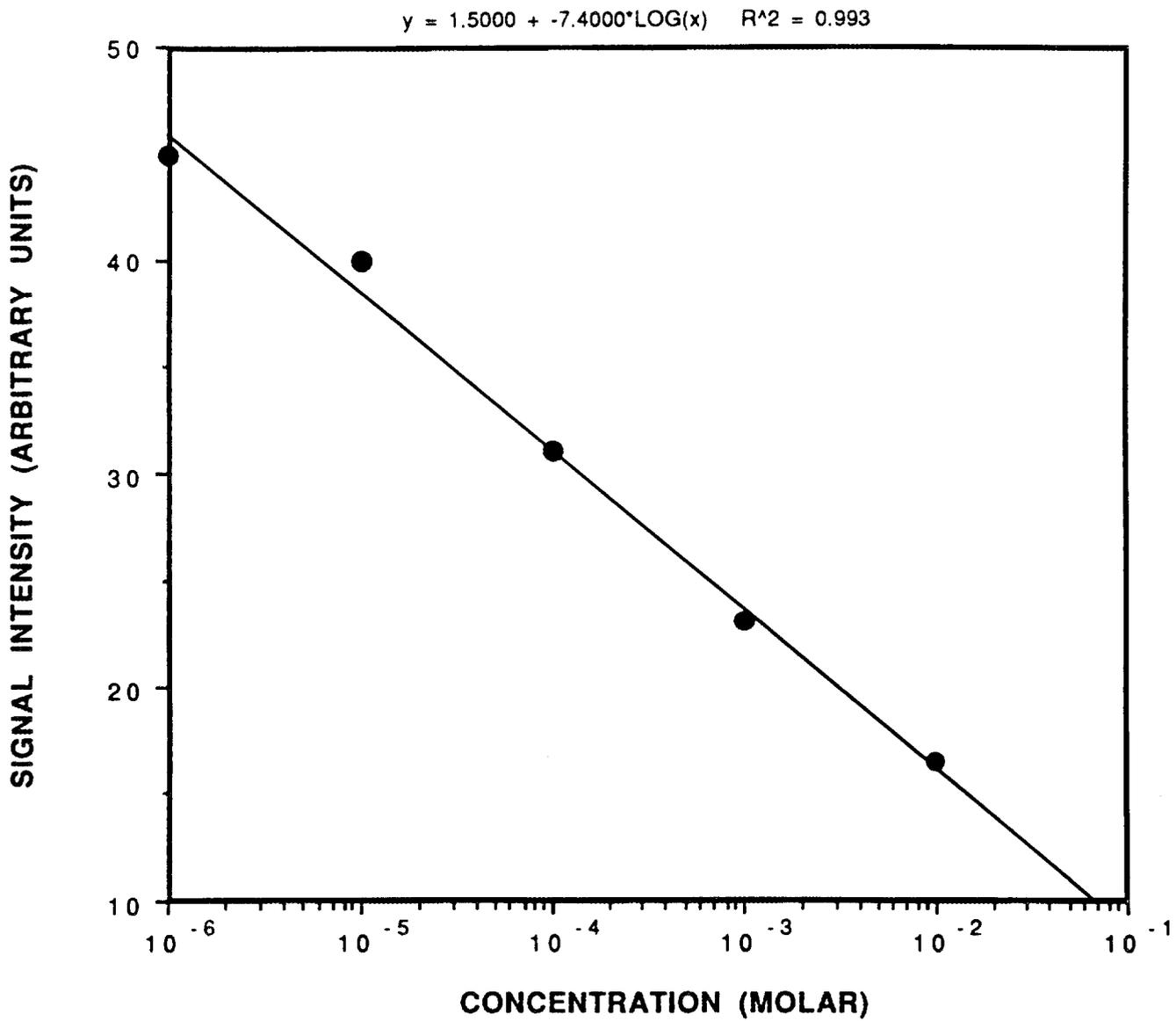


Figure 4. Calibration curve for DMMP via fluorescence quenching of phenanthrene on W-41 filter paper substrate

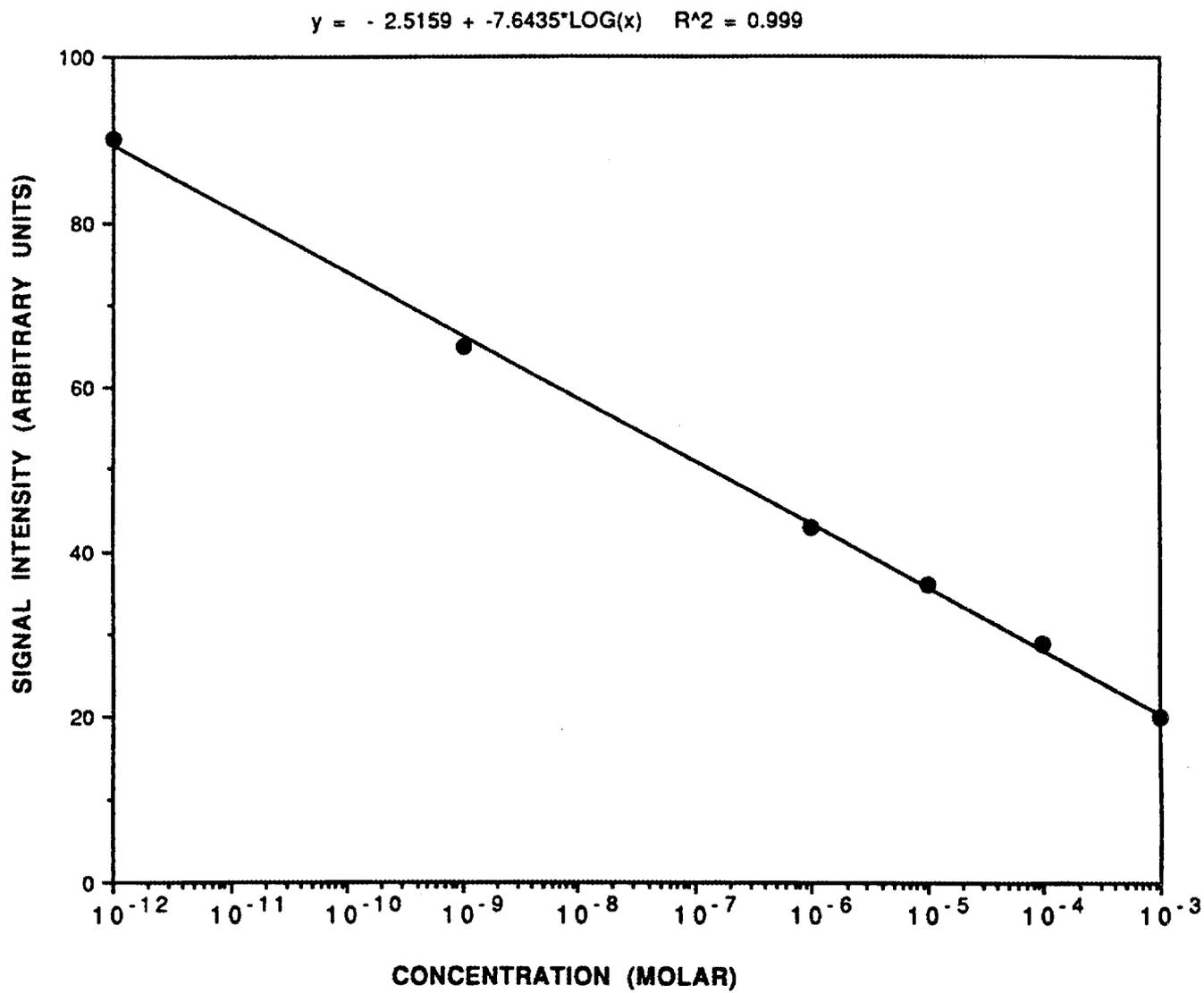


Figure 5. Calibration curve for malathion via fluorescence quenching of phenanthrene on W-41 filter paper substrate

3.3 STUDY OF PERMEATION

Extensive SM measurements were performed to determine the rate at which chemicals diffused through a variety of protective materials. The SM experiments also provided the individual breakthrough times for each chemical. Figures 6 and 7 illustrate the results of experiments in which luminescence quenching measurements were performed on phenanthrene exposed to permeation of malathion and DBS through Playtex® neoprene plastic for progressive 15-min intervals over an 8-hr challenge period. These calibration plots illustrate the fluorescence intensities as a function of permeation, using the emission and excitation wavelengths at 390 and 325 nm respectively. The emission signals were recorded at 410-nm using a 10-nm spectral bandwidth. In these experiments, the breakthrough time was defined as the time required for the first detectable (by fluorescence quenching) quantity of challenge compound to permeate through the protective clothing materials onto the filter paper treated with phenanthrene. An example of breakthrough time studies for DIMP through several protective materials is summarized in Table 1.

A comparison of the two different emission spectral curves illustrated in Figure 6 (DBS through Playtex® neoprene plastic) and Figure 7 (DMMP through Playtex®) reveals noticeable differences in breakthrough times. In particular, breakthrough in Figure 7 occurs later (15 min after the beginning of exposure) and at a significantly slower rate than that shown in Figure 6 (10 min). The curves in Figures 6 and 7 illustrate the utility of the SM measurements to determine permeation rates for various compounds. Quantitative calibration involving normalization against the quenching of the IC luminescence by known amounts of specific chemicals can provide quantitative information about the breakthrough curves and rates of permeation of specific compounds of interest. With a standard challenge time, the SM technique may be used as a practical and cost-effective testing protocol to provide a preliminary ranking which can serve as a guide for more detailed studies of breakthrough times and rates of penetration of chemical agents through protective materials.

4. CONCLUSIONS

This study demonstrates that the SM procedure is a practical and efficient tool for monitoring toxic chemical compounds. The sensitivity of the procedure is excellent since the fluorescence quenching techniques can detect subnanogram amounts of chemicals of interest. The main advantages of the SM technique are its simplicity and practicality. A large number of IC substrates can be mounted onto exposure cells and analyzed sequentially on a routine basis. The SM technique could also lead to the development of patch-type monitors that could be mounted inside clothing and gloves for field monitoring.

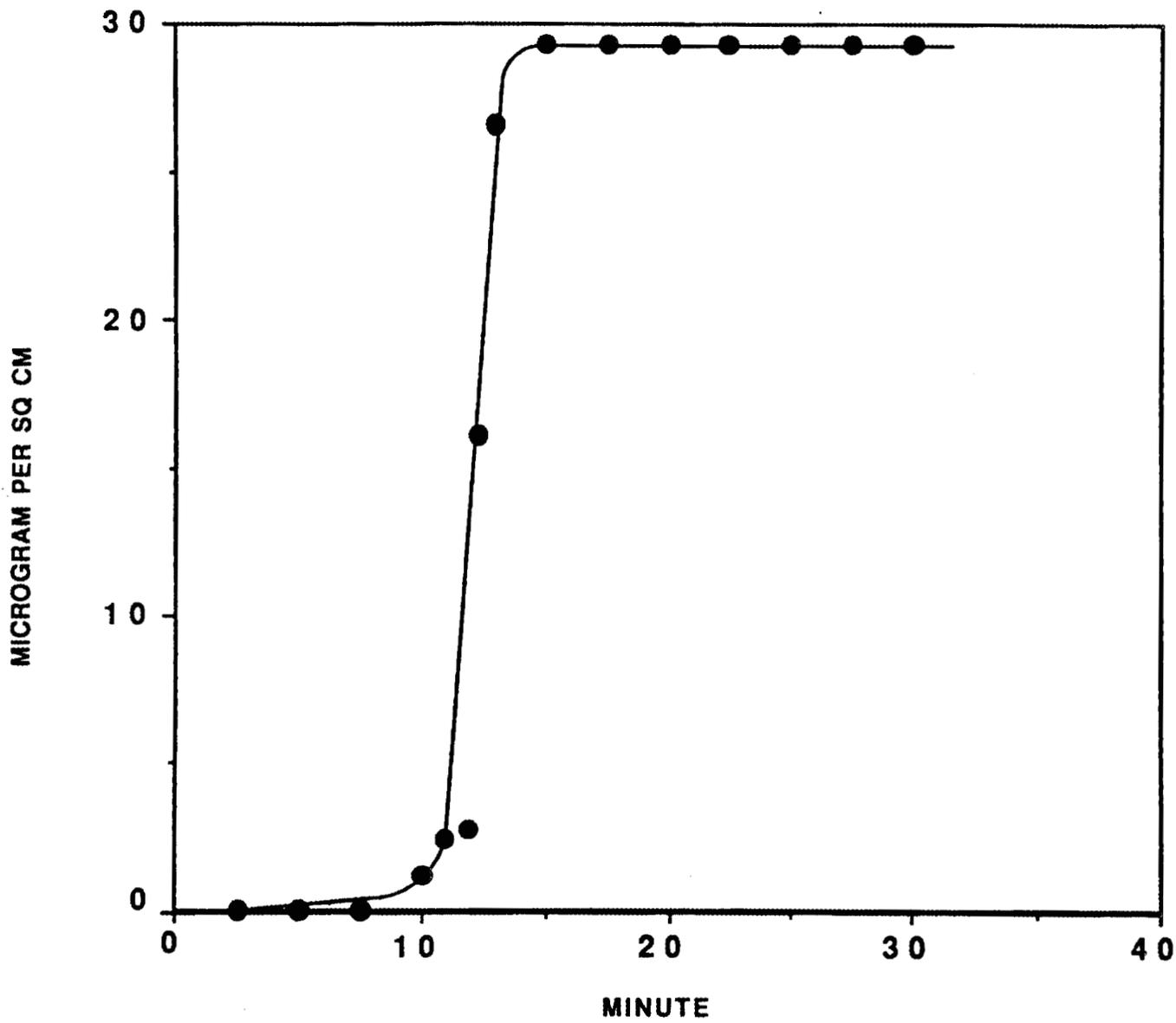


Figure 6. Permeation of DBS through Playtex® neoprene plastic at 25° C

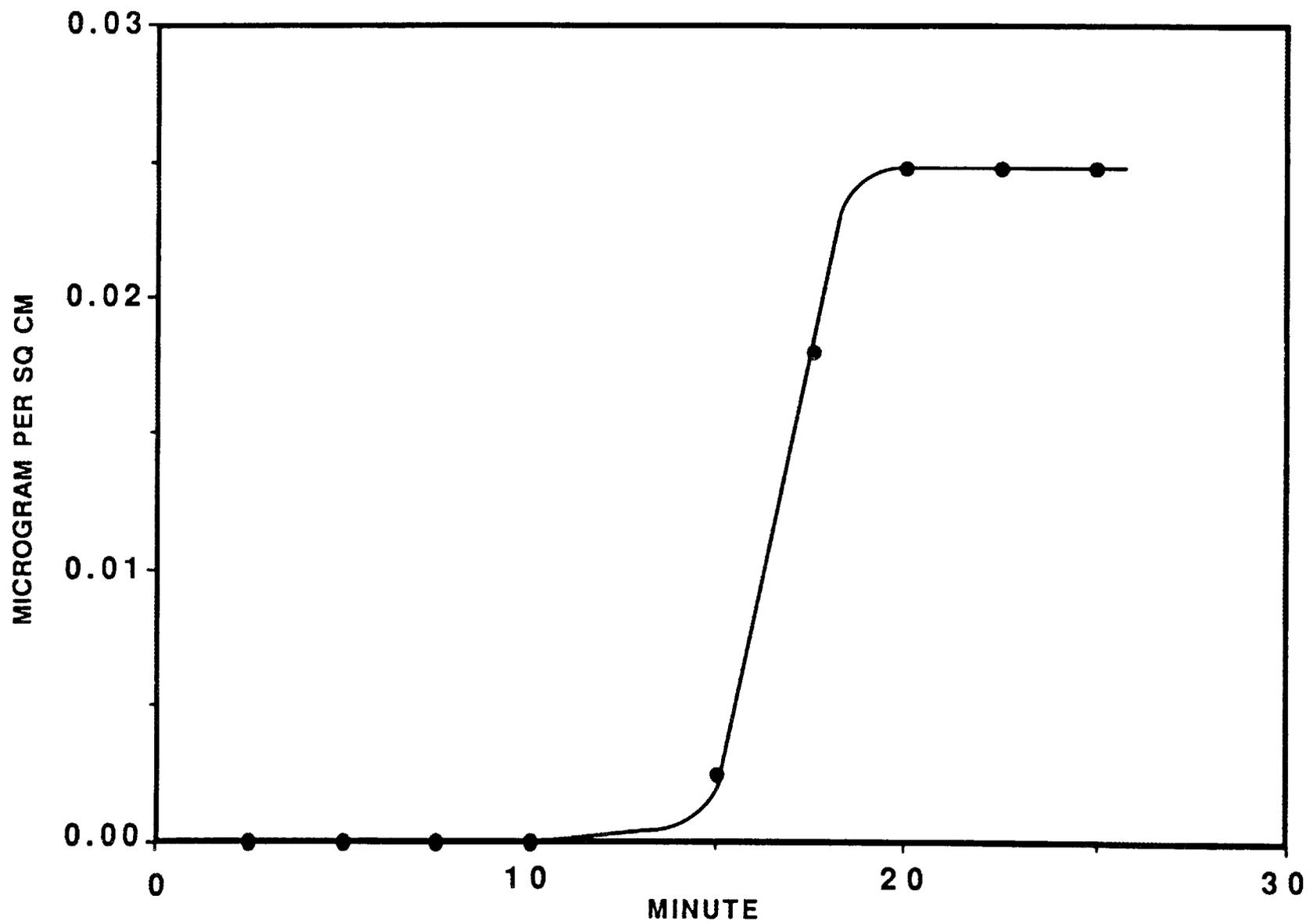


Figure 7. Permeation of DMMP through Playtex® neoprene plastic at 25° C

Table 1. Permeation of DIMP through several protective materials

<u>Protective Materials</u>	<u>Breakthrough Time</u>
Polyvinyl Chloride (PVC)/Nylon/PVC ("305 PVC/BA," Fyrepel Products)	10 min
Butyl Nitrile glove material ("Pioneer Gatorhide," Pioneer Industrial Products)	1 h
Teflon/Kevlar/Teflon ("Force Field™," Fyrepel Products)	> 24 h
Tyvek® (a spunbonded olefin material)	30 min
Neoprene plastic glove material (Playtex®)	45 min

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