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Feasibility of Using Radioactive Tracers for Studies of Permeation of Chemicals Through Protective Clothing Materials

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16. Abstract

This report describes the examination of the feasibility of using radicactive tracers, i.e., carbon-14, in studies of permeation of chemicals through protective clothing. The primary method in the feasibility study has been microscale autoradiography. The technique, well known from biological science, has been modified for work with highly diffusible chemicals and polymers. As a result, the concentration profile inside the material from a given carbon-14 labeled permeant is obtained for one specific chemical exposure time. Separate experiments, using different chemical exposure times, yield visual information on the propagation versus time of the permeant front inside the test material. The present technique uses a layered "sandwich" to maintain contact between the test material during film exposure while minimizing evaporative losses. The individual steps in the technique are carried out at temperatures between -40 and -130 degrees centigrade. Calibration of the autoradiographic results is mainly based on "diskotomy," i.e., slicing of the test material parallel to the exposed surface followed by determination of the carbon-14 activity in the individual slices. Dry-combustion of exposed aliquots of the test material followed by liquid scintillation counting of the evolved and trapped carbon-14 carbon dioxide has also been used with success in the calibration and in the determination of decontamination efficiency.

This report describes the method development and future needs for improvements. The report includes application results on Viton/chlorobutyl rubber laminate, neoprene, Teflon-coated Nomex and seams of Teflon-coated Nomex with the permeants: acetone, nitrobenzene, vinyl acetate and methylene chloride.

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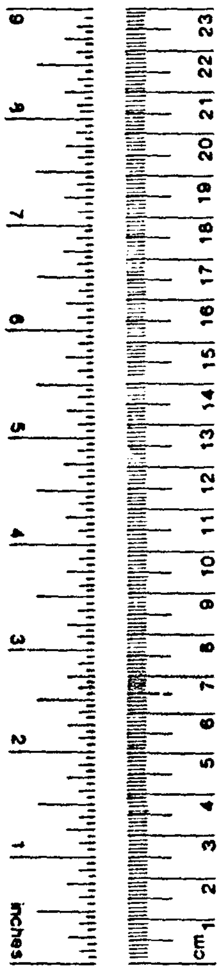
METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

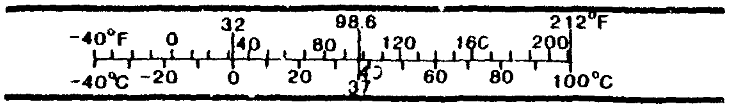
Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (WEIGHT)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (EXACT)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures. Price $2.25. SD Catalog No. C13.10.286.



Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (WEIGHT)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	0.125	cups	c
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (EXACT)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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NOTE: The names Saran, Teflon and Nomex are registered trademarks.

INTRODUCTION

The purpose of this study has been to investigate the feasibility of using radioactive tracer techniques to elucidate mechanisms of chemical permeation.

By the aid of autoradiography and related techniques it was hoped that concentration gradients within a protective clothing membrane could be visualized for one given chemical exposure time. Sequential experiments would then reveal the progress of the permeant front during the process of permeation.

Information gained from such experiments could contribute to the understanding of the theoretical framework governing permeation.

Autoradiography is a well established technique within biological science (1). Despite its potential it has hitherto only been used rarely in combination with polymer membranes (2,3). The main reasons for this are due to the inherent problems caused by incompatibilities between the materials used in normal autoradiography and the polymers tested in this study, and the general difficulties of working with highly diffusible chemicals such as acetone. In order to fix the organic permeant within the protective clothing material all the individual steps have to be carried out at very low temperatures (4,5).

The present study has been carried out under contract with the U.S. Coast Guard ("Radioactive Tracers to Elucidate Mechanisms of Chemical Permeation of Protective Clothing Materials - A Feasibility Study", contract DTCG39-85-R-80272).

Objectives of this report are to describe the development of the techniques, their present state and current limitations. The applications of the techniques are presented and needs for future development discussed.

The work has been limited to three types of materials, [Viton/chlorobutyl laminate, neoprene and Teflon-coated Nomex (both ordinary material and seams)] and four carbon-14 labeled test chemicals (acetone, nitrobenzene, vinyl acetate and methylene chloride).

Besides looking at permeant concentration gradients within these materials after chemical exposure tests, special attention has been given in some cases to the efficacy of decontamination and the use of the techniques in this concept.

Some of the results of the feasibility study were presented earlier at the Second Scandinavian Symposium on Protective Clothing against Chemicals and other Health Risks arranged by NOKOBETEF, 5-7 November in Stockholm, 1986 (6), and at the Second International Symposium on the performance of Protective Clothing arranged by ASTM Committee F-23, 19-22 January in Tampa, Florida, 1987 (7).

DEVELOPMENT OF METHODS

Briefly, the principle of the technique is as follows:

An ordinary chemical exposure test using a carbon-14 labeled test chemical is conducted using an ASTM 1" cell. By the end of the exposure the test material is removed from the test cell and, in order to keep the test chemical in a fixed position, the material is frozen at -120 °C using liquid nitrogen. A cross-section of the test material is obtained by cutting with a cryomicrotome (cryotomy). After cutting a nuclear emulsion is put on top of the sectioned material, and following a suitable autoradiographic exposure time the emulsion-coated section is processed by conventional photographic techniques (autoradiographic procedures). Silver grains induced by radioactivity now reveal the position of the test chemical within the cross-section of the test material. The final visualization and quantification is done in a light microscope (microscopic evaluation). The number of silver grains within a given area is a measure of the concentration of the test chemical. The calibration is done by various methods (calibration/diskotomy). In some cases a decontamination is carried out after the chemical exposure before the autoradiographic procedure for specific examination of the effect of decontamination.

The different experimental steps are further described in the following sections.

Chemical exposure

In general the guidelines followed for the chemical exposures are those given in ASTM F739-85, "Test Method for Evaluation of Protective Clothing Materials for Resistance to Permeation by Liquid and Gaseous Chemicals", (8). It should, however, be emphazised that several deviations were instituted in the development phase. It was considered more important to get the carbon-14 labeled test chemical into the test material so that the autoradiographic techniques could be checked.

Distilled water was used as the only collecting medium. Discrete sampling with replenishment was employed. Radioactivity in the samples was determined by liquid scintillation counting.

A procedure is available for a gaseous collecting medium (open loop with discrete sampling). This procedure has the same sensitivity as the procedure with distilled water as collecting medium. It was not used, however, in this study.

For testing of pure solutions a specific activity of between 5 and 20 MBq/mL is preferred. In the initial phases a specific activity of 0.5 MBq/mL was used.

Chemical exposure tests are preferably carried out in an ASTM 1" cell. A small modification of the test cell, i.e. adding of an outlet vent to challenge chamber, was necessary in order to facilitate handling of the carbon-14 labeled test chemical after the end of the exposure period (see Appendix A-1). This cell was used in all experiments with Viton/chlorobutyl laminate/acetone, Teflon coated Nomex/acetone and neoprene/nitrobenzene.

In order to increase sensitivity of the methods and/or to cut down use of very expensive labeled compounds, several other cells have been constructed and used. Appendices A-2 and A-3 show two cell types. The one in Appendix A-2 was only used in one occasion (Teflon coated Nomex/vinyl acetate). It had a very small collecting chamber (0.85 mL), but was found impractical for experimental work. The cell in Appendix A-3 had a very low leakage rate (<10^{-5} g per hour). After the chemical exposure the challenge chamber of this cell was removed and turned up side down (see Appendix A-3). The lower part of the chamber containing the carbon-14 labeled test chemical was then cooled in liquid nitrogen (to minimize loss), while the exposed membrane was removed. This cell type was found very effective, but not convenient for sampling during normal chemical exposure test. It was used in most of the experiments with Teflon coated Nomex/methylene chloride.

The cell type used for the final tests (seams of Teflon coated Nomex/methylene chloride) is shown in Figure 1 (p 4).

Before the chemical exposure 2.0 mL of the carbon-14 labeled test chemical is placed in the challenge chamber at A on Figure 1. The "finger" is emerged in liquid nitrogen while the cell is mounted with the test material. Before the experimental start the test chemical is quickly brought to +20^{o}C, and the whole chamber turned with the challenge chamber upwards. At the end of the chemical exposure the cell is again turned upside down and the test chemical frozen by immersion of the "finger" in liquid nitrogen. Subsequently, the cell is dismantled.

Testing of seams has called for some minor modifications of the Teflon gasket supplied with the ASTM 1" cell to obtain an acceptably tight joint. The original gasket was replaced with a "Gore-Tex Joint Sealant" gasket. With this material a leakage rate less than 10^{-3} g per hour was obtained in the case of seams of Teflon coated Nomex and methylene chloride.

Cryotomy

After the chemical exposure the cell is dismantled and the exposed membrane divided into a suitable number of disks. Later

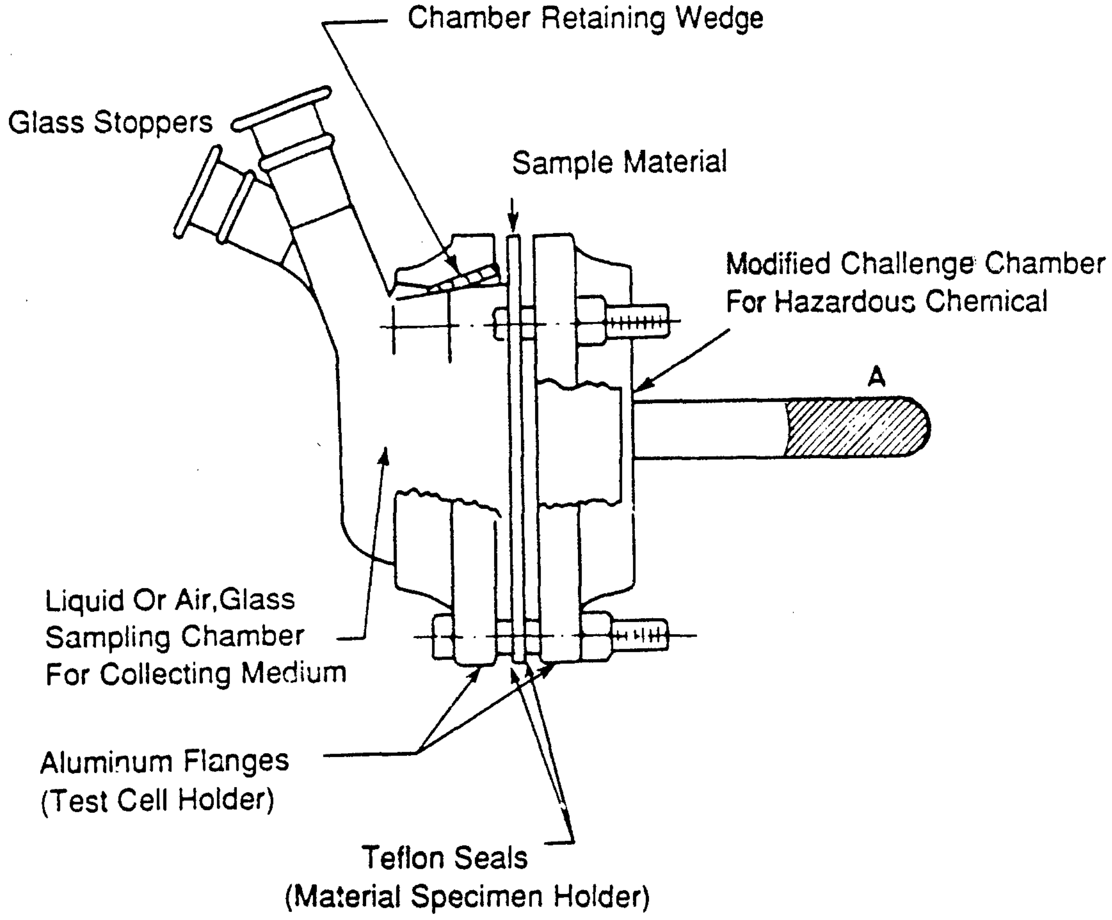

Figure 1. Modified ASTM 1" Cell Used During the Last Phase of Feasibility Study

in the project it was found convenient to wrap the disks in a polymer film, e.g. Saran, in order to minimize evaporation loss.

The exposed membrane disks were frozen quickly to fix the radioactive permeant within the disks. Freezing directly in boiling nitrogen, using a traditional embedding medium, is not convenient. The embedding medium, e.g. carboxymethyl cellulose, becomes porous and the subsequent cryotomy, i.e. cutting of slices at low temperatures with a microtome, is impeded. It has also been found, that the structure of the test material can be damaged by such a procedure.

The procedure used throughout the project involved positioning of the material above boiling nitrogen, in order to achieve an adequate freezing rate. The material is partially surrounded by the embedding medium and frozen in a specially designed high density silicone rubber cylinder, see Figure 2 (p6).

Depending on the test material, cryosectioning is performed with or without support material.

In the latter part of the project a Leitz 1720 digital cryostat was used. This state-of-the-art cryostat makes it possible to minimize variation in the thickness of consecutive sections, which is essential in quantitative autoradiography.

With many polymer materials, the selection of cutting temperature may be decisive in determining the quality of the sections. Previously, cutting temperatures were chosen at some point between -10° and -40°C, with a preference for the lower temperatures. Preferred section thickness is approximately 25 micrometers.

Autoradiographic procedure

The normally described procedure (1) involves tissues, and encounters no problems in the adhesion of the exposed specimen to the nuclear emulsion. This is primarily due to the protein content in biological tissues. When dealing with protective clothing materials special precautions were necessary to keep the specimen and the nuclear emulsion in unchangeable contact during the photographic development procedures. Problems in getting sections thin enough to allow visibility through the specimen also meant, that mounting the specimen above the emulsion precluded the possibility of making microscopic evaluation of the autoradiograms (an autoradiogram is the result of the finally processed emulsion-covered section).

To solve the above mentioned problems, an approach was adapted based on a technique described by Wedeen (8) using a stripping film. Using this approach, unchangeable contact between the specimen and the film during all autoradiographic steps is feasible, with the specimen beneath the film. Briefly described the technical approach is as follows:

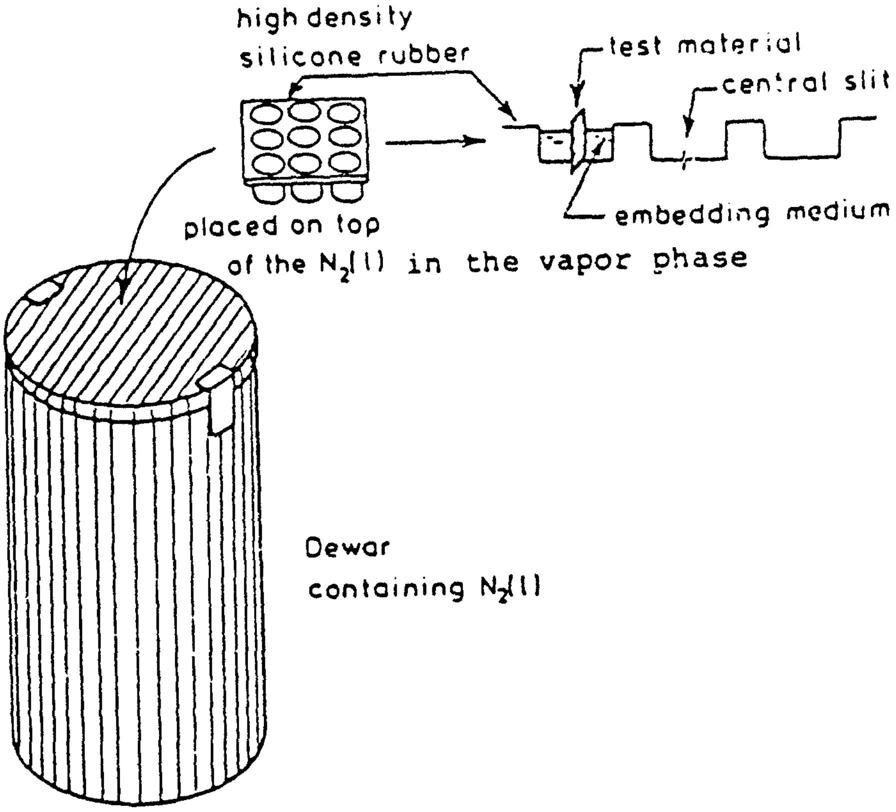

Figure 2. Equipment Used for Freezing Exposed Material

The cut sections are collected directly from crysectioning with a Scotch 3723 low temperature tape.

After collection the sections are transferred at -50°C to the darkroom. The sections are then glued to a stripping film with ethylcyanoacrylate. This step involves heating the specimen to approximately 10-20°C for 2-5 minutes to make the glue polymerize. In spite of many efforts to avoid this heating step no alternative method has been found yet.

The stripping film used at present is KODAK Fine-Grain Autoradiographic Stripping Plate, AR 10.

The resulting autoradiographic "sandwich" is shown in Figure 3 (p 8).

During the autoradiographic exposure the temperature is lowered to between -120°C to -150°C. After 2 and 9 days the emulsion coated sections are processed by conventional autoradiographic developing techniques. Silver grains generated by the carbon-14 radioactivity now reveal both the position and a concentration equivalence of the permeant chemical within the cross section of the test material.

The procedure detailed above does not, however, work satisfactorily in all cases, e.g. in the case of severe chemographic effects. Theoretically chemographic effects can be caused by the test material as well as the test chemical, but in the case of aggressive organic solvents the latter is most likely. The chemographic effects are of two types: (1) positive chemography caused by a direct chemical induction of a latent image, in which case a positive signal is obtained, although not induced by radioactivity; (2) negative chemography caused by latent image fading resulting in a diminution of the signal.

In the latter part of the project, the autoradiographic "sandwich" was supplemented with a clear protective layer of 12 um Saran in order to reduce possible chemographic effects. The Saran layer was placed between the nuclear emulsion and the section as shown in Figure 4 (p8). Besides reducing chemographic effects the extra Saran layer also diminishes possible evaporation loss. It is calculated, however, that the extra Saran layer per se reduces the carbon-14 beta radiation intensity by approximately 25%.

Microscopic evaluation

Mounting the photo-processed autoradiograms can cause problems. Normal mounting techniques used for biological materials, are not sufficient, and might result in either opti-

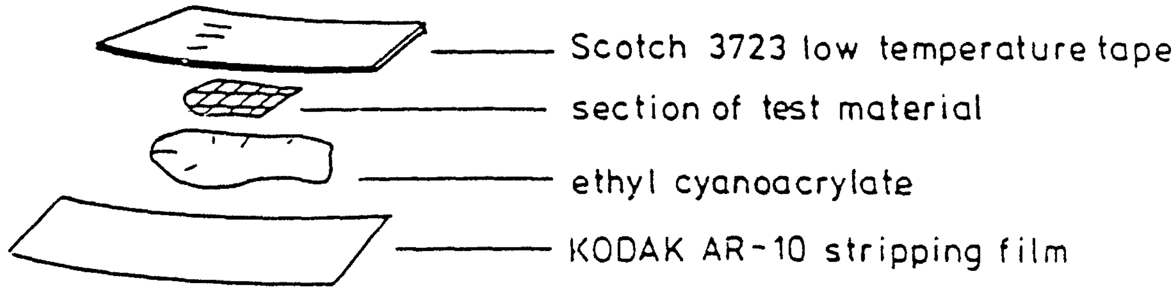

Figure 3. Autoradiographic "Sandwich" Using the Kodak AR-10 Stripping Film

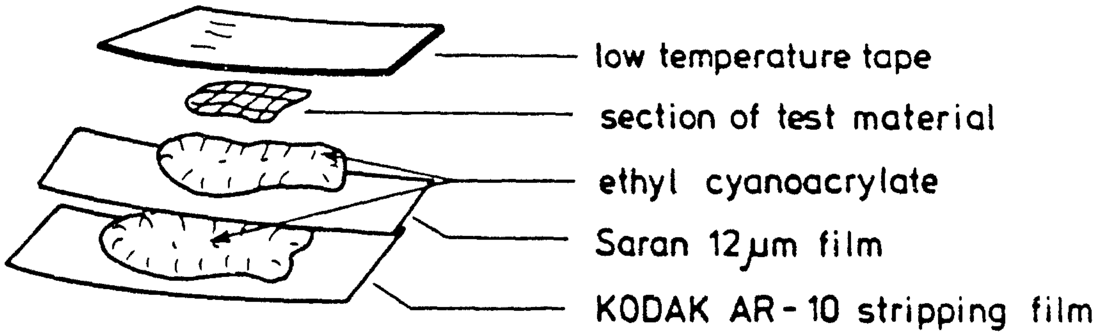

Figure 4. Autoradiographic "Sandwich" Supplied with a 12 μm Transparent Saran Film to Reduce Chemographic Effects

cally very poor slides or simply deterioration of the autoradiograms.

Of four different mounting media, i.e. depex, epon, aquamount and limpid polyester, the limpid polyester in combination with a pressure technique provided the best results. The optical quality is, however, not always good. The use of high-quality microscopes can relieve this problem partially.

The microscopes used in most of the project were a Leitz Orthoplan or a Leitz Metallux 3. Nomarski optics were provided on both microscopes.

The autoradiograms were qualitatively evaluated in the microscope using an area-calibrated counting grid. Either normal transmitted bright field or incident dark field illumination was used. With an improved version of the Metallux 3 successful countings were carried out with a graduated light mixing of incident dark field (95%) and transmitted bright field (5%), both with polarized light. The incident polarized light was very effectively reflected by the silver grains without going through the rather thick sections (25 microns), thus giving an acceptable optical quality. The transmitted light was used for orientation and measuring of distances within the sections. In the case of the opaque neoprene, incident light is indispensable.

Calibration/diskotomy

Conversion of the grain density to concentration units can be carried out in two ways. Either using a calibrated certified polymer reference standard kit in pre-cut strips containing a selected range of known specific activities (Amersham), or by cutting thin sections parallel to the exposed surface of the test materials (in the autoradiographic cryotomy procedure perpendicular sections are cut). The thin parallel sections are extracted, and the extract counted by liquid scintillation. By the comparison with a standard of the radioactive test chemical the concentration in the parallel sections is obtained directly. The concept of parallel sectioning is called DISKOTOMY. Sectioning is performed at approximately -30°C, with a section thickness of approximately 15-25 um.

The use of the calibrated polymer reference standard kit can provide a relation between grain density and nCi per g, see Appendix Figure A-4. But this relation cannot be used directly on the actual samples due to differences in thickness between standard and samples. Instead the standard should be sectioned in a thickness similar to that of the sectioned test materials, and positioned together with these. In this way it would be possible to correct for differences between the individual autoradiograms caused by individual processing. If no chemographic effects and no evaporation losses are present a direct conversion of grain densities to concentration is also possible. This is, however, often not the case.

It is therefore found, that the most reliable conversion of the profiles obtained by autoradiography should be based on DISKOTOMY.

Besides being used for calibration, diskotomy also produces complementary results for the autoradiography. Furthermore a concentration gradient is always obtained, although of poorer spatial resolution. Unlike autoradiography diskotomy results do not provide a direct link to the contour nor to the structure of the tested material. In the autoradiography the concentration of the test chemical is observed by placing the developed film directly on top of the material in the microscope. Especially in the case of multilayered membranes like the seams of Teflon coated Nomex this is a unique advantage.

The concept of extraction followed by liquid scintillation counting and comparison with a standard can also be used for verification of the procedures, e.g. determination of evaporative loss. In some cases the procedure is supplemented with combustion of a part of the exposed test material in a LECO combustion device, followed by liquid scintillation counting of the evolved and trapped carbon-14 CO_2.

Decontamination

Two different decontamination procedures have been used, i.e. (1) immersion in Freon 113 for 10 min, and (2) thermal exposure for 24 hours at 100°C in a circulating hot-air oven.

Decontamination is performed on a disk of the exposed test material. The decontamination efficiency is determined by dry combustion on an exposed disk and an exposed, decontaminated disk. The combustion is performed in a LECO combustion device, and is followed by liquid scintillation counting of the evolved and trapped carbon-14 CO2.

Evaluation of the decontamination procedure is further done by autoradiography and diskotomy.

Concluding remarks

It should be emphasized, that the cryogenic, microautoradiographic approach cannot be considered a fully developed routine method. Problems may and do still arise when the technique is applied to new combinations of materials and chemicals.

The feasibility study has mostly been carried out using available equipment. During the last phases of the feasibility study The Danish Isotope Centre aquired new, state-of-the-art equipment, and it has been shown, that this equipment is mandatory for many of the more specialized applications. The equipment consists of:

Leitz 1720 Digital Cryostat with differential cooling on knife and specimen
Leitz Metallux 3 microscope with Nomarski optics and Leitz Vario Orthomat camera
LECO combustion device
Packard Tri-Carb 2000CA with low-level device
Dewars for storage between -90°C to -150°C.

During the study some of the great advantages of using labeled compounds for normal permeation tests, i.e. measurements of breakthrough and steady state permeation rate, have been revealed. With the new Packard Tri-Carb 2000 CA with low-level counting device the sensitivity has been further improved by a factor of 20-50. Specific attention on these capabilities will not be given in this context.

APPLICATIONS

In this secton, the results of the applications carried out during the feasibility study will be described. It should be emphasized, that the technical approach has been currently under development during the applications. As mentioned in the preceding paragraph there are still improvements to be made in the technical approach, and this should be borne in mind, when looking at the results.

Results, however, clearly show, that the technical approach is indeed feasible.

The applications carried out during the feasibility study are summarized in Table 1 (p 12). The applications are listed in time-sequential order.

In the following sections the individual applications are detailed.

Viton/chlorobutyl laminate/acetone

For the Viton/chlorobutyl laminate, chemical exposure tests have been performed at four different exposure times using acetone with a specific activity of 0.47 MBq/g. The exposure times have been: 20 minutes, 2 hours, 20 hours and 72 hours. The cell shown in Appendix A-1 was used, and discrete sampling with replenishment and water as collecting medium was employed.

The permeation curve including discrete samples up to 72 hours is shown in Figure 5 (p13).

From the permeation curve a steady state permeation rate, reached after 3.5 hours, is calculated to be 0.49 $mg/m^2/s$. Breakthrough is significantly seen in the first sample collected after 2 min. Using ordinary GC technique and unlabeled acetone a breakthrough time of 54 min was found.

TABLE I
APPLICATIONS CARRIED OUT DURING THE FEASIBILITY STUDY
TYPE AND EXTENT OF EXPERIMENTS

	Permeation curve	Exposure times Autoradiography	 Diskotomy
Viton/chlorobutyl laminate vs. acetone	yes	20 min, 2h, 20 h, 72 h	20 min 20 h, 72 h
Neoprene vs. nitrobenzene	yes	[a]2 sec, 75 min	[a]2 sec 75 min
Teflon coated Nomex vs. acetone	yes	no success (early in the project)	not tried
Teflon coated Nomex vs. vinylacetate	yes	[b]done, but too low sensitivity (200 min)	not tried
Teflon coated Nomex vs. methylene chloride	yes	[a]15 min, 90 min not successful	[a]15 min 90 min
Teflon coated Nomex, seams vs. methylene chloride	yes	20 min, 75 min results, but problems still present	20 min 75 min

a results from decontamination, Freon 113 and hot-air oven
b results from decontamination, hot-air oven

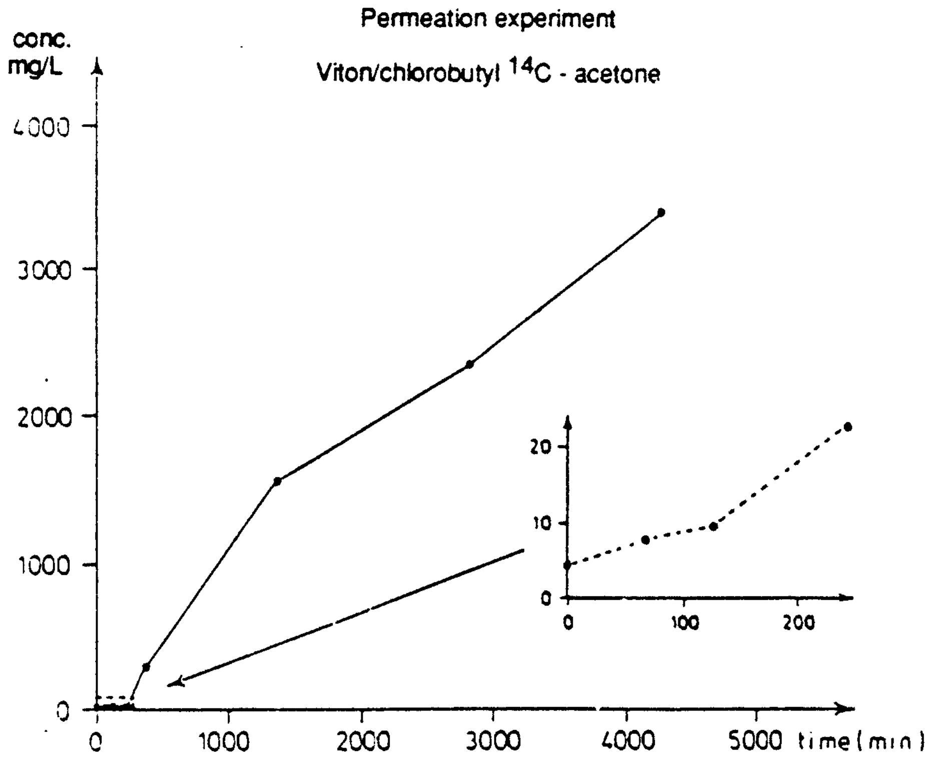

Figure 5. The Concentration (mg/L) vs Time (min) for Viton/Chlorobutyl Laminate Tested with Carbon-14 Labeled Acetone (0.47 MBq/g) as Permeant

In Figure 6 (p15), an autoradiogram of Viton/chlorobutyl laminate exposed to carbon-14 labeled acetone for 72 hours is shown. Figure 6 shows only part of the 340 um thick Viton/chlorobutyl laminate. A picture in a smaller magnification (100x) is shown in Appendix Figure A-5.

The carbon-14 labeled acetone is indicated in Figure 6 by the specks on top of the exposed Viton/chlorobutyl laminate. A diminishing gradient from the exposed exterior side of the material towards the inside can be seen.

The results (in grains per 100 um^2) based on autoradiograms from the four different chemical exposure times (21 days autoradiographic exposure) are shown in Appendix Figures A-6 to A-9. Variation in section thickness and lack of standardization of development and mounting procedures in these first experiments means that conversion from grain density to concentration units could not be done on the basis of autoradiographic standards.

Calibration was instead based on diskotomy and high temperature combustion techniques, but only for the chemical exposure times 20 minutes, 20 hours and 72 hours. The calibrated results are shown in Figure 7 (p16) as eyefitted curves.

Comparison of the 3 curves in Figure 7 shows, that the descendent gradient of the activity versus penetration depth is very steep for the 20-minute exposure time, while it tends to flatten out at the 20-hour chemical exposure time. The curve for the 72-hour chemical exposure time is not significantly different from that for 20 hours. This is in accordance with the permeation characteristics of the acetone for Viton/chlorobutyl laminate, where a steady state permeation rate is found after 3.5 hours.

The drop in concentration towards the exposed side is probably due to inevitable evaporation loss during the autoradiographic steps.

Neoprene/nitrobenzene

The neoprene elastomer was tested against carbon-14 labeled nitrobenzene at two different exposure times, i.e. 2 secs (splash test) and 75 minutes. The tests were carried out with the cell shown in Appendix A-1. Discrete sampling with replenishment was employed using water as collecting medium.

For each of the chemical exposure times, decontamination was carried out as described in the method development paragraph.

A permeation curve including samples up to 75 minutes is shown in Figure 8 (p17).

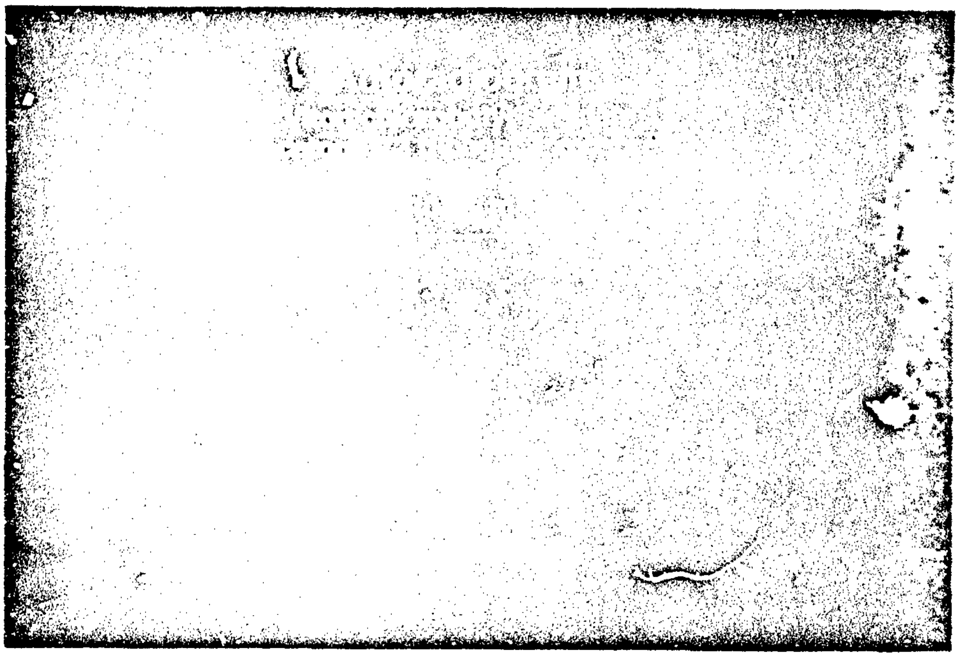

Figure 6. Autoradiogram (Kodak AR-10 Stripping Film, Sandwich Technique) of Viton/Chlorobutyl Laminate Exposed to Carbon-14 Labled acetone for 72 Hours. Autoradiographic Exposure Time 3 Days, Normal Light Microscopic Optics (Magnification 1000x). Exposed Side to the Right

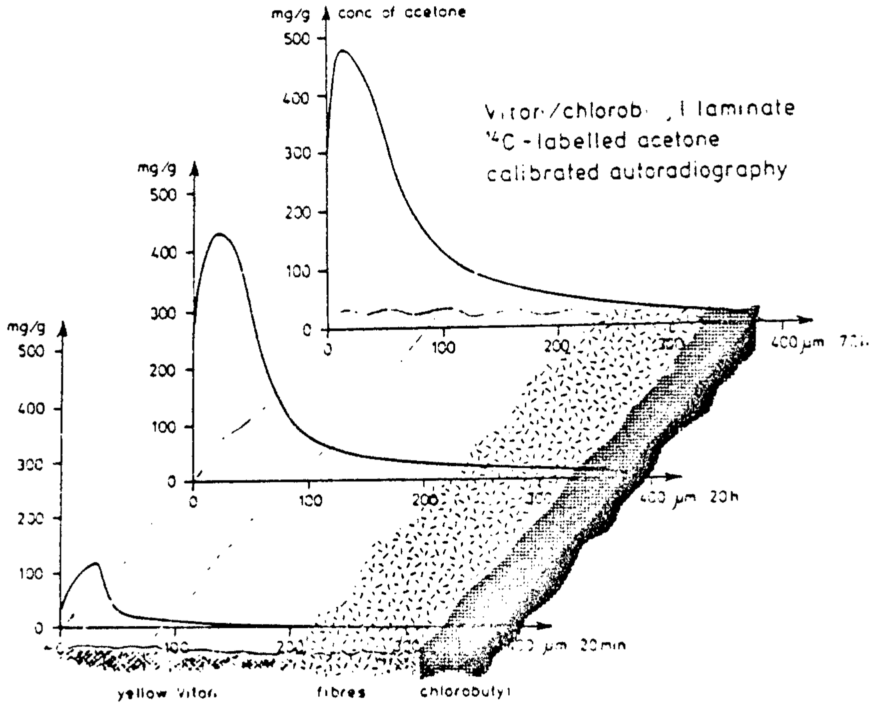

Figure 7. Autoradiographic Results. Concentrations (mg/g) vs Penetration Depth (µm) Calibrated Using Diskotomy and High Temperature Combustion. Viton/Chlorobutyl Laminate/Acetone, Chemical Exposure 20 Minutes, 20 Hours and 72 Hours

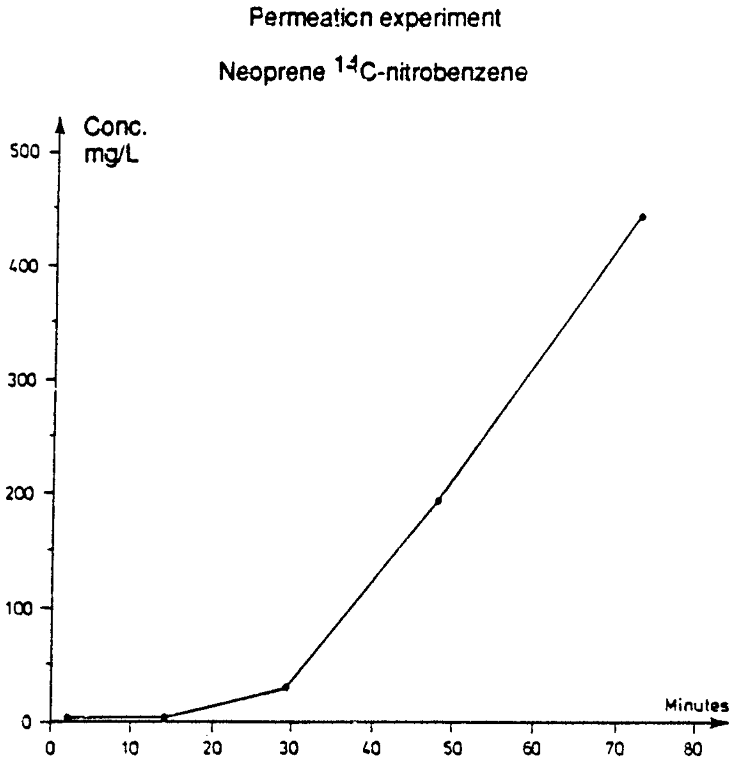

Figure 8. The Concentration (mg/L) vs Time (min) for Neoprene Tested with Carbon-14 Labeled Nitrobenzene (0.5 MBq/g) as Permeant

A steady state permeation rate is reached after 30 minutes. The steady state permeation rate is calculated to 5.9 $mg/m^2/s$. Significant breakthrough is seen in the first sample after 2 seconds in the splash test.

In Appendix Figures A-10 and A-11, the autoradiograms of neoprene/nitrobenzene exposed for 2 secs are shown. For the 75 minutes exposure very high grain densities were found, and the autoradiograms could only be evaluated qualitatively. For this exposure time the quantitative results are therefore mostly based on diskotomy.

In Figure 9 (p19), the diskotomy-calibrated results are shown for both exposure times.

In the autoradiograms after the 2 secs splash test a slightly descendent grain density from the exposed exterior side to the unexposed side is found. In the outermost 15 um the concentration was 142 mg/g, but already after 20-30 um the concentration has decreased to 90 mg/g. Near the unexposed side the concentration has decreased to less than 30 mg/g.

After 75 minutes chemical exposure the concentration at the outermost 15 um is 545 mg/g with a single peak value on 767 mg/g at 30 um (the peak is not visible on the smooth curve). Near the unexposed side the concentration is 450 mg/g.

The results for the decontamination experiments measured using dry combustion and liquid scintillation counting of the trapped carbon-14 CO_2 are shown in Tables II and III.

A high variation in the nitrobenzene content in the untreated neoprene exposed for 2 secs (Table II) is seen. This is possibly due to the short chemical exposure time.

No apparent differences in decontamination efficiencies were seen for the two different exposure times (Freon 113: 79.2 and 87%. Hot air oven: 99.9 and 99.9%).

Thermal decontamination results in a very high decontamination efficiency, 99.9%. A significant residue of 0.08-0.12% was found, however.

Autoradiographic results are only obtained after the Freon 113 decontamination and only for the 75 minutes chemical exposure. The residual nitrobenzene was homogeneously distributed with a mean value of 4.3 grains per 100 um^2. For the other experiments the applied specific activity (0.5 MBq/g) was not sufficient to leave autoradiographically detectable amounts of carbon-14 labeled nitrobenzene within the neoprene.

Teflon-coated Nomex/acetone

With the Teflon-coated Nomex an experiment with carbon-14

TABLE II
DECONTAMINATION - NEOPRENE/NITROBENZENE AFTER CHEMICAL EXPOSURE FOR 2 SECS AT 20°C

Treatment after chem. exposure	dpm per unit * (exposed) membrane (dry combustion)	% nitrobenzene residue	% ** decontamination efficiency
none	13414 +/- 2012	(100)	
Freon 113 for 10 min at 20°C	2796 +/- 215	20.8 +/- 3.5	79.2 +/- 3.5
Thermal hot air oven 100°C for 24 hours	16.3 +/- 2.0	0.12 +/- 0.02	99.9 +/- .02

* 1 unit membrane is a circular disc of 5 mm diameter

** % decontamination efficiency = ((Ca-Cb)/Ca)*100, where Ca is the contaminant concentration in the unwashed, exposed disc and Cb is the contaminant concentration in the washed, exposed disc

TABLE III
DECONTAMINATION - NEOPRENE/NITROBENZENE AFTER CHEMICAL EXPOSURE FOR 75 MINUTES AT 20°C

Treatment after chem. exposure	dpm per unit * (exposed) membrane (dry combustion)	% nitrobenzene residue	% ** decontamination efficiency
none	119600 +/- 1555	(100)	
Freon 113 for 10 min at 20°C	15000 +/- 1050	12.5 +/- 0.9	87 +/- 1
Thermal hot air oven 100°C for 24 hours	90 +/- 32	0.08 +/- 0.03	99.9 +/- 0.1

* 1 unit membrane is a circular disc of 5 mm diameter

** % decontamination efficiency = ((Ca-Cb)/Ca)*100, where Ca is the contaminant concentration in the unwashed, exposed disc and Cb is the contaminant concentration in the washed, exposed disc

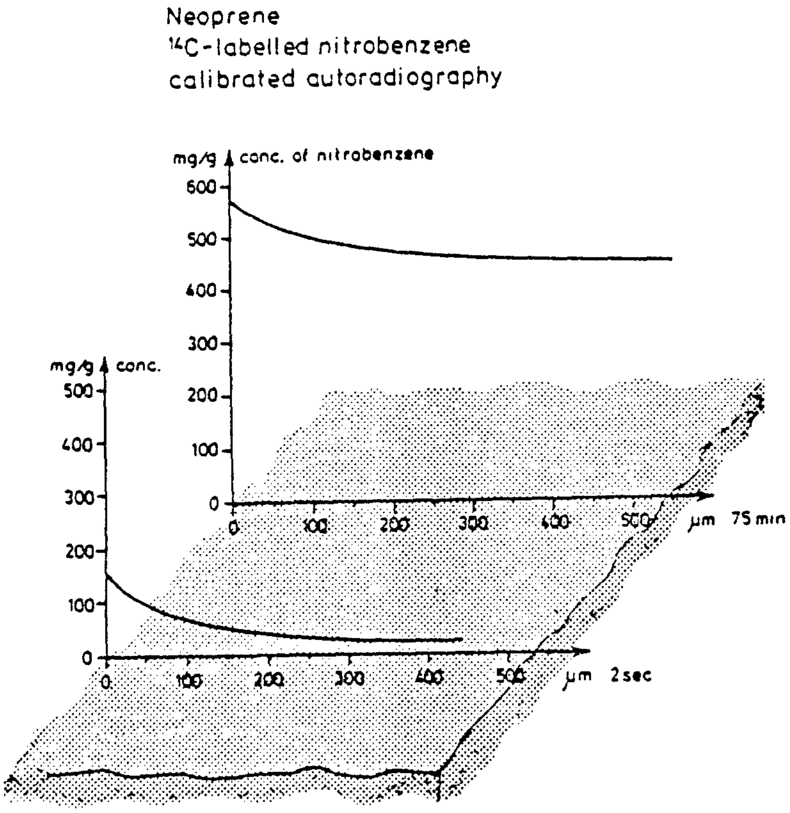

Figure 9. Autoradiographic Results, Concentrations (mg/g) vs Penetration Depth (µm) Calibrated Using Diskotomy and High Temperature Combustion. Neoprene/ Nitrobenzene, Chemical Exposure 2 Seconds and 75 Minutes

labeled acetone (0.47 MBq/g) was performed in the beginning. The experiment was carried out in the cell shown in Appendix A-1 and discrete sampling with replenishment and water as collecting medium was employed.

The permeation curve is shown in Appendix Figure A-12. Breakthrough time of less than 45 minutes was found, and the steady state permeation rate was calculated to 0.0024 $mg/m^2/s$. A permeation experiment using ordinary GC-technique and unlabeled acetone did not give breakthrough within 240 minutes.

No autoradiographic results were obtained.

Teflon coated Nomex/vinyl acetate

The Teflon coated Nomex has been tested against carbon-14 labeled vinyl acetate (0.4 MBq/g). The test cell shown in Appendix Figure A-2 was used. Chemical exposure time was 200 minutes. Water was used as collecting medium and discrete sampling with replenishment employed. Due to the special construction of the test cell and the small sample volume no blind sample could be taken prior to introduction of the radioactive vinyl acetate into the challenge chamber.

Decontamination experiments were carried out for the Teflon coated Nomex/vinyl acetate. Only the hot air oven procedure was employed.

The resultant permeation curve is shown in Appendix Figure A-13. A rather big off-set (blind value) is seen, which might be due to problems in the cell assembly. Because of the low permeation rate and the relatively low specific activity of the vinyl acetate (0.4 MBq/g), the resulting concentrations in the collecting medium are close to the detection limit. A permeation rate could still be calculated from the slope of the curve, and it was estimated to be 0.0079 $mg/m^2/s$ within the first 200 minutes.

The low permeation rate resulted in a mean concentration of vinyl acetate within the membrane of approx. 1 mg/g (determined by dry combustion and liquid scintillation counting of the trapped carbon-14 CO_2). This low mean concentration combined with the specific activity of 0.4 MBq/g implies that no results are attainable with the autoradiography. The autoradiograms are shown in Appendix Figure A-14.

The decontamination results are shown in Table IV.

As for the other results the low permeation rate combined with the specific activity of 0.4 MBq/g means that the decontamination results are very uncertain. Experiments should be repeated with a higher specific activity.

TABLE IV
DECONTAMINATION - TEFLON-COATED NOMEX/VINYL ACETATE AFTER CHEMICAL EXPOSURE FOR 200 MINUTES AT 20°C

Treatment after chem. exposure	dpm per unit * (exposed) membrane (dry combustion)	% ** decontamination efficiency
none	85/197	
Thermal hot air oven 100°C for 24 hours	<10/22	75-100

* 1 unit membrane is a circular disc of 5 mm diameter

** % decontamination efficiency = (Ca-Cb)/Ca*100, where Ca is the contaminant concentration in the unwashed, exposed disc and Cb is the contaminant concentration in the washed, exposed disc

Teflon coated Nomex/methylene chloride

The off-white Teflon coated Nomex has been tested against carbon-14 labeled methylene chloride (8.4 MBq/g). Due to the high price of carbon-14 labeled methylene chloride, a new and smaller cell with a very low leakage rate was used, see Appendix Figure A-3.

For other experiments, water was used as collecting medium, and discrete sampling (0.5 mL) with replenishment was employed.

Exposure tests were conducted six times; three at a chemical exposure time of 15 minutes and three at 90 minutes. For each chemical exposure time, decontamination was carried out by two methods as described under the method development paragraph.

For each exposure, the exposed membrane was divided into four equal-sized pieces. One piece was used for autoradiography, two for dry combustion and the last one for diskotomy.

The permeation curve up to 90 minutes is shown in Figure 10. Breakthrough is significant in the first sample collected after 5 minutes. The steady state permeation rate within the first 90 minutes was calculated to 0.073 $mg/m^2/s$.

Autoradiography has been performed at all six exposure tests. In Figure 11 the structure of the Teflon coated Nomex membrane is seen. No grains are visible at this magnification. In Figure 12 the membrane is shown at a higher magnification. Very few autoradiographic grains are visible.

Generally, all autoradiograms of the Teflon-coated Nomex looked like the ones in Figures 11 and 12, even after decontamination. The number of grains per 100 um^2 were generally not significantly above background, and in some cases negative net grain densities were observed even after 21 days of autoradiographic exposure. This is not consistent with earlier findings, e.g. Viton/chlorobutyl laminate/acetone. Results from both d y combustion and diskotomy of the methylene chloride-exposed-Teflon coated Nomex show that the amount of radioactivity inside the membrane was at least 7.4 KBq/g for the 15 minutes chemical exposure and 15 KBq/g for the 90 minutes chemical exposure. Compared to our previous experiences with the Kodak AR10 stripping emulsion these specific activities should produce average grain densities from 5 to 20 grains/100 um^2 after 9-20 days autoradiographic exposure at -120°C.

The explanation for the very low grain densities found on all autoradiograms of the methylene chloride-exposed Teflon-coated Nomex might be that the carbon-14 labeled methylene chloride had evaporated during the short warm-up period, when the

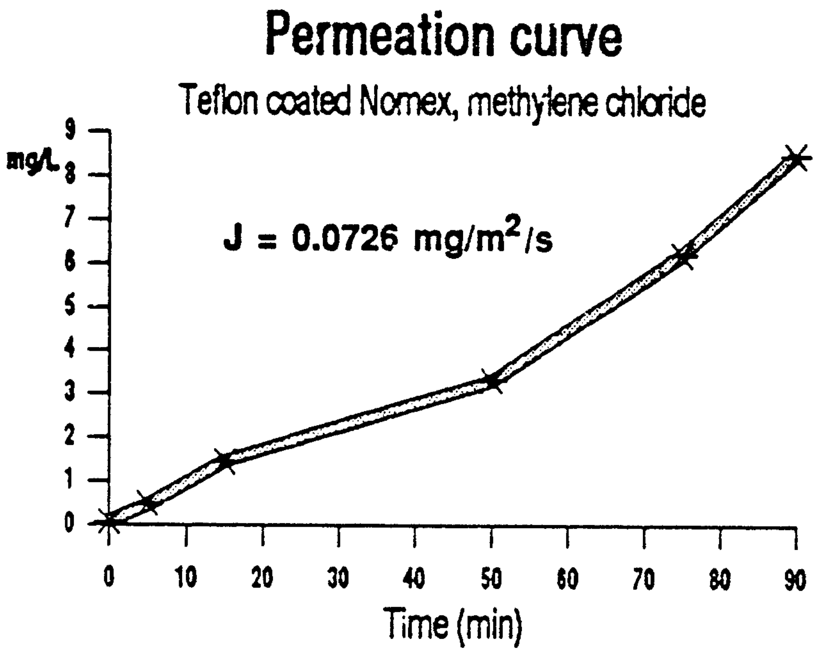

Figure 10. The Concentration (mg/L) vs Time (min) for Teflon-coated Nomex with Carbon-14 Labeled Methylene Chloride (8.4 MBq/g) as Permeant

Figure 11. Autoradiogram of Teflon-coated Nomex Exposed to Carbon-14 Labeled Methylene Chloride for 15 Minutes. Incident Polarized Light (Magnification 250x). Grain Density is Below Background

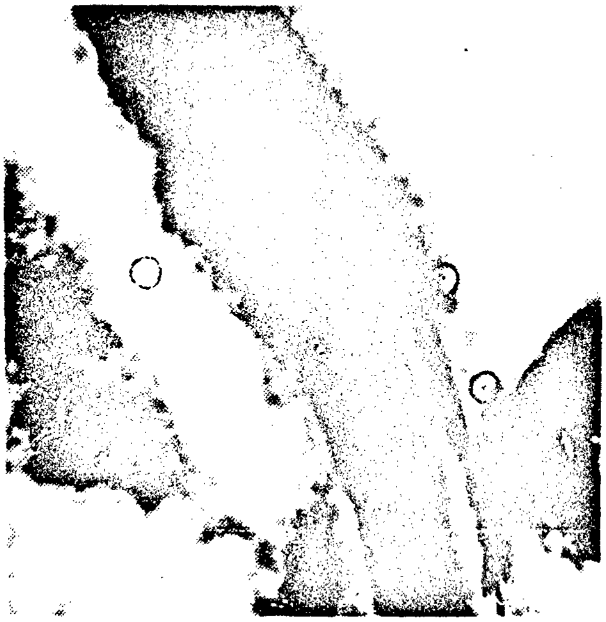

Figure 12. Autoradiogram of Teflon-coated Nomex Exposed to Carbon-14 Labeled Methylene Chloride for 90 Minutes. Transmitted Bright Field (Magnification 1250x). Grain Density is Very Low. Circles Depict Autoradiographic Grains

autoradiographic sandwich is prepared (5 minutes at 15°C). The finding of very low background densities over the sections, however, points in the direction of a severe negative chemography generated by the methylene chloride, but it cannot be excluded, that both phenomena could have occurred simultaneously. These possibilities have not been checked within the current project.

Both the untreated exposed membranes and the decontaminated exposed membranes were analyzed by diskotomy and dry combustion. A summary of the results is presented in Tables V and VI.

It should be noted, that the Teflon had a bad adhesion to the frozen embedding medium. As a consequence only the outermost 200 um could be sliced in the diskotomy before the remaining 250 um broke off in one piece. The concentration in the remaining uncut piece is consequently determined as an average concentration.

The diskotomy results in Tables V and VI have been obtained by accumulation of the chemical amounts observed in each slice through out the whole membrane piece. A reasonably good agreement between these results and those obtained by dry combustion is observed. The two methods have been applied on membrane aliquots from the same exposed piece but are analytically independent.

Decontamination efficiency seems to be relatively independent of chemical exposure time. Between 59% and 73% is found for the Freon 113 wash, while the heat treatment is more effective with results between 97.0% and 99.7%. Even after the heat treatment methylene chloride is found in the ug/g range inside the membrane.

The discontinuous concentration gradient from the diskotomy are shown in Appendix Figures A-15 and A-16 as a succession of bars. The uncertainty on the concentrations and on the distance from the exposed side is not exactly known. A rough estimate suggest that the uncertainty for both these parameters, especially from slices no. 1 and 3, is considerable - on the order of +/-50%. The results suffer from the lack of autoradiographic results which have a far better topographical resolution. It should be emphasized, that the diskotomy results were obtained using an old cryotome, and not the new Leitz 1720 Digital Cryostat. With this cryotome a better reproducibility can be obtained.

From Appendices A-15 and A-16, it is nevertheless evident that methylene chloride permeates into the Teflon-coated Nomex. When the results from the different chemical exposure times are compared, methylene chloride seems to permeate deeper and with increasing amounts into the membrane with time.

Teflon coated Nomex, seams/methylene chloride

Seams of off-white Teflon coated Nomex were tested against

TABLE V
DECONTAMINATION - TEFLON-COATED NOMEX/METHYLENE CHLORIDE AFTER CHEMICAL EXPOSURE FOR 15 MINUTES AT 20°C

Treatment after chem. exposure	Dry-combustion conc. (mg/g)	Dry-combustion decontamination* efficiency %	Diskotomy** conc. (mg/g)	Diskotomy** decontamination* efficiency %
none	0.638 +/- 0.070		1.02	
Freon 113 for 10 min. at 20°C	0.260 +/- 0.021	59.2	0.272	73.3
Thermal hot air oven 100°C for 24 hours	0.0193 +/- 0.0012	97.0	0.00751	99.3

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* % decontamination efficiency = (Ca-Cb)/Ca*100, where Ca is the contaminant concentration in the unwashed, exposed disc and Cb is the contaminant concentration in the washed, exposed disc

** accumulated amounts from whole transsection

TABLE VI
DECONTAMINATION - TEFLON-COATED NOMEX/METHYLENE CHLORIDE AFTER CHEMICAL EXPOSURE FOR 90 MINUTES AT 20°C

Treatment after chem. exposure	conc. (mg/g)	Dry-combustion decontamination* efficiency %	conc. (mg/g)	Diskotomy** decontamination* efficiency %
none	1.97 +/- 0.14	1.69		
Freon 113 for 10 min. at 20°C	0.655 +/- 0.059	66.8	0.594	64.9
Thermal hot air oven 100°C for 24 hours	0.0095 +/- 0.0005	99.5	0.00471	99.7

---

* % decontamination efficiency = (Ca-Cb)/Ca*100, where Ca is the contaminant concentration in the unwashed, exposed disc and Cb is the contaminant concentration in the washed, exposed disc

** accumulated amounts from whole transsection carbon-14 labeled methylene chloride. The test cell shown in Figure 1 (modified ASTM 1" cell) was used. Water was used as collecting medium, and discrete sampling (0.5 mL) with replenishment was employed.

Exposure tests were conducted at two different exposure times, i.e. 20 minutes and 90 minutes. A specific activity of 1.28 MBq/g was used for the 20 minutes exposure, while the specific activity in the 75 minutes experiment was 6.28 MBq/g.

For each exposure the exposed membrane was divided into five equal-sized pieces. One piece was used for autoradiography, two for dry combustion and the last two for diskotomy.

Figure 13 shows an overview of the seam in incident light dark field at a low magnification. Arrows indicate the side to be exposed to methylene chloride.

The thickness of the exposed area of the seam varied from 1333 um in the mid-area to 480 um at the sides of the seam. Figure 14 shows a transection of the seam mid-area at a higher magnification. Ten white (Teflon) layers are seen. The number of such layers is decreasing towards the side of the seam, where the material proceed in the normal 2-layered Teflon coated Nomex. Different areas in the seam might thus consist of a varying number of layers (4-10).

The permeation curve up to 75 minutes is shown in Figure 15. Breakthrough is significant in the first sample collected after 5 minutes. An average steady state permeation rate is calculated to 0.00074 $mg/m^2/s$.

After each chemical exposure, autoradiography was carried out. Due to the expected problems with negative chemography and/or evaporation loss the modified "sandwich" technique was used. This technique consists of a thin Saran layer between the nuclear emulsion and the exposed section (see Figure 4). For cryosectioning the Leitz Digital cryotome was used, providing a better cutting reproducibility.

Results were only obtained for the 75 minute chemical exposure.

In Figure 16 a survey is shown of the autoradiographic grain densities observed. These results indicate, that the highest concentrations of methylene chloride are found in the 12-14 um thick black layers on both sides of the white Teflon layers. (The lowest concentrations are observed in the Teflon layers).

At the chemically exposed side of the seam grain densities are not as high as expected (compared to diskotomy, see later).

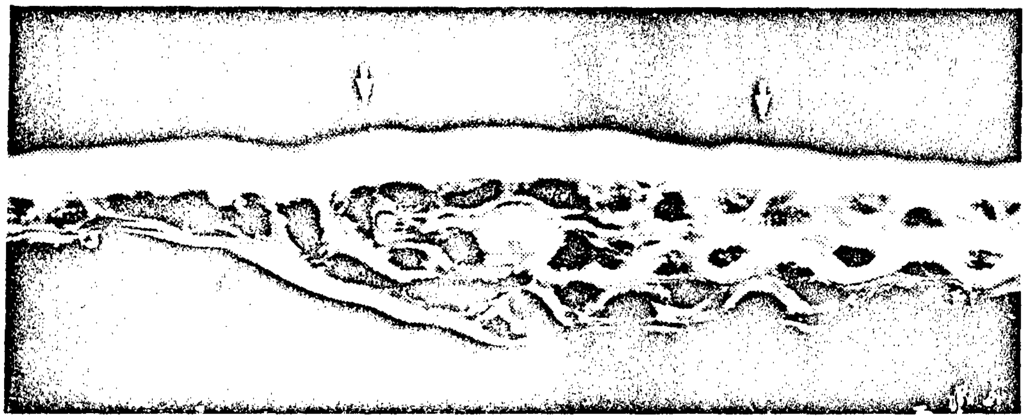


Figure 13. Teflon-coated Nomex Seam (Nonexposed), Transection to Show the Structure and Folding of the Seam. Incident Light, Darkfield (Magnification 20x)

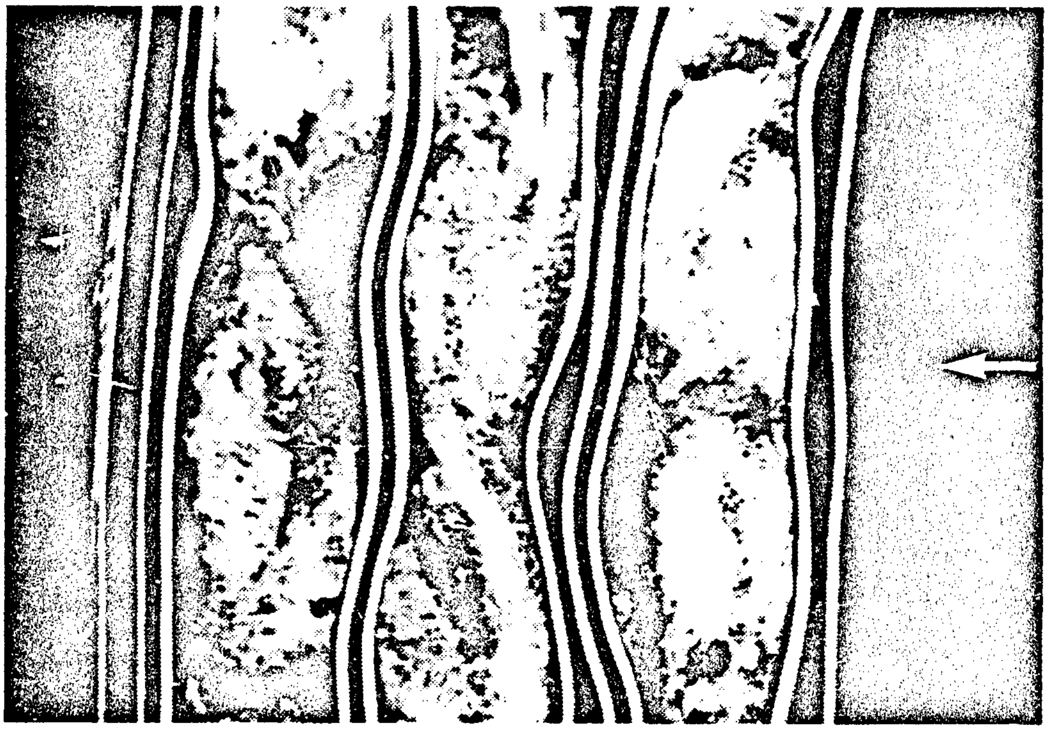


Figure 14. Teflon-coated Nomex Seam Exposed to Carbon-14 Labeled Methylene Chloride for 75 Minutes. Transection of the Mid-Area. Arrow Indicates the Exposed Side. Incident Light, Darkfield (Magnification 80x)

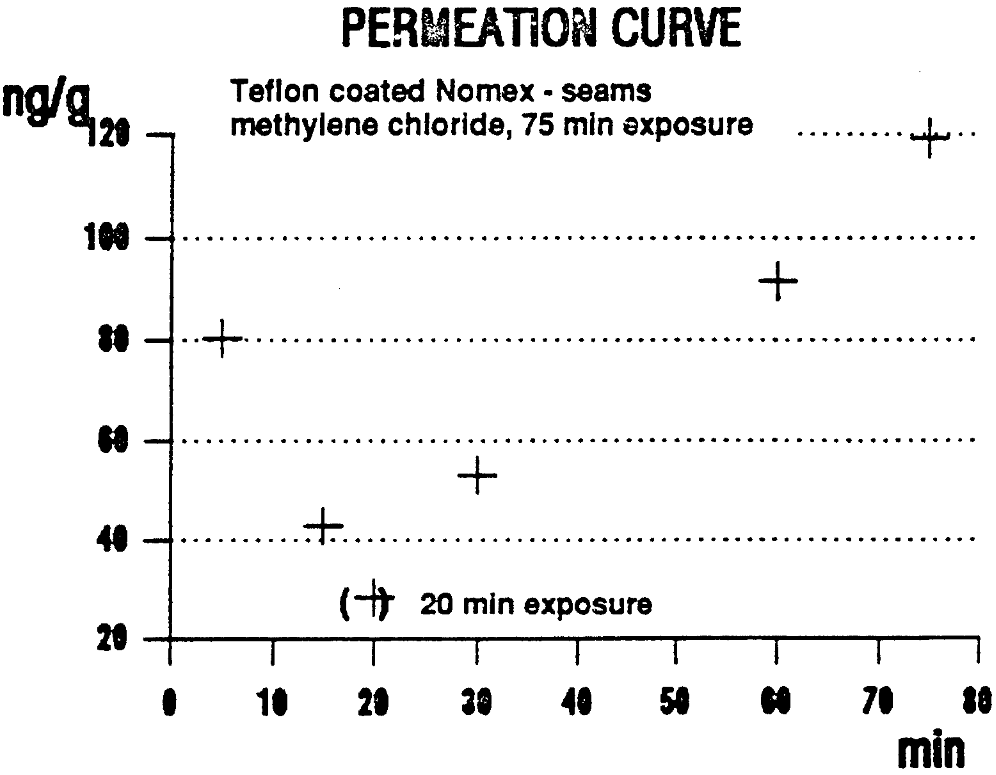
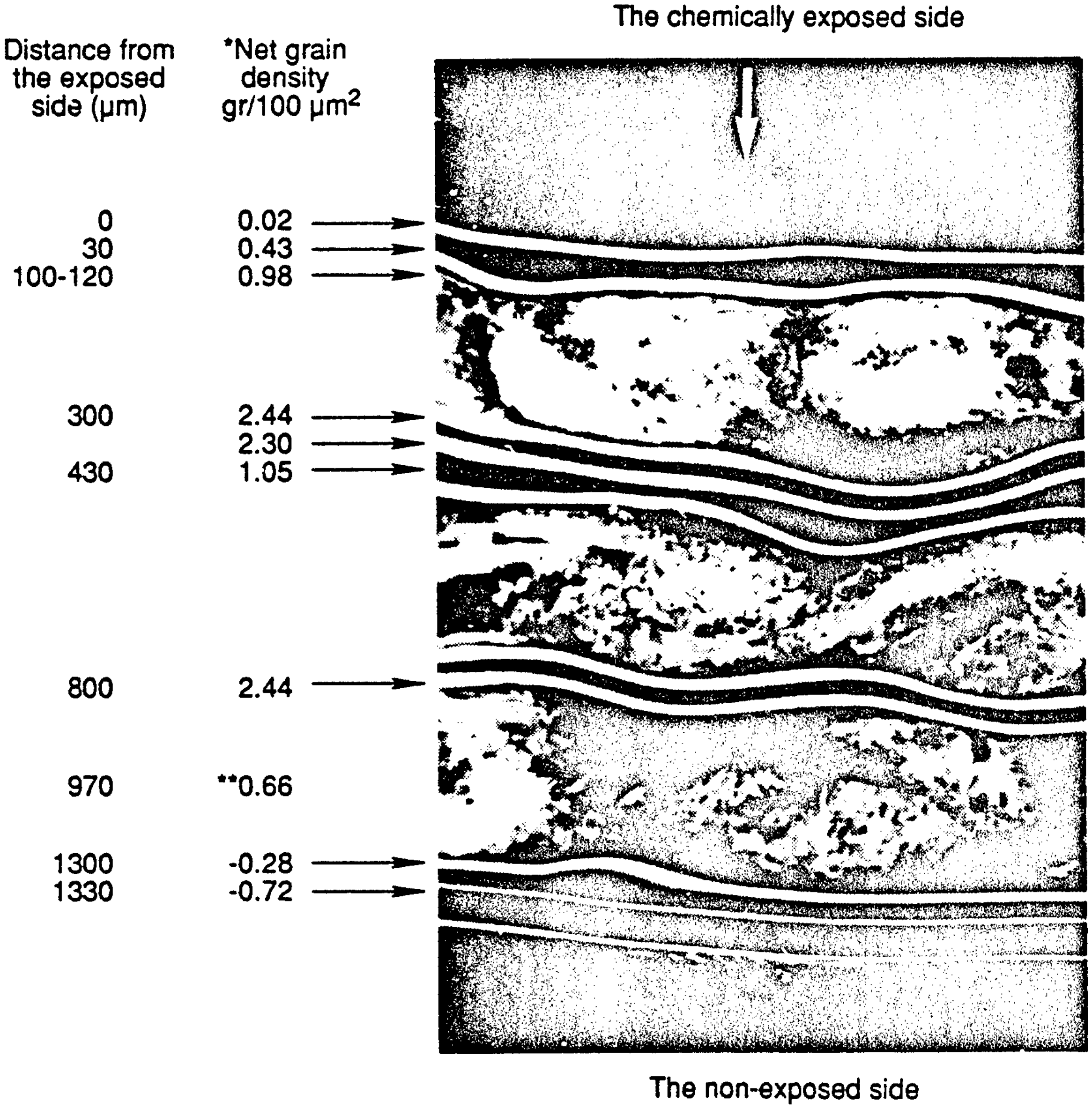


Figure 15. The Concentration (ng/g) vs Time (min) for Teflon-coated Nomex Seam Tested with Carbon-14 Labeled Methylene Chloride (6.28 MBq/g) as Permeant



* Net grain density above the 12-14 µm thick "brownish" layers adjacent to the Teflon layer

** Net grain density above the fibrous layer

Figure 16. Teflon-coated Nomex Seam Exposed to Carbon-14 Labeled Methylene Chloride for 75 Minutes. Survey of Autoradiographic Results. The Net Grain Densities were Below or Equal to Back-ground, Especially Above the Teflon Layers (White Layers). Incident Light, Darkfield

An explanation could be that the evaporation was most severe at that side. The negative grain densities at the non-exposed side indicate that the background setting was too high.

The grain densities in Figure 16 are generally too small to make reliable conclusions. They should only be used indicatively. It appears as if the autoradiographic procedure with a 12 um protective Saran layer beneath the nuclear emulsion diminishes the problems of evaporation and chemography, but further improvements are needed.

In Appendix Figures A-17 to A-19, autoradiograms are shown at 1600x magnification. Some silver grains are visible.

The results from diskotomy and dry-combustion are presented in Figures 17 and 18 and in Table V.

In Figure 17 the concentration versus distance from the exterior side after 20 minutes chemical exposure is shown. A maximum concentration of 1.01 mg/g is seen about 120 um from the exterior exposed side. The slightly lower values in the most outlying disks at the exposed side indicate, that some evaporation has taken place, presumably in connection with the dismounting of the ASTM cell at the end of the exposure period. 300 um from the exposed side only trace amounts of methylene chloride are seen (below 0.005 mg/g). At the non-exposed side the concentration is 0.04 mg/g.

In Figure 18 the results of the 75-minute experiment are presented.

The two different curves in Figure 18 represent two adjacent samples from the same experiment. The concentrations at the exposed side are in the range of 2 to 3 mg/g. About 300 um from the exposed side and the non-exposed side both curves show minimum values of about 0.2 mg/g. Between 300 um and close to the non-exposed side slightly higher values about 0.3 to 0.5 mg/g are seen.

Due to the inherent variation in the seam the two parallel pieces are not necessarily identical. The two curves in Figure 18 nevertheless give a rough picture of the reproducibility of the diskotomy procedure. The largest deviations are seen for the outermost disks. After the first 50 to 100 um, the progress of the two curves are quite consistent.

In Table VII the diskotomy results are compared with results from dry-combustion.

The diskotomy results have been obtained by cumulation of the chemical amounts observed in each disk throughout the whole membrane punch. The dry-combustion technique is considered the most reliable technique for measuring of the total contained or incorporated amount of a carbon-14 labeled chemical in almost any

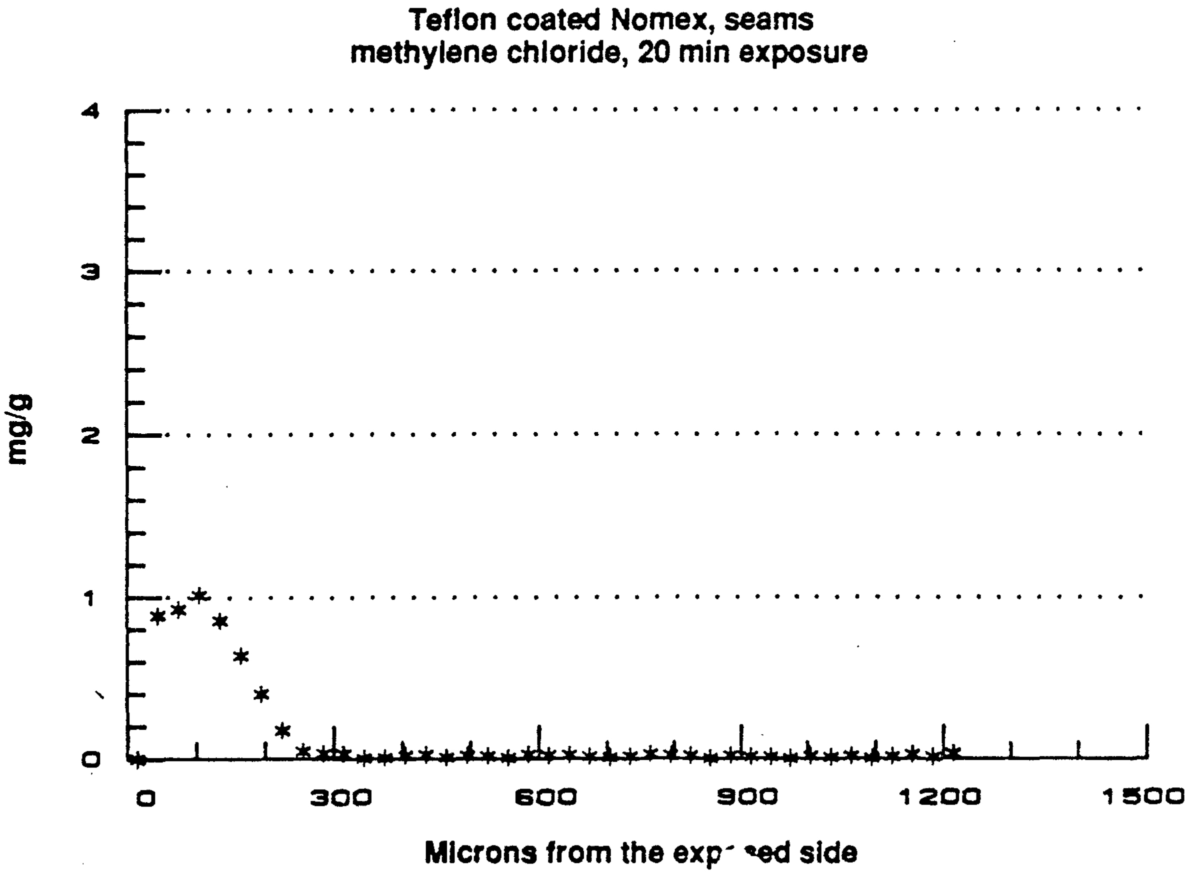


Figure 17. Teflon-coated Nomex Seam Exposed to Carbon-14 Labeled Methylene Chloride (1.28 MBq/g) for 20 Minutes. Diskotomy Results — Concentration (mg/g) vs Penetration Depth (µm)

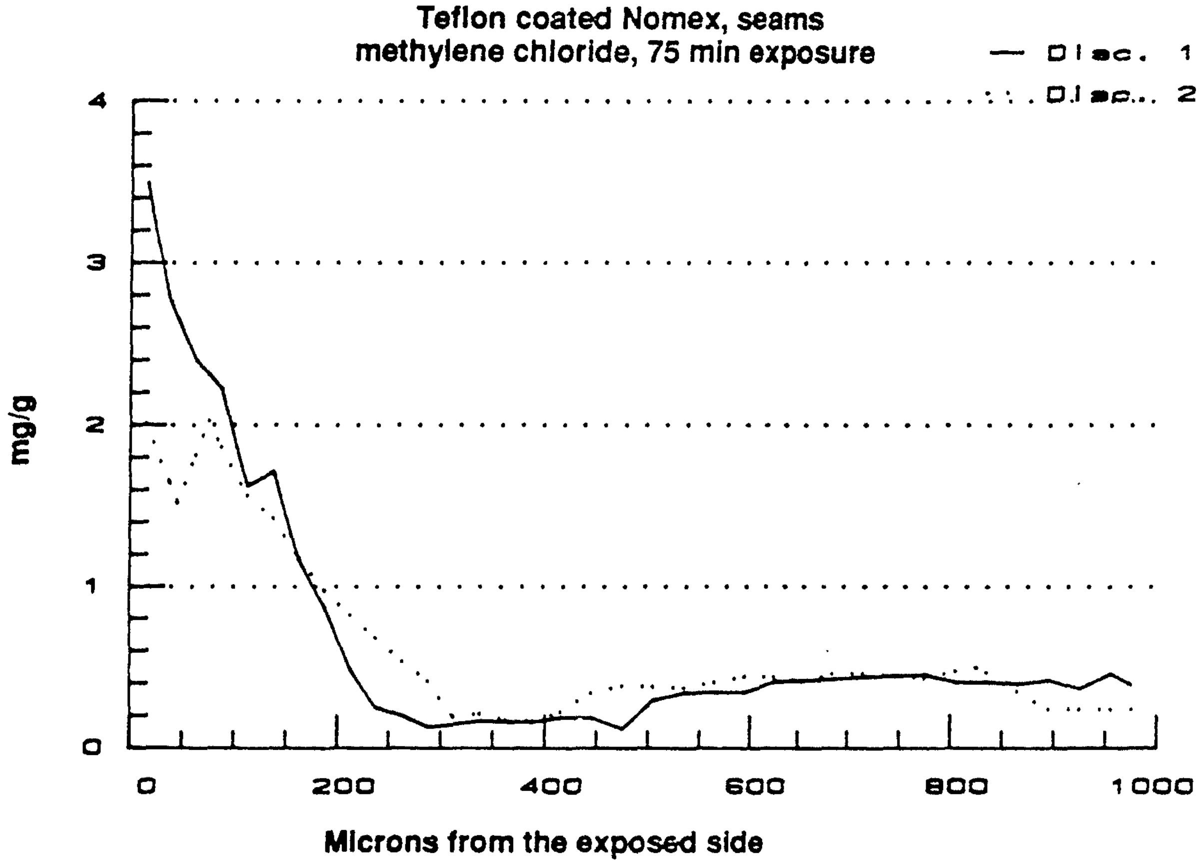


Figure 18. Teflon-coated Nomex Seam Exposed to Carbon-14 Labeled Methylene Chloride (6.28 MBq/g) for 75 Minutes. Diskotomy Results — Concentration (mg/g) vs Penetration Depth (μm)

TABLE VII
TEFLON-COATED NOMEX SEAMS EXPOSED TO CARBON-14 LABELED METHYLENE CHLORIDE - ISOTOPE MASS BALANCE, DISKOTOMY AND DRY-COMBUSTION

Specific activity MBq/g	Chemical exposure time min	Diskotomy cumulated amount mg/cm^2	Dry-combustion mg/cm^2	Diff.* %
1.28	20	0.0506	0.0712 +/- 0.0003	-29
6.28	75	0.0867 +/- 0.0001	0.1065 +/- 0.0026	-19

* ((diskotomy - dry-combustion)/dry-combustion)*100

kind of material.

From Table VII can be seen, that activity has been lost in the diskotomy procedure. In the 20 minute experiment 30% of the carbon-14 activity was lost compared to only 19% in the 75 minute experiment.

Compared to normal Teflon-coated Nomex base material, it is evident, that the seam of the same material is more resistant to methylene chloride, and that lower concentrations are found inside the membrane seam.

CONCLUSIONS AND FUTURE WORK

It has been shown, that radioactive tracers are indeed feasible for elucidating mechanisms of chemical permeation of protective clothing materials.

However, the use of radioactive tracers of highly diffusible substances in combination with autoradiography in microscale cannot yet be considered a routine method. Expensive state-of-the-art equipment and experience in dealing with the techniques on many different materials are considered mandatory for successful results.

The techniques developed during the feasibility study are by no means perfect and improvements are still needed. The techniques at their present state and used in the combinations described in this report are nevertheless considered good enough to produce reliable results even in highly sophisticated applications like seams of Teflon-coated Nomex. It is therefore concluded, that experiments can be carried out beyond the feasibility level, while concurrent improvements are being made.

Some drawbacks have been identified with the technique, especially in the application on Teflon-coated Nomex and methylene chloride. These drawbacks are presumably related to evaporative loss of the highly volatile methylene chloride, and possibly by chemographic effects.

Future development effort should be focused on:

(1) The need to develop another gluing procedure in the preparation of the autoradiographic sandwich to prevent temperature rise above -10°C.

(2) Refinement of the mounting procedure, which is desirable in order to permit more advanced data evaluation using image-analysis.

(3) More detailed checking of the evaporative loss by mass balances (already done partly).

(4) Making calibration of individual autoradiograms using a radioactive standard more operational.

(5) Comparison of the results of more simple experiments with theoretical elucidations.

ACKNOWLEDGMENT

The idea of using radioactive tracers for visualization of concentration gradients within protective clothing was originally inspired by Dr. Alan Bentz, U.S. Coast Guard R&D Center.

The work carried out within this project using unlabeled compounds was done by DANTEST, Denmark, who worked as a subcontractor for the Danish Isotope Centre.

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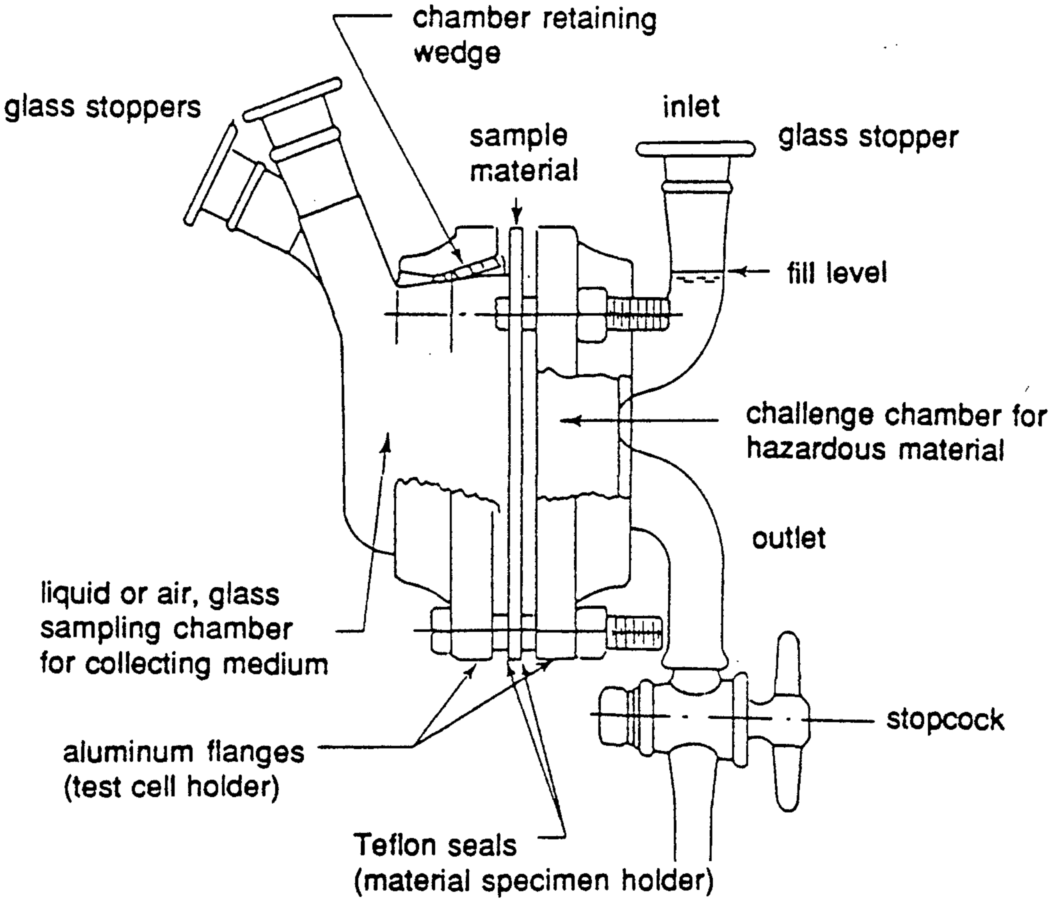
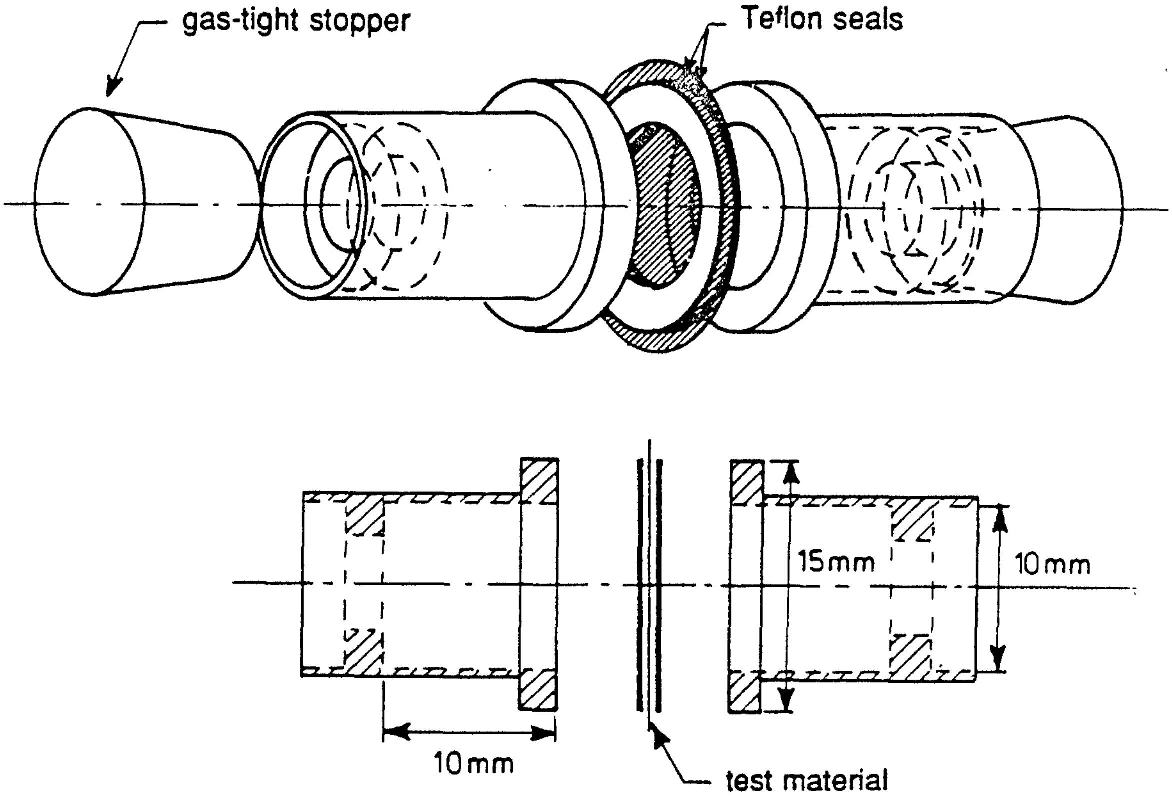
APPENDIX

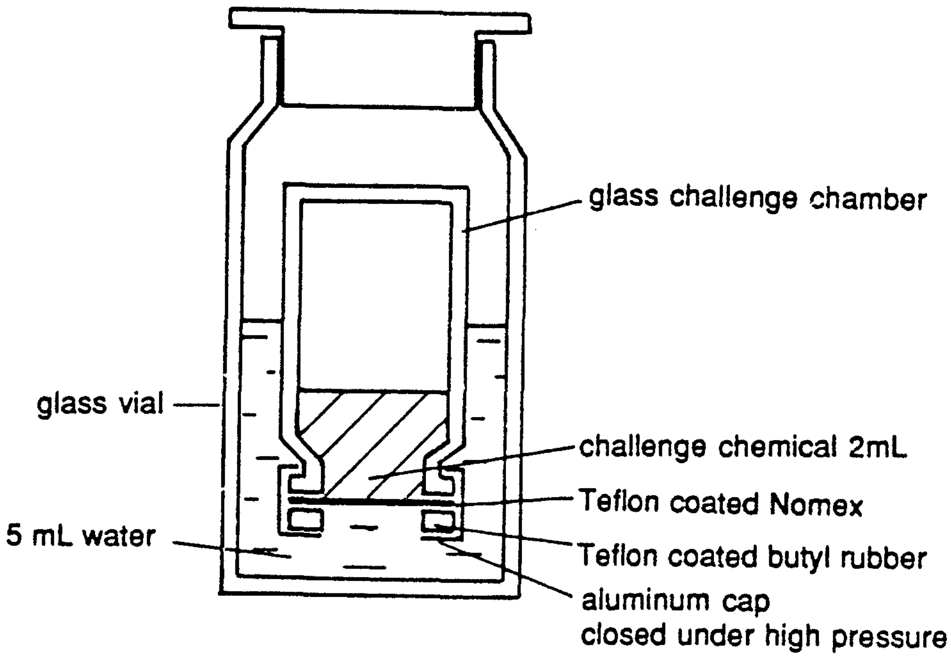
SUPPLEMENTARY FIGURES



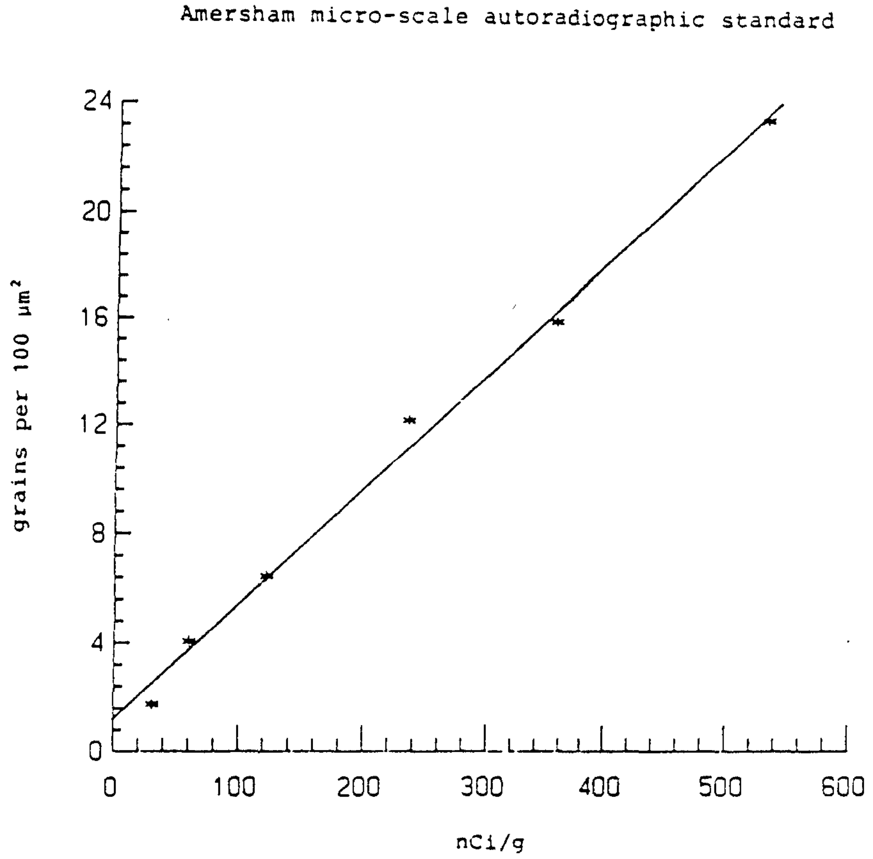
A-1 Early modification of ASTM 1" cell. Adding an outlet vent to the challenge chamber.



A-2 Test cell (0.85 mL) used for the Teflon coated Nomex/vinyl acetate

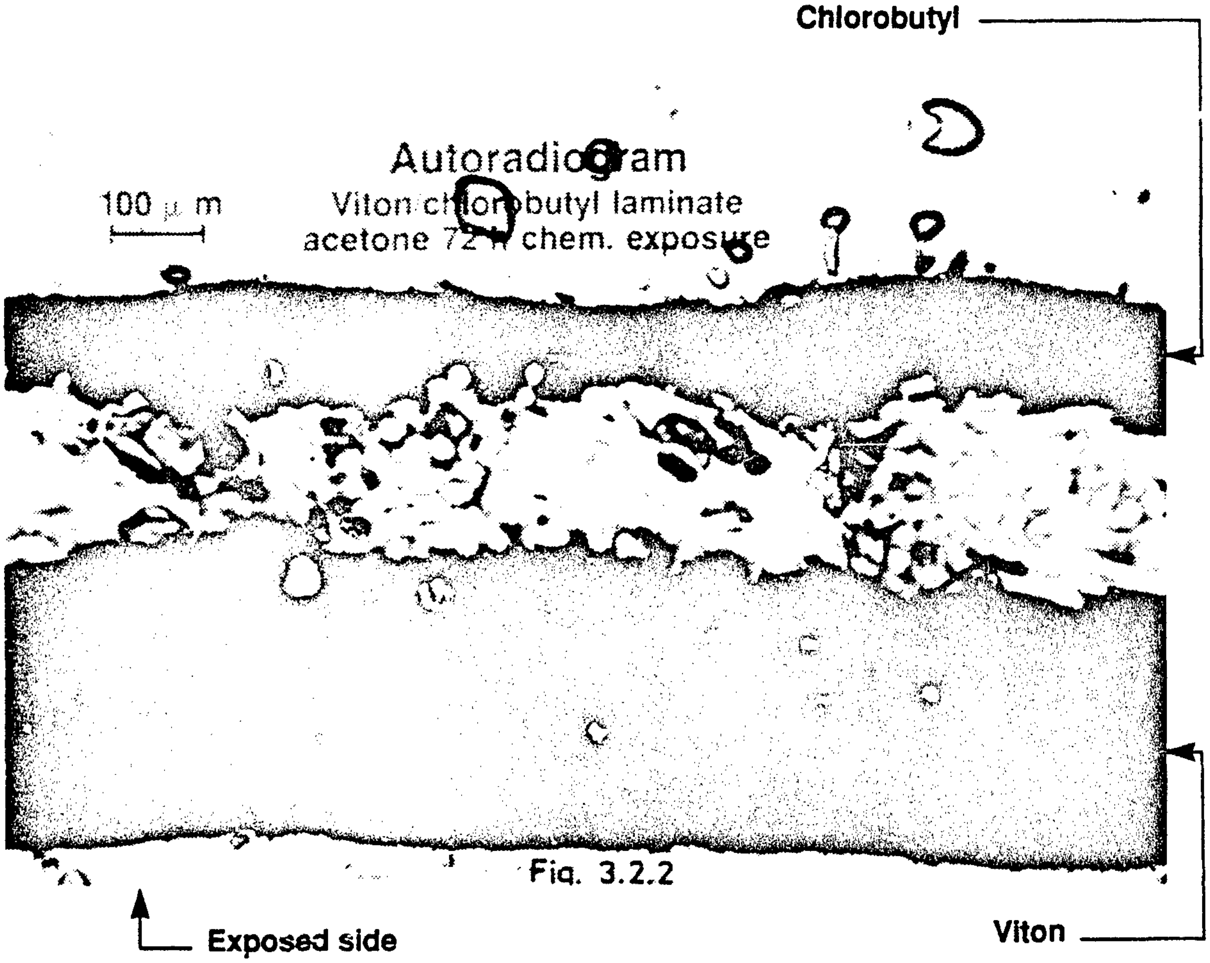


A-3 Modified minicell for obtaining highest possible carbon-14 specific activity in relation to cost.

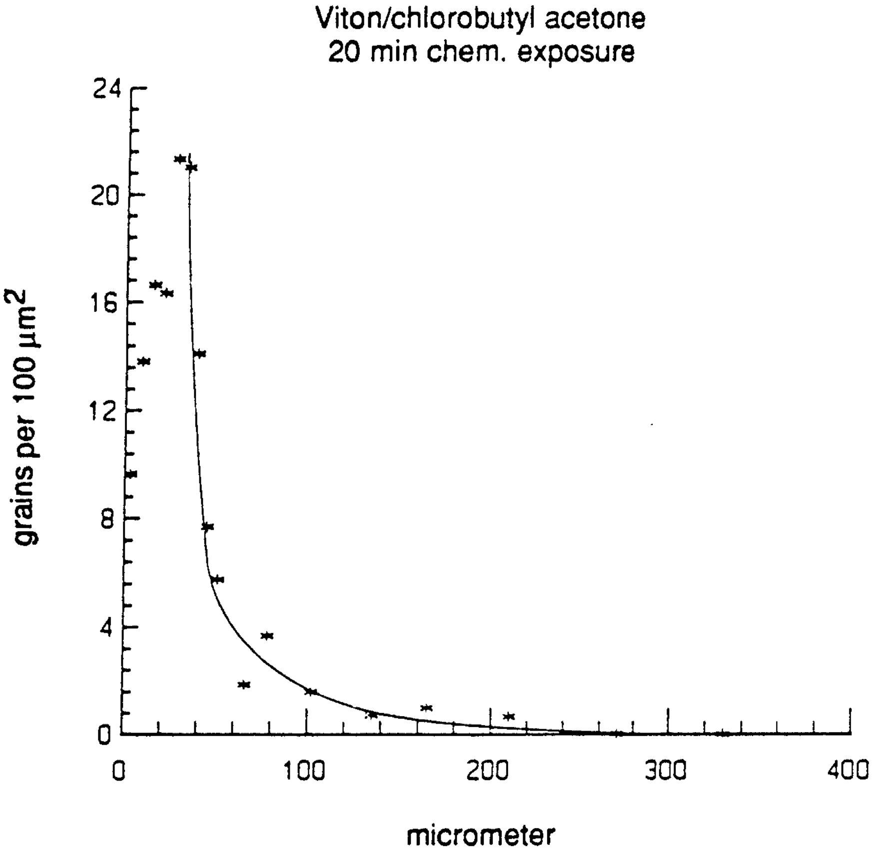


Amersham micro-scale autoradiographic standard

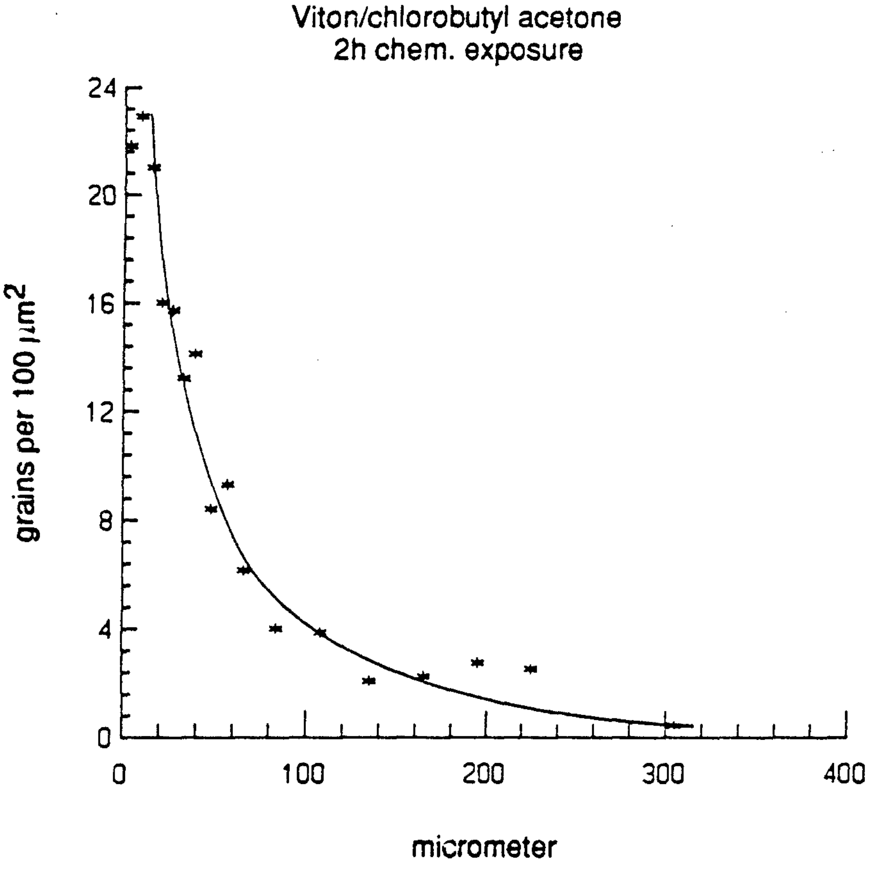
A-4 Amersham micro-scale autoradiographic standard. Grain density vs nCi/g.



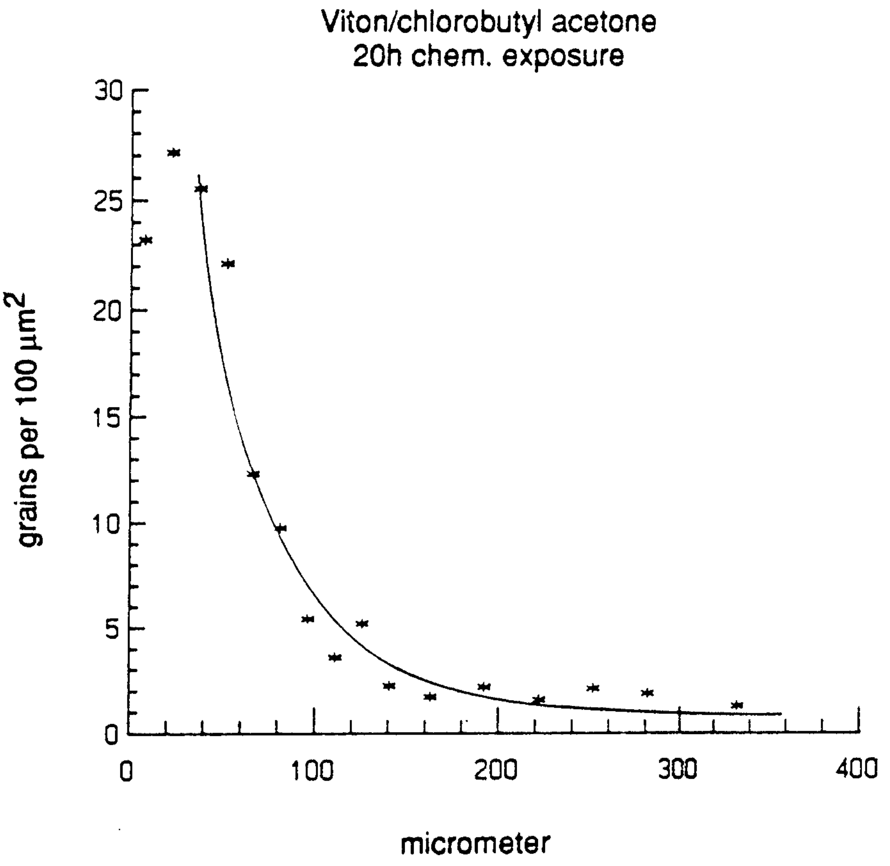
A-5 Autoradiogram (Kodak AR10 stripping film - "sandwich" technique) of Viton/chlorobutyl laminate exposed to carbon-14 labeled acetone for 72 hours. Autoradiographic exposure time 3 days, normal light microscopic optics (magnification 100x). Exposed side to the bottom.



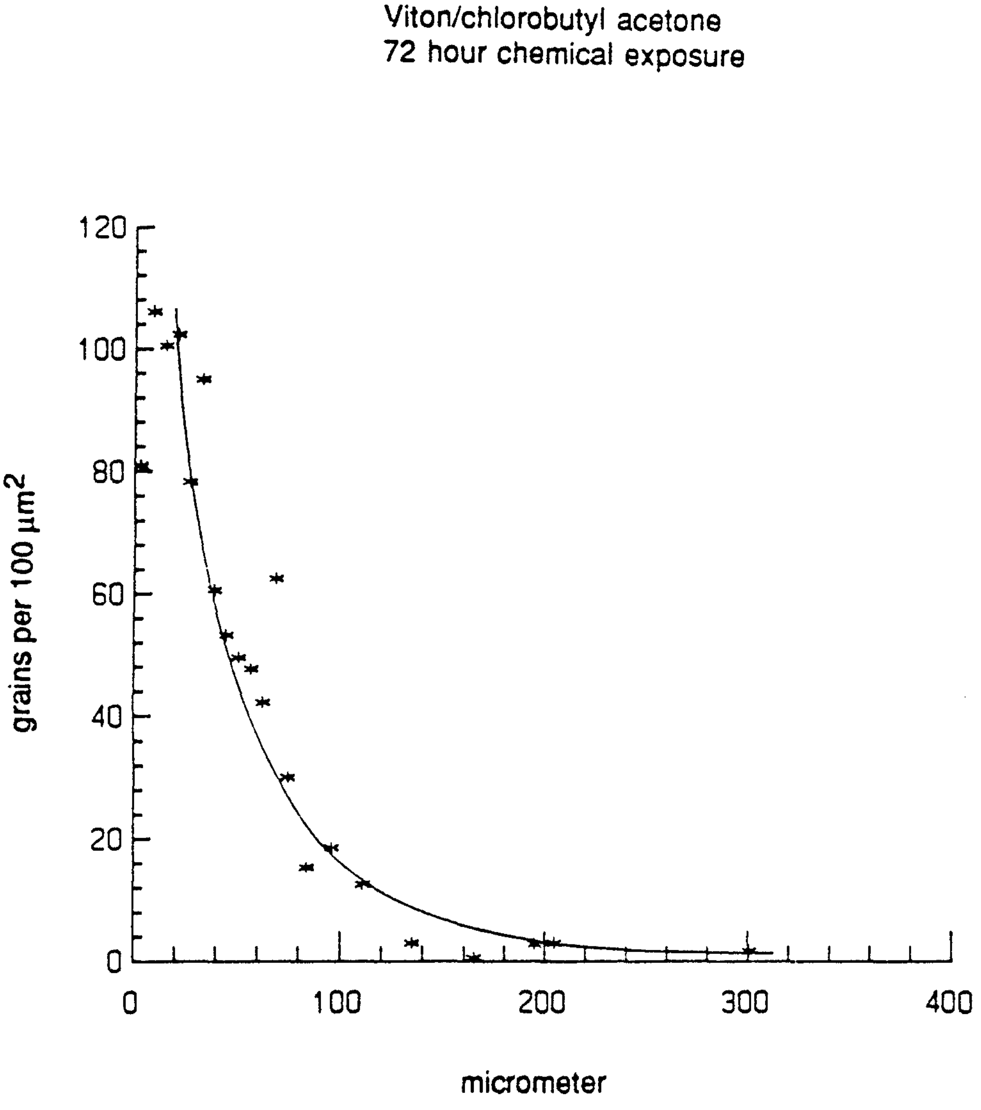
A-6 Results for Viton/chlorobutyl laminate autoradiogram, carbon-14 acetone exposed (Kodak AR10 stripping film "sandwich" technique), 21 days autoradiographic exposure. Net grain density per 100 μm^2 vs penetration depth (μm). 20 minutes chemical exposure time.



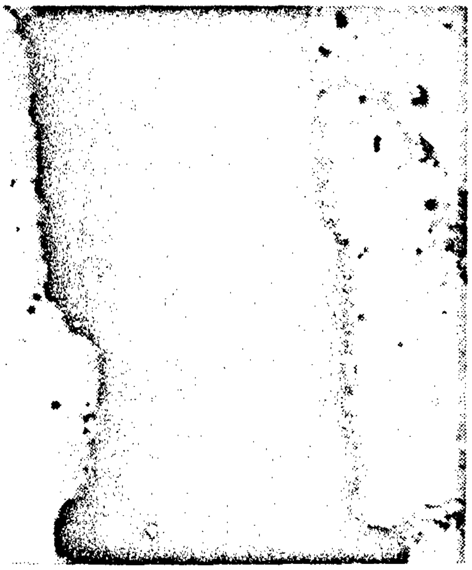
A-7 Results for Viton/chlorobutyl laminate autoradiogram, carbon-14 acetone exposed (Kodak AR10 stripping film "sandwich" technique), 21 days autoradiographic exposure. Net grain density per 100 μm^2 vs penetration depth (μm). 2 hours chemical exposure time.



A-8 Results for Viton/chlorobutyl laminate autoradiogram, carbon-14 acetone exposed (Kodak AR10 stripping film "sandwich" technique), 21 days autoradiographic exposure. Net grain density per 100 μm^2 vs penetration depth (μm). 20 hours chemical exposure time.

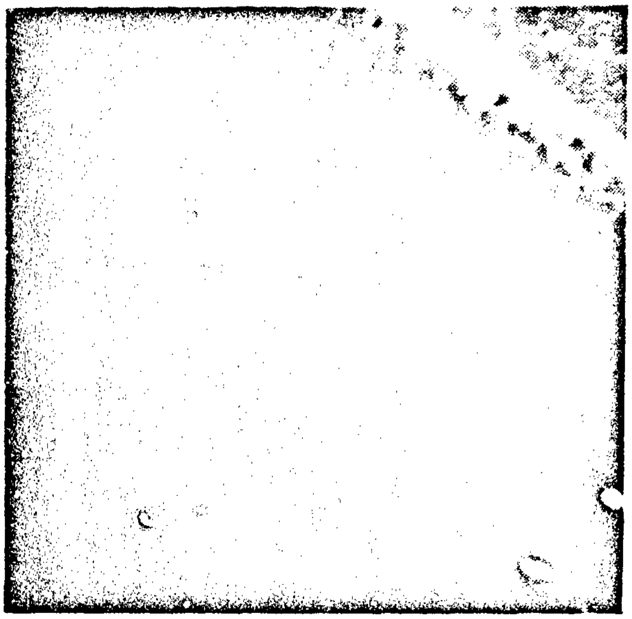

Viton/chlorobutyl acetone
72 hour chemical exposure

A-9 Results for Viton/chlorobutyl laminate autoradiogram (carbon-14 acetone exposed Kodak AR10 stripping film "sandwich" technique, 21 days autoradiographic exposure). Net grain density per 100 μm^2 vs penetration depth (μm). 72 hours chemical exposure time.



Cross section of the black opaque membrane at a low magnification. The total thickness of the membrane is 480 µm which is 30% more than the unexposed membrane (after 75 minutes the thickness is 580 µm which is 45% above normal). Incident light

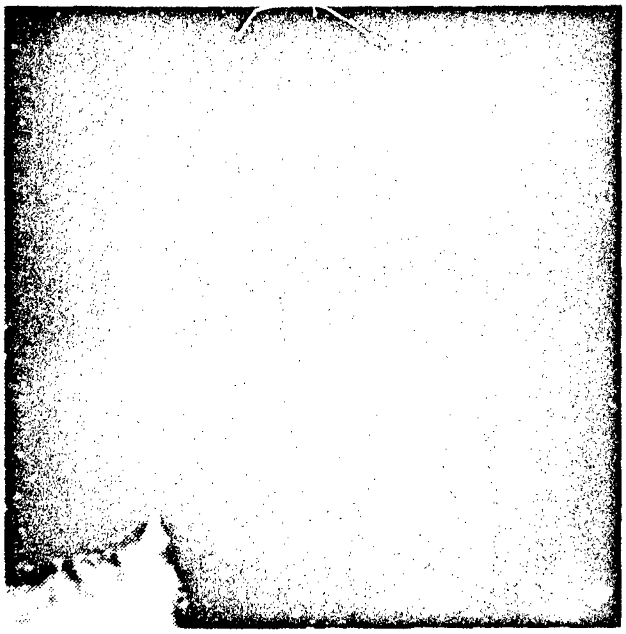
500 µm



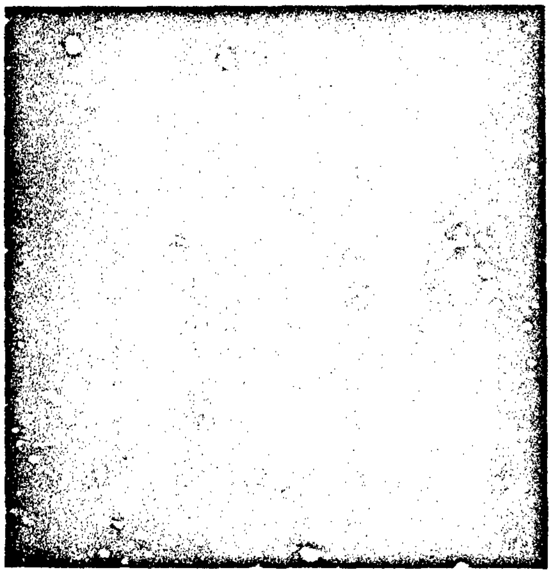
The membrane cross section at a higher magnification. It is noticed that the cross section surface has a wooly appearance. Incident light

50 µm

A-10 Autoradiograms, neoprene exposed to carbon-14 labeled nitrobenzene for 2 seconds (splash test), 65x and 310x magnification

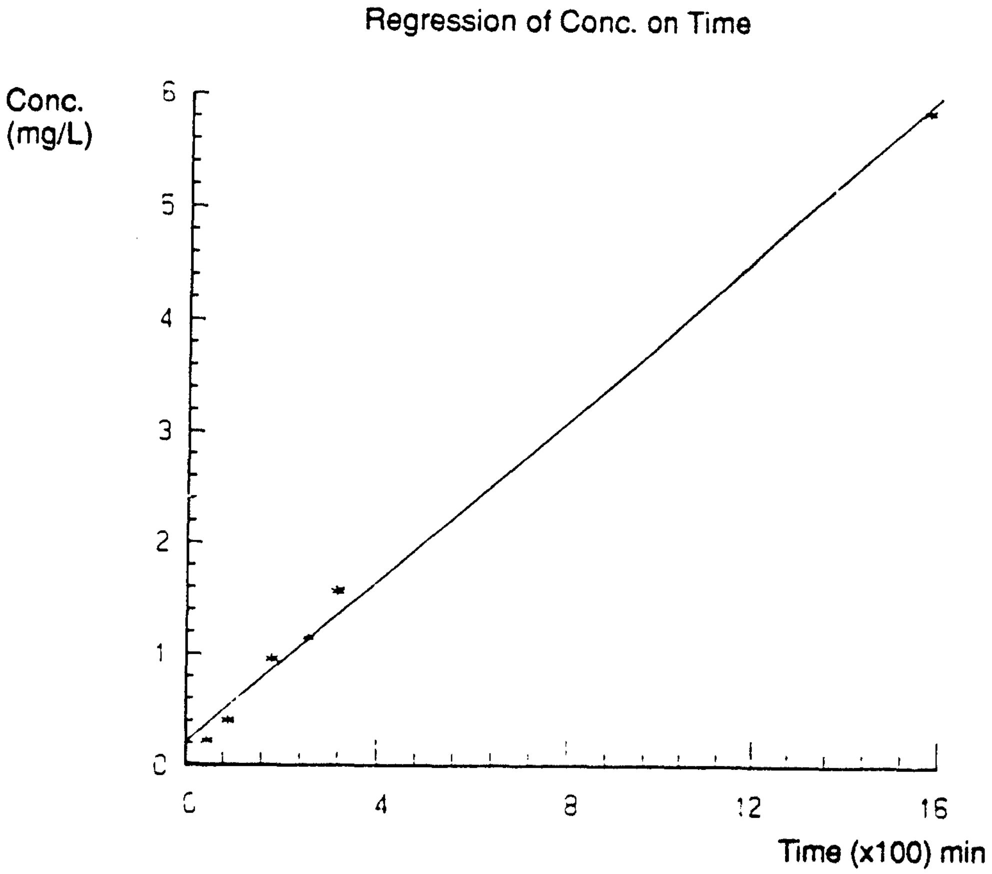


The reflected light from the superposed silver grains is visible as light specks. Incident light

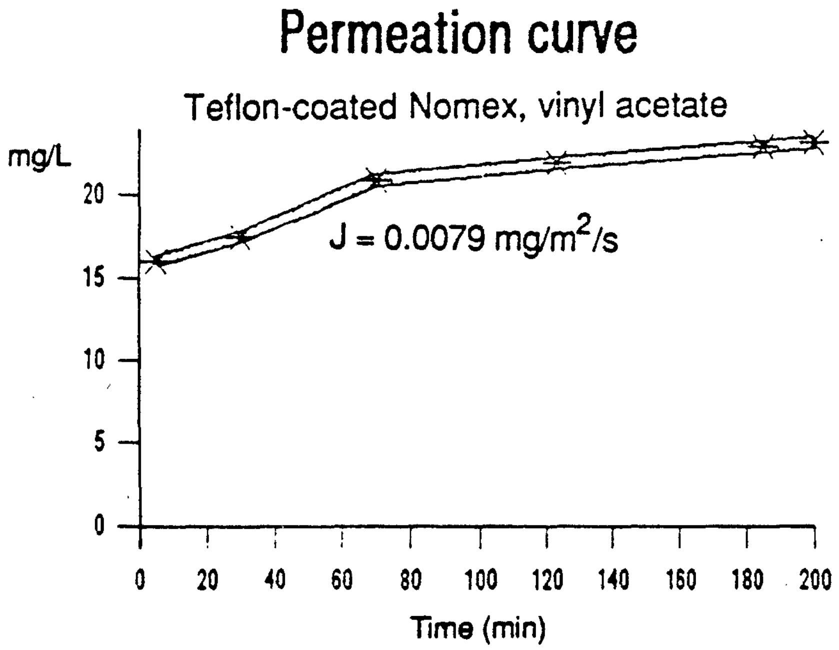


The same area at higher magnification. The reflected light from the silver grains is seen very clearly. By turning the plane of the polarized light it is possible with this technique to exclude about 95% of the reflectance from the cross section. Incident polarized light

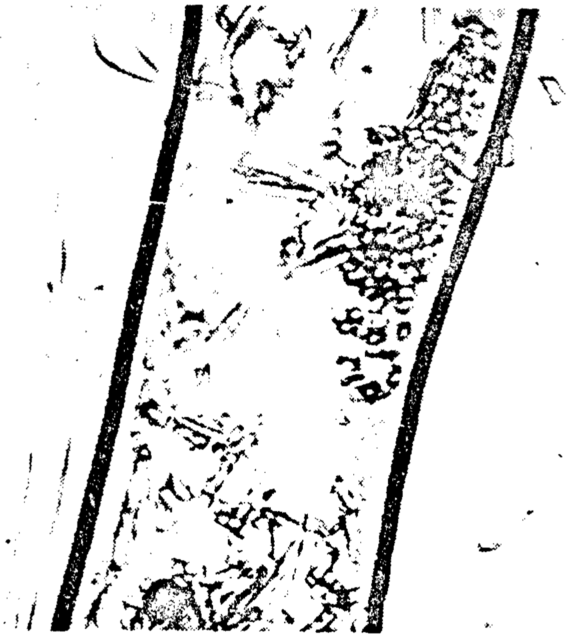
A-11 Autoradiograms, neoprene exposed to carbon-14 labeled nitrobenzene for 2 seconds (splash test), 700x and 840x magnification



A-12 The concentration (mg/L) vs time (Minutes) for Teflon coated Nomex with carbon-14 labeled acetone (0.47 MBq/g) as permeant



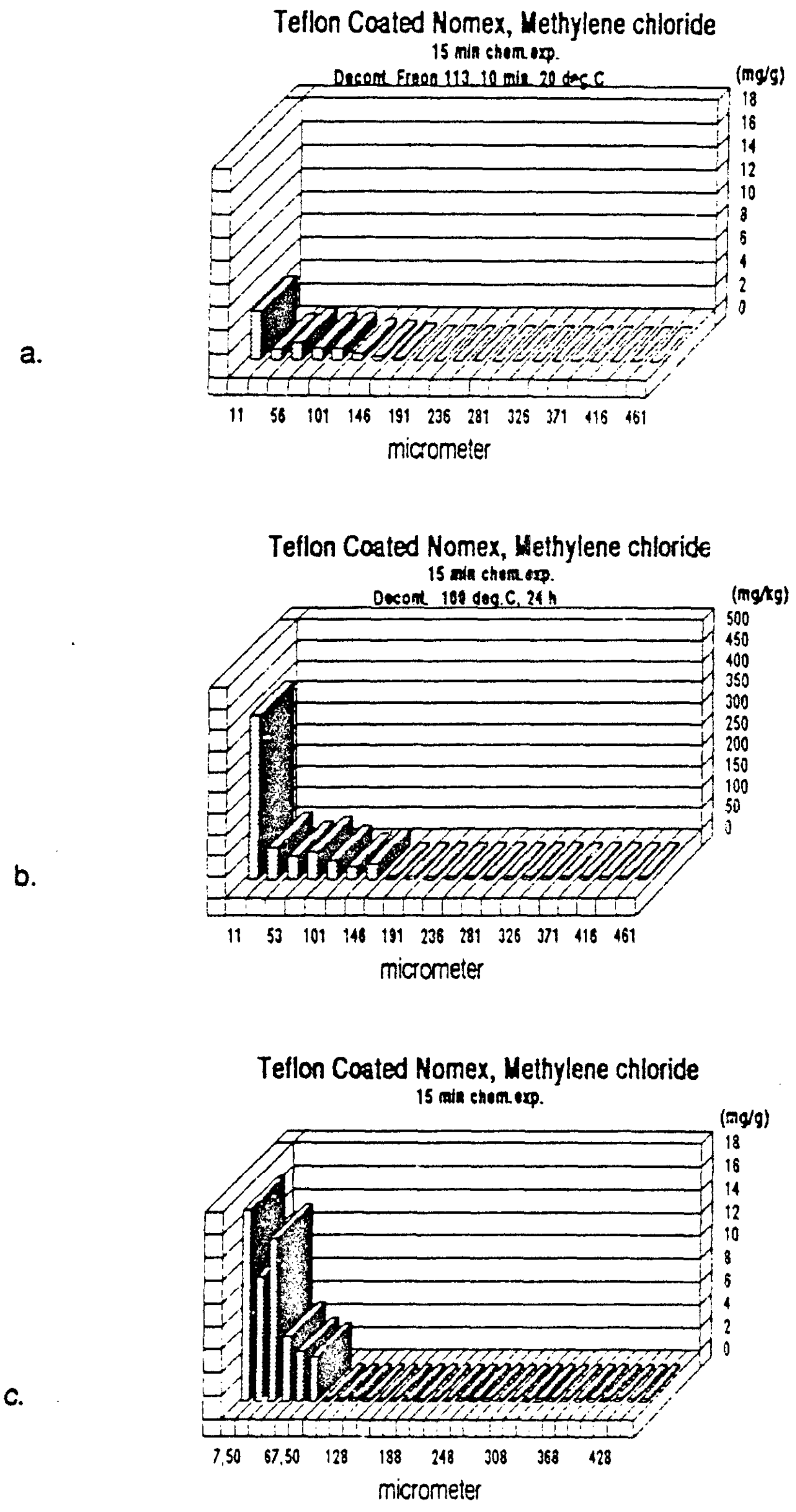
A-13 The concentration (mg/L) vs time (Minutes) for Teflon coated Nomex with carbon-14 labeled vinyl acetate (0.4 MBq/g) as permeant



Overview of cross section. The exposed side to the left. The Saran film is visible outside the exposed side.

Enlargement of the exposed side. Silver grains are visible. Grain density not significant.

A-14 Autoradiograms, Teflon coated Nomex exposed to carbon-14 labeled vinyl acetate for 200 minutes, 100x and 1000x magnification.

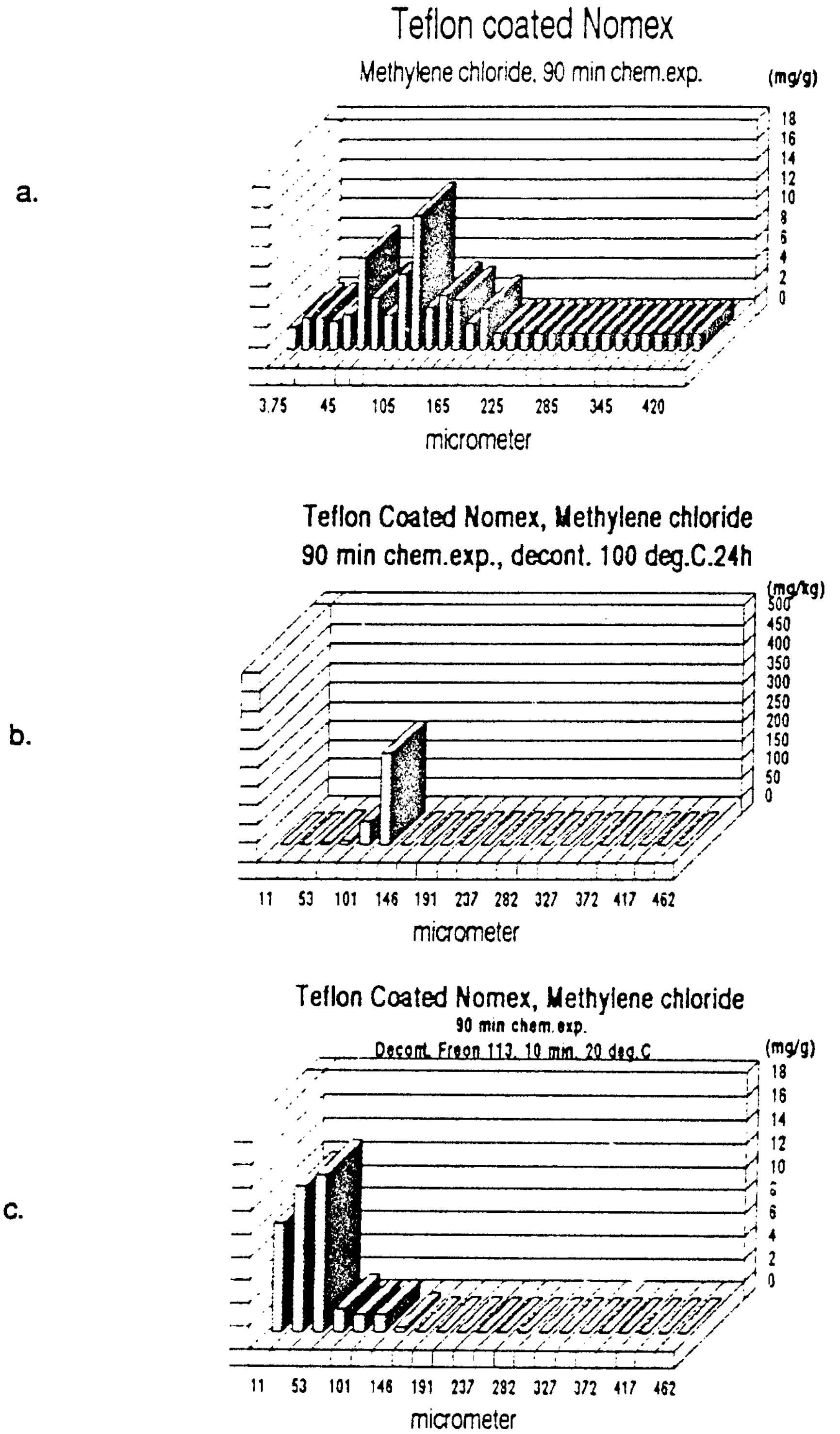


Teflon Coated Nomex, Methylene chloride
15 min chem.exp.
Decont. Freon 113, 10 min, 20 deg.C

Teflon Coated Nomex, Methylene chloride
15 min chem.exp.
Decont. 100 deg.C, 24 h

Teflon Coated Nomex, Methylene chloride
15 min chem.exp.

A-15 Teflon-coated Nomex exposed to carbon-14 labeled methylene chloride (8.4 MBq/g). Diskotomy results after nomal exposure (15 minutes) and two decontamination procedures, concentrations vs penetration depth (µm).



a. Teflon coated Nomex

Methylene chloride. 90 min chem.exp.

b. Teflon Coated Nomex, Methylene chloride

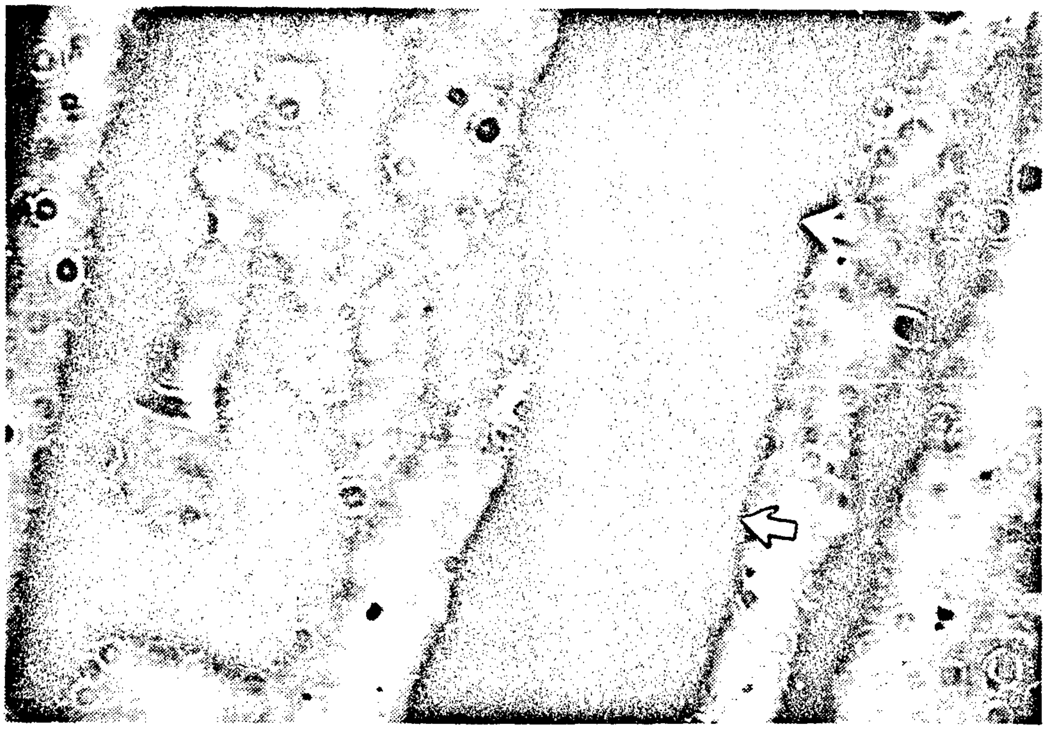
90 min chem.exp., decont. 100 deg.C.24h

c. Teflon Coated Nomex, Methylene chloride

90 min chem.exp.

Decont. Freon 113. 10 min. 20 deg.C

A-16 Teflon-coated Nomex exposed to carbon-14 labeled methylene chloride (8.4 MBq/g). Diskotomy results after nomal exposure (90 minutes) and two decontamination procedures, concentrations vs penetration depth (μm).



A-17 Autoradiogram, Teflon-coated Nomex exposed to carbon-14 labeled methylene chloride for 75 minutes. Arrows indicate the Teflon layer at the chemically exposed side. Few autoradiographic silver grains (black specks) are visible. Transmitted bright field (1600x).

A-18 Autoradiogram, Teflon-coated Nomex seam exposed to carbon-14 labeled methylene chloride for 75 minutes. The double Teflon layer (2 dark lines) about 380 µm from the chemically exposed side are seen. Some autoradiographic silver grains (black specks) are visible. Transmitted bright field (1600x).

A-19 Autoradiogram, Teflon-coated Nomex seam exposed to carbon-14 labeled methylene chloride for 75 minutes. The black specks are the autoradiographic silver grains above the fibrous area 1000µm from the chemically exposed side. Transmitted bright field (1600x).