THE DEVELOPMENT OF A TEST SYSTEM FOR THE EVALUATION OF REVERSE OSMOSIS WATER PURIFICATION MEMBRANES

Final Report Submitted in June 1984

by

Capt. Stephen J. Walker, Jr.
Robert E. Martin
Vincent P. Olivieri

Supported By

FORT BELVOIR RESEARCH & DEVELOPMENT COMMAND

Contract No. DAAK70-82-K0267

The Johns Hopkins University
School of Hygiene & Public Health
Division of Environmental Health Engineering
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INTRODUCTION

As a result of ten years of extensive research and development, the US Army has developed a trailer-mounted reverse osmosis water purification unit (ROPU) which effectively treats brackish water, sea water, and chemically contaminated freshwater. The treatment processes consist of high rate filtration followed by the reverse osmosis system. Under the present concept there will be two units: one will produce 600 gallons per hour and the other 3,000 gallons per hour of potable water.

The smaller unit was designed to operate for 20 hours a day at a production rate equivalent to 600 gallons per hour on freshwater and 400 gallons per hour on sea water. A climatic requirement to operate at temperatures ranging between 1.6°C and 40°C (35°F and 105°F) at relative humidities as high as 90 percent was established to provide a world wide operational capability. The water quality standards which the product water had to meet were established by the US Army Surgeon General.

The use of simulants for chemical warfare agents and the search for better simulants have greatly escalated because of the ban on open-air testing of agents. No compound can exactly match all the properties of an agent and yet be non-toxic because of the interrelationship between toxicity and chemical structure. The structural features that determine toxicity may also uniquely determine the chemical and physical properties of the compound. The properties to be matched in any application are those that determine the specific parameter under investigation (dissemination, decontamination, detection, removal from water, etc.).

Cont'd Pg. 2

The specific mechanisms of the rejection of chemical compounds by reverse osmosis have not been firmly established. Selection of a simulant for this process must therefore be based on empirical investigations. The removal rates of chemical compounds is partly a function of the configuration and composition of the specific membrane employed. To evaluate all membranes for all possible chemical contaminants of water would be an excessively expensive and laborious task. A test system of indicator compounds would prove cost-effective as a preliminary evaluation before extensive testing is undertaken. A lower initial testing cost should also expand the competition of suppliers, possibly producing an overall reduction in unit cost and a more effective membrane.

LITERATURE REVIEW

REVERSE OSMOSIS

Reverse osmosis (RO) is a membrane process in which the input water is pressurized to a value above the osmotic pressure. Pure water passes through the membrane leaving most of the soluble salts behind. At the same time, a large part of particulate matter, including microorganisms and suspended colloids, is removed.

The mechanisms by which RO membranes allow the transport of certain solutes are still a matter of conjecture. Various theories have been proposed, but as yet, no one theory has enjoyed universal acceptance. Three of the more common approaches to membrane transport are shown in Figure 1 (Blais 1977) representing the solution-diffusion (Panel A), the sieve transport (Panel B) and the preferential sorption (Panel C) models.

The solution diffusion model (Lonsdale et al., 1965) envisions a transport corridor in the interstices between the molecules composing the "thin film" rejection area of the membrane. A size estimate of these species places it in the range of 6-20 Å for membranes with high salt rejections, which is of the same order of magnitude as intermolecular distances in swollen polymers (Blais 1977). In this mode, actual passage of solute and solvent first requires a dissolving into the membrane followed by diffusion through the rejection layer. A modified form of this theory includes imperfections in the casting process to allow for some pore transport (Pusch 1977; Sherwood et al., 1967).

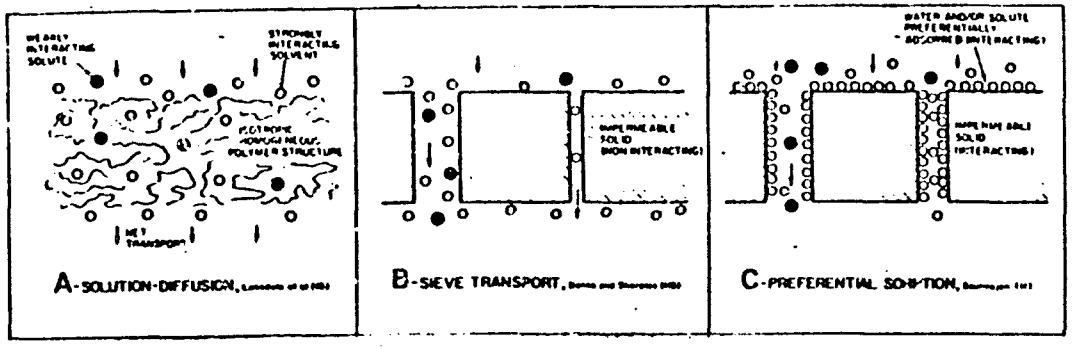


Figure 1. Schematic of three models for the transport of materials across reverse osmosis membranes (Blais, 1977).

Passage of water through the membrane would be governed by diffusive transport according to the following equation, which relates to permeate quantity:

$$F = K_1(Pa - Po) \qquad (1)$$

where:

F = Product (permeate) water flux in gal/(sq ft of membrane area) (day)

K_1 = Constant in gal/(sq ft) (day) (psi)

Pa = Applied pressure in psi

Po = Osmotic pressure in psi

According to equation (1), no product water is produced when the applied pressure is less than the osmotic pressure. However, above the osmotic pressure, the more the pressure, the more product water. Seawater, for example, has an osmotic pressure of approximately 350 psi and would require pressure greater than 350 psi to yield permeate.

Permeate quality would be governed by equation (2):

$$S = K_2 (Cr - Cp) \qquad (2)$$

where:

S = Salt flux in grams/sq ft of membrane area/day

K_2 = Constant in gal/(sq ft) (day)

Cr = Concentration of salt in raw water in grams/gal

Cp = Concentration of salt in product (permeate) water in grams/gal

The constants K_1 and K_2 depend on a variety of factors including temperature, viscosity, electrical resistance, diffusion and partition

coefficients as well as membrane potential. As yet, the specific interrelationships and mechanisms are not clearly understood. (Spiegler and Lavial, 1980; Lindsten, 1972)

The sieve transport model (Banks and Sharples, 1964) detailed a non-interactive method of membrane rejection based on steric exclusion. In the sieve approach, it is the membrane matrix with its associated pore structure that governs the rejection of solute and solvent. As shown in Figure 1 (Panel B), the distribution of pore sizes allows for varying rejection between solute and solvent. Compounds such as phenol, however, which would be rejected at higher rates than sodium and chloride ions based on their size, tend to penetrate membranes at much higher rates. This type of information supports the premise that transport processes also depend on membrane chemistry and its interaction with the solute. The steric parameters of a molecule are important for larger species, for whatever the model, there must be a physical space for movement.

The preferential sorption model (Sourirajan, 1970) evaluates three molecular parameters as determining factors of solute rejection by RO membranes: molecular size and the molecule's polar and nonpolar characteristics. The steric factor determines passage based on the bulk of a molecule in relation to the size of the transport corridor. The polar and nonpolar parameters attempt to quantify the chemical interaction between the solute and the membrane. With membranes thought to have specific polar and nonpolar regions (Chian et al., 1975) these two parameters determine both aqueous type reactions as well as hydrophobic interactions. This model theorizes a sorption at the membrane-solution

interface that would show marked differences in a concentration profile across the membrane solution junction.

There are obviously common elements among these theories. For certain membrane configurations all may apply but one may be most appropriate. The diffusion coefficient used in the Lonsdale model is determined by the interaction between solute and membrane, interaction that the Scurirajan model attempts to quantify with certain solute characteristics. The models account for unexplained rejections by including factors for membrane imperfections.

The configuration of the membrane will have a direct bearing on the relationship between the rate of rejection and the amount of potable water produced. The U.S. Army has adopted membranes in the spiral wound configuration as shown in Figure 2.

The pressurized water passing along the length of a RO element is continuously "dewatered." Therefore, the feed becomes more concentrated and the quality of the product continually deteriorates through the system as more salt migrates through the membrane and less water passes through to dilute it. At the end of the system, the concentrated feed is discharged as the waste stream. A graphic representation of this cross flow process is shown in Figure 3. Alleviation of the concentration problem is achievable by operation at a low "water recovery," i.e., maintaining a high feed rate so that the product output is a small fraction of the feed. However, when a highly concentrated waste stream is desired, such as when processing wastewater, low "water recovery" is undesirable. Also, low "water recovery" results in a comparatively high energy requirement. A

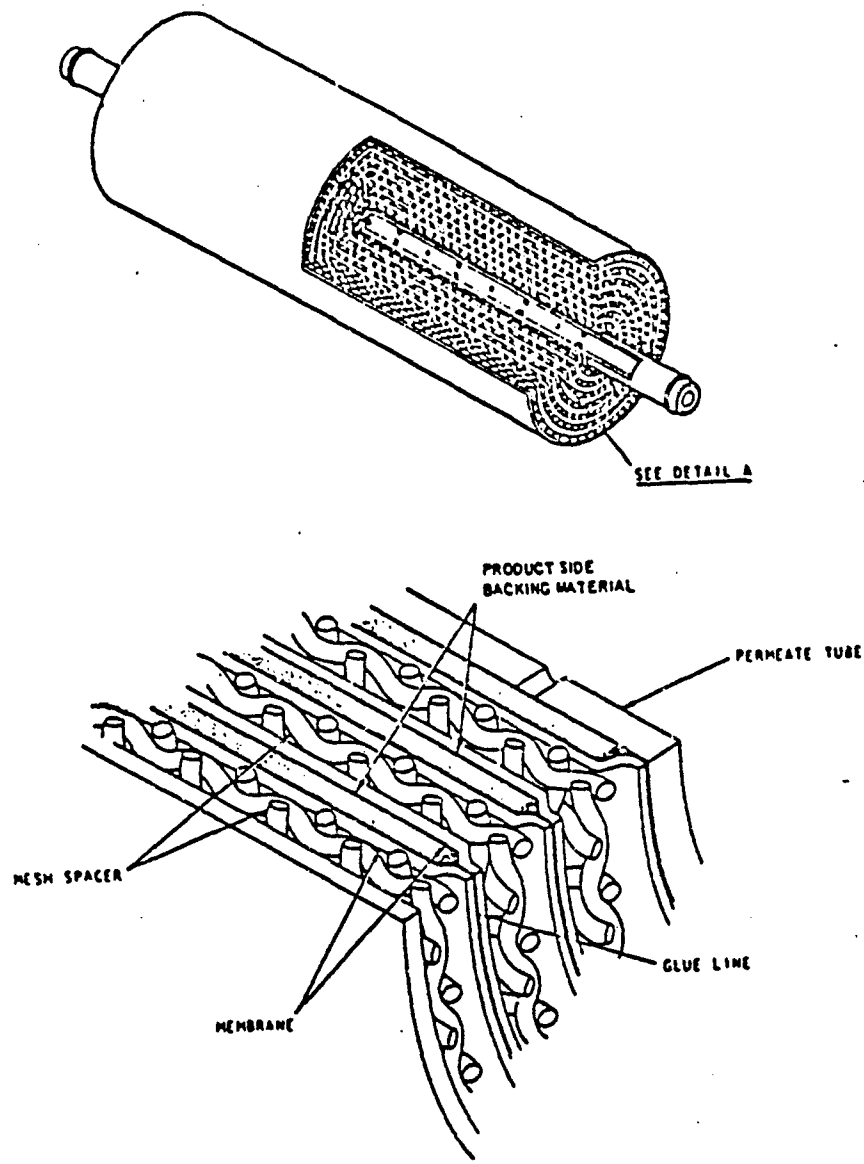


Figure 2. Schematic of construction of spiral wound membrane module (Sliger and Quinn 1975).

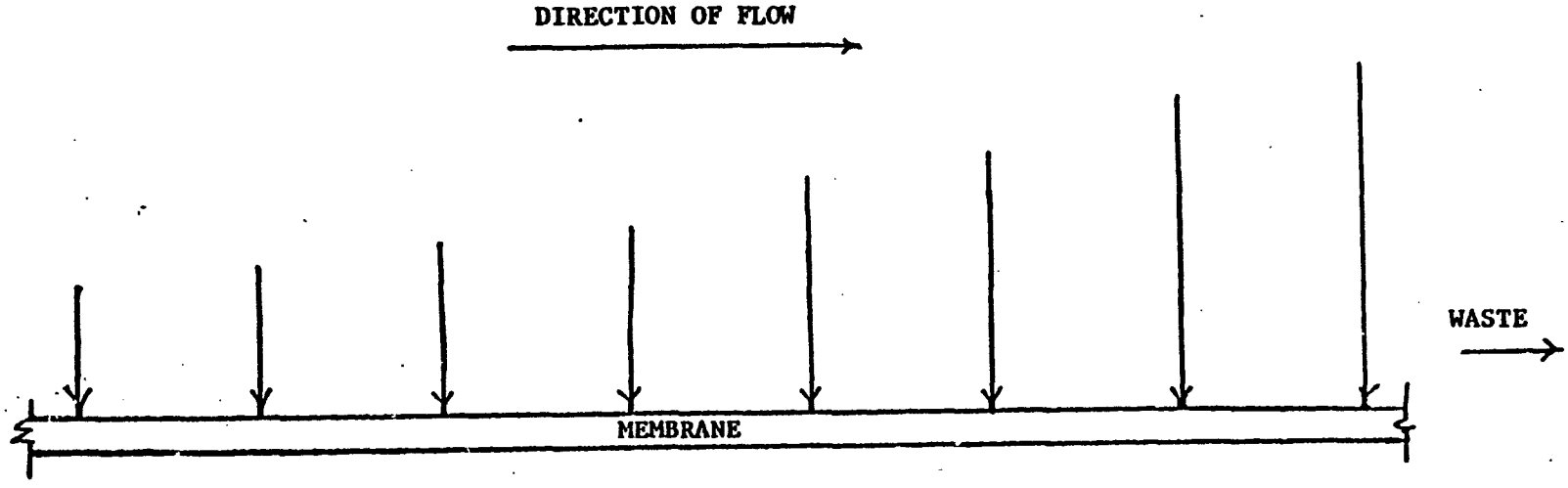


Figure 3. Solute concentration profile along the length of a spiral wound membrane module (Nusbaum 1981). Height of arrow indicates relative solute concentration.

drop in flux as a function of time is a commonly encountered occurrence. It is believed that this phenomenon is a direct result of increased flow resistance due to any or all of the following reasons: (a) compaction of the porous membrane substructure; (b) release of tiny pinpoints of air or dissolved gas on and in the membrane; (c) electrical charge buildup due to streaming potential; (d) deposition of raw water turbidity (including microorganisms, clay, organic turbidity, suspended iron and manganese, and colloidal particles); (e) deposition of scale due to the precipitation of sparingly soluble dissolved salts; (f) growth of biological films; and (g) accumulation of ions adjacent to the membrane surface, which is responsible for "concentration polarization." (Nusbaum 1981, Lindsten, 1972)

SIMULANTS

The chemical agent data center at the Edgewood area of Aberdeen Proving Ground was used to perform a search of the literature based on chemical properties that would be related to membrane rejection (Coon et al. 1982). The chemical and physical properties used and their units were:

1. Molecular weight
2. Vapor pressure, mm Hg at 25°C
3. Molecular diffusion coefficient, cm^2/sec at 25°C
4. Solubility in water, gm/l at 25°C
5. Hildebrand solubility parameter, $(cal/cm^3)^{1/2}$

The additional considerations and general guidelines outlined in the contract proposal listed below were also considered during the selection of simulants.

1. Stability in aqueous solutions
2. Similar molecular structure
3. Simple analytical methods
4. Reasonable detectable limits
5. Non-toxic characteristics
6. Past use as indicator compounds

The criteria used for the selection of these compounds were that values of the specific chemical properties fall within a plus or minus 10 percent range around the value for a volatile nerve agent (GB) and a non-volatile nerve agent (VX). The range was expanded to plus or minus 20 percent when limited output was generated for various combinations of these properties. The 20 percent bracket is shown in Table 1 for both GB and VX. The data base checked the Technical Library at the Chemical Research and Development Command (CRDC) and various Department of Defense literature surveys to identify the approximately 800 references contained in its files. Typical of the material contained in this data base are two Department of Defense Publications. Arthur D. Little, Inc. (1982) reported chemical properties, toxicological data, and analytical procedures for various simulants. Bagley et al. (1977) at Dugway Proving Ground, reviewed simulants and compared chemical properties of simulants to agents.

TABLE 1. A 20 PERCENT RANGE OF SELECTED PROPERTIES OF A VOLATILE NERVE AGENT (GB) AND A NON-VOLATILE NERVE AGENT (VX)

Property	AGENT	
	GB	VX
Molecular Weight	112.0 - 168.1	213.9 - 320.9
Vapor Pressure mm Hg at 25°C	2.32 - 3.48	0.00050 - 0.00074
Molecular Diffusion Coefficient cm^2/sec at 25°C	0.049 - 0.073	0.028 - 0.041
Solubility in Water gm/l at 25°C	Miscible	0.05
Hildebrand Solubility Parameter $(Cal/cm^3)^{1/2}$	7.24 - 10.85	6.40 - 9.60

The candidate simulants developed from the literature are listed in Table 2. While a literature search was a useful tool, a careful evaluation of the results must be performed. Highlighting the requirement of this follow up was that one of the compounds selected by the search, diethyl pthalate was insoluble in water even though solubility was one of the parameters to be matched on. Diisopropyl methyl phosphonate (DIMP) was chosen for initial study.

TABLE 2. CANDIDATE NERVE AGENT SIMULANTS

1. Bis (2-ethyl hexyl) phosphonate
2. Diethyl glycol dimethyl ether
3. Diethyl phosphonate
4. Diethyl phthalate
5. Diethyl sebacate
6. Diethyl sulfite
7. Diisopropyl methyl phosphonate (DIMP)
8. Dimethoxy methyl phosphonate (DMMP)
9. Ethyl dimethyl phosphite

METHODS

PREPARATION AND ANALYTICAL METHODS

Sample Preparation, Handling and Storage

Glassware Preparation—

All glassware was washed with detergent, rinsed with distilled water and maintained at 400°C for one hour to remove organics.

Preparation of Simulant Standards—

DIMP standards in water and acetone were prepared from 1,000 mg/l stock solutions. An aliquot of 0.200 ml DIMP was added to 200 ml of solvent in a volumetric flask. DIMP in water standards of 10.0, 1.00 and 0.100 mg/l were made up in 2,000 ml volumetric flasks. DIMP in acetone standards of 20.0, 10.0, 5.00, 1.00 and 0.100 mg/l were made up in 100 ml volumetric flasks. A 0.050 mg/l standard and a 0.025 mg/l standard were made by diluting the 0.100 mg/l standard.

Aqueous Samples—

Aqueous samples were collected and stored in 150 ml screw cap bottles. Caps were lined with aluminum foil which had been heated at 400°C for at least one hour to remove organics. Samples were stored at 4°C.

DIMP in Acetone Samples—

DIMP in acetone samples included standard solutions and extractions of aqueous samples. Standard solutions were stored in 10 ml serum bottles with teflon faced septa. Sample extractions resulted in a 2 ml volume of DIMP in acetone. These were transferred to 1.8 ml screw cap vials with open top caps and teflon faced septa. All septa were scrubbed with acetone before placement on vials.

Sample Extraction Procedure

A schematic illustrating the extraction procedure appears in Figure 4. Aqueous DIMP samples were poured through silica gel columns (Baker 10 3PE disposable reversed-phase extraction columns, octylsilane bonded silica gel) under low vacuum to collect and concentrate the DIMP on the sorbent bed. The retained DIMP was then eluted with acetone into a volumetric flask. A detailed description is given below. Multiple extractions were conducted simultaneously on a vacuum manifold.

Sample Extraction Steps

1. Column Preparation

   1.1 Place column on manifold (one column per extraction).

   1.2 Fill column with HPLC grade methanol.

   1.3 Turn on vacuum and draw methanol through column.

   1.4 Turn off vacuum immediately to avoid drying the column.

2. Extraction

   2.1 Using a volumetric pipet, apply desired volume of sample to the column and draw through with vacuum.

3. Elution

   3.1 Remove column from manifold and place on a volumetric flask of the appropriate size.

   3.2 Using a volumetric pipet, add chromatography grade acetone to the column and force it through with compressed air.

   3.3 Remove the column from the flask and adjust the volume to the mark with acetone.

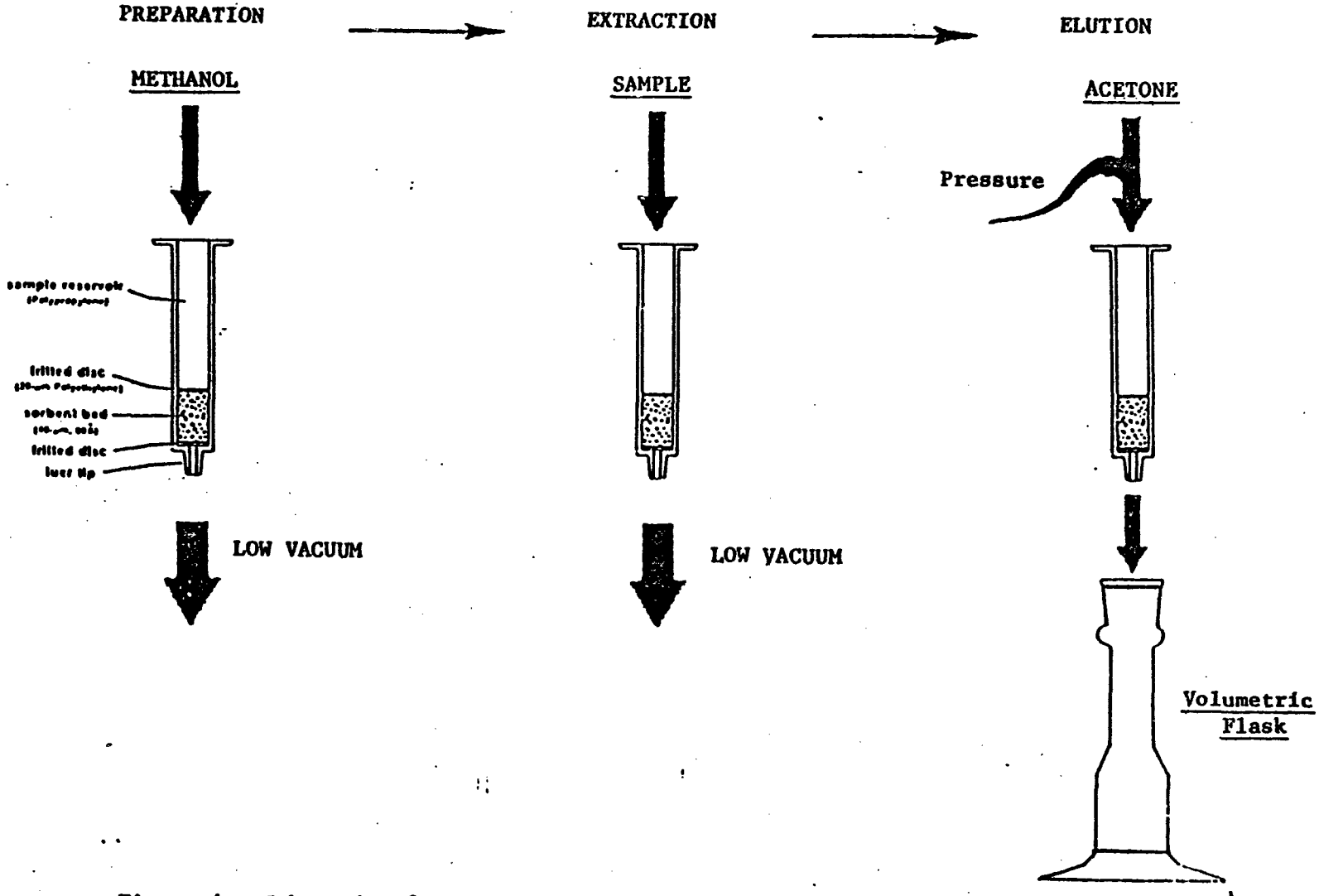


Figure 4. Schematic of extraction procedure with Baker 10 SPE disposable reversed - phase extraction columns. Sorbent bed: octylsilane bonded silica gel.

4. Storage

4.1 Transfer extracted sample to an appropriately sized vial and seal with septum cap.

Gas Chromatographic Analysis

Equipment--

Gas chromatographic analysis was performed with a Hewlett-Packard 5830A gas chromatograph equipped with a carbowax column and a nitrogen-phosphorous detector (N-P detector). The specific chromatographic conditions are listed below.

Chromatographic Conditions

1. Detector: Hewlett-Packard nitrogen-phosphorous flame ionization detector (HP 18847A/8A) with long wide bore jet.
2. Column: 10% Carbowax 20M on 80/100 chromosorb W-HP. Type: glass. Length: 2 meters. Outside diameter: 1/4 inch. Inside diameter: 2 mm.
3. Carrier gas: Helium, 99.995% minimum purity with inline molecular sieve drying.
4. Support gases: Hydrogen, 99.995% minimum purity and 'dry' quality air, both with inline molecular sieve traps.
5. Injection port: On column injection. Septum: Thermogreen LB-1 (Supelco 2-0659).

Operating conditions—

All results were obtained under the following operating conditions:

Operating Conditions

1. Gas flows, measured with soap bubble flow meter: helium 30 ml/min, hydrogen 3 ml/min, air 60 ml/min;

2. Oven temperature: 165°C, isothermal;

3. Injection port temperature: 220°C;

4. Detector temperature: 300°C.

5. Offset: set at approximately 100 mm at the start of each series of analyses.

Injections were performed manually by the solvent flush technique using acetone as the solvent. Injection volumes were approximately 2 microliters. In order to minimize the effects of detector sensitivity variations, samples were grouped according to approximate DIMP concentration and the groups were analyzed in order of increasing concentration. A DIMP in acetone standard of approximately the same concentration was injected with each set of samples in a fixed sequence. The sequence was repeated for three to five replicate injections. Any variations in sensitivity thus did not exert an inordinate influence on any one sample.

For each injection, the peak area and injection volume were recorded. The response was then calculated as peak area per microliter injected and averaged for replicate injections. Calculation of the corresponding DIMP concentration was based on a least squares line of best fit for calibration data. The calibration curve was adjusted for day to day variations in sensitivity on the basis of responses to standards analyzed at the same time as the samples. Reported concentrations were adjusted for the density and purity of DIMP.

EXPERIMENTAL PROTOCOL

Stability of pH

The stability of the pH of tap water from the Edgewood area of Aberdeen Proving Ground, Building 1956, was evaluated over a thirty hour period under various conditions of pH and salt concentration. A five gallon sample of filtered tap water was collected in a carboy which had been washed and rinsed three times with triple distilled water. The sample was dechlorinated by aeration for 48 hours followed by the addition of sodium thiosulfate sufficient to remove the remaining residual. The absence of chlorine residual was confirmed by regular determinations with N,N-diethyl-p-phenylene-diamine (DPD) according to Standard Methods for the Examination of Water and Wastewater (1981).

Aliquots of the dechlorinated tap water and salt solutions containing 35,000 and 5,000 mg/l NaCl were dispensed in brown glass bottles. For each trial, the pH was adjusted to 5, 7 or 9 with 0.1 N solutions of sulfuric acid or sodium hydroxide. The bottles were stored at room temperature.

The pH was determined electrometrically with a Beckman Zeromatic Model II pH meter according to Standard Methods for the Examination of Water and Wastewater (1980). Samples were agitated with a magnetic stirrer during the measurement.

Evaluation of Extraction Procedure

Efficiency--

The efficiency of the extraction procedure was evaluated for 10.0, 1.00 and 0.100 mg/l DIMP in dechlorinated tap water and brackish water (5,000 mg/l NaCl in dechlorinated tap water) solutions at pH values of 5, 7, and

9. These solutions were prepared as described above. Dechlorination of the tap water and pH adjustment were described in the previous section. The efficiency was determined by comparing the response (area per microliter) for an extracted aqueous sample with that for a DIMP in acetone standard of the same nominal concentration.

Variability—

The variability of the extraction procedure was assessed by performing six replicate extractions each of a feed water sample and a product water sample from the Johns Hopkins University reverse osmosis test stand. Five replicate injections of each extraction were made.

Stability of DIMP in Acetone

To determine the stability of DIMP in acetone, solutions containing 10.0, 1.00 and 0.100 mg/l DIMP were prepared as described above. Aliquots of each were stored under three different conditions: 1) at 25°C, with normal diurnal variations in light; 2) at 25°C, in the dark; and 3) at 4°C, in the dark. On each day that the samples were analyzed, the gas chromatograph was calibrated with fresh standards. Analyses were performed on days 0, 1, 6 and 20.

Stability of DIMP in Aqueous Solution

The stability of DIMP in aqueous solution was determined for 10.0, 1.00 and 0.100 mg/l DIMP in dechlorinated tap water and brackish water at pH values of 5, 7 and 9. Extractions were performed on days 0 and 14. Having established the stability of DIMP in acetone, the day 0 extractions were stored and analyzed at the same time as the day 14 extractions. The percent change in response between the two provided an indication of the stability.

Rejection of DIMP by Reverse Osmosis

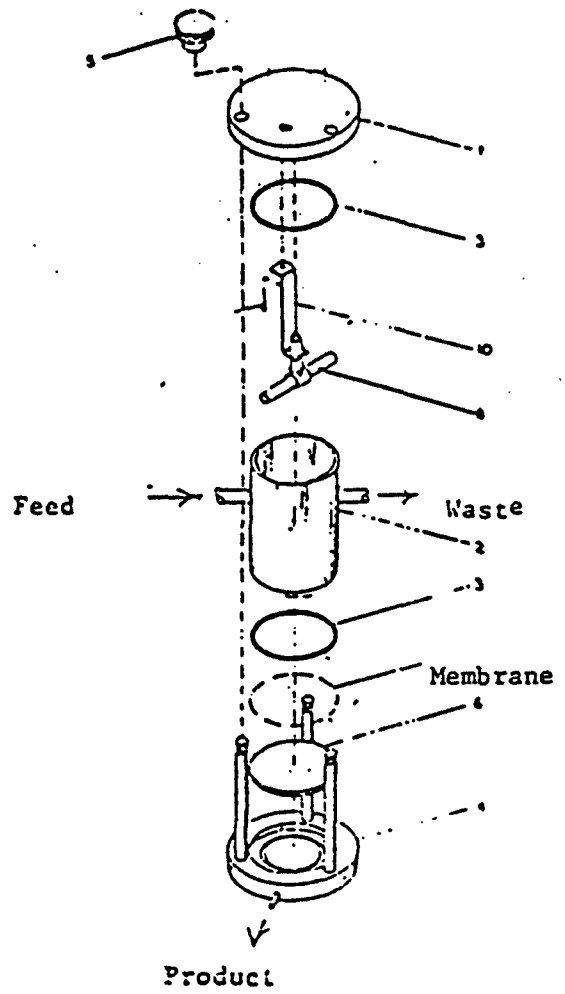
Bench Scale Test Cell--

The RO test cells were assembled with 47 mm diameter pieces of UOP TFC-801 membrane material. The flow system for these smaller units was a once through system. The feed solutions were prepared, as needed, in 100 liter containers with tap water filtered through a 10 micron cotton filter for removal of rust and scale. The tap water was dechlorinated with the addition of 15 mg/l of sodium thiosulfate. Dechlorination was confirmed by the determination of chlorine concentration by the DPD technique as described above. Required levels of NaCl were added to the 100 liter batch and mixed for one half hour by a chemical mixer. A schematic of the bench scale test cell is shown in Figure 5.

The test cell system incorporated high pressure pumps capable of operating the system at pressures up to 800 psi. Complete mixing was obtained by rotating magnetic stirrers at 400 rpm. On exiting the cells, the waste stream was returned to atmospheric pressure through a pressure relief valve.

Four Inch Module Test Stand--

The four inch module reverse osmosis test stand was supplied by the Ft. Belvoir Research and Development Command. The evaluation of rejection was performed using a recirculation mode of operation shown in Figure 6. The reservoir was a 500 gallon water storage tank. The energy dissipation on return to atmosphere caused an increase of temperature of the feed water over the course of a run, necessitating the recording and inclusion of temperature as an additional variable. The tank was cleaned when received



Index No.	Description
1	Top Cap
2	Sleeve
3	O-ring (large; sleeve)
4	Bottom Cap
5	Locking Knobs
6	Porous Membrane Support Disk
7	Stirring Bar
8	Tube Fitting Assembly
9	Magnetic Stirring Assembly

Figure 5. Schematic of bench scale test cell.

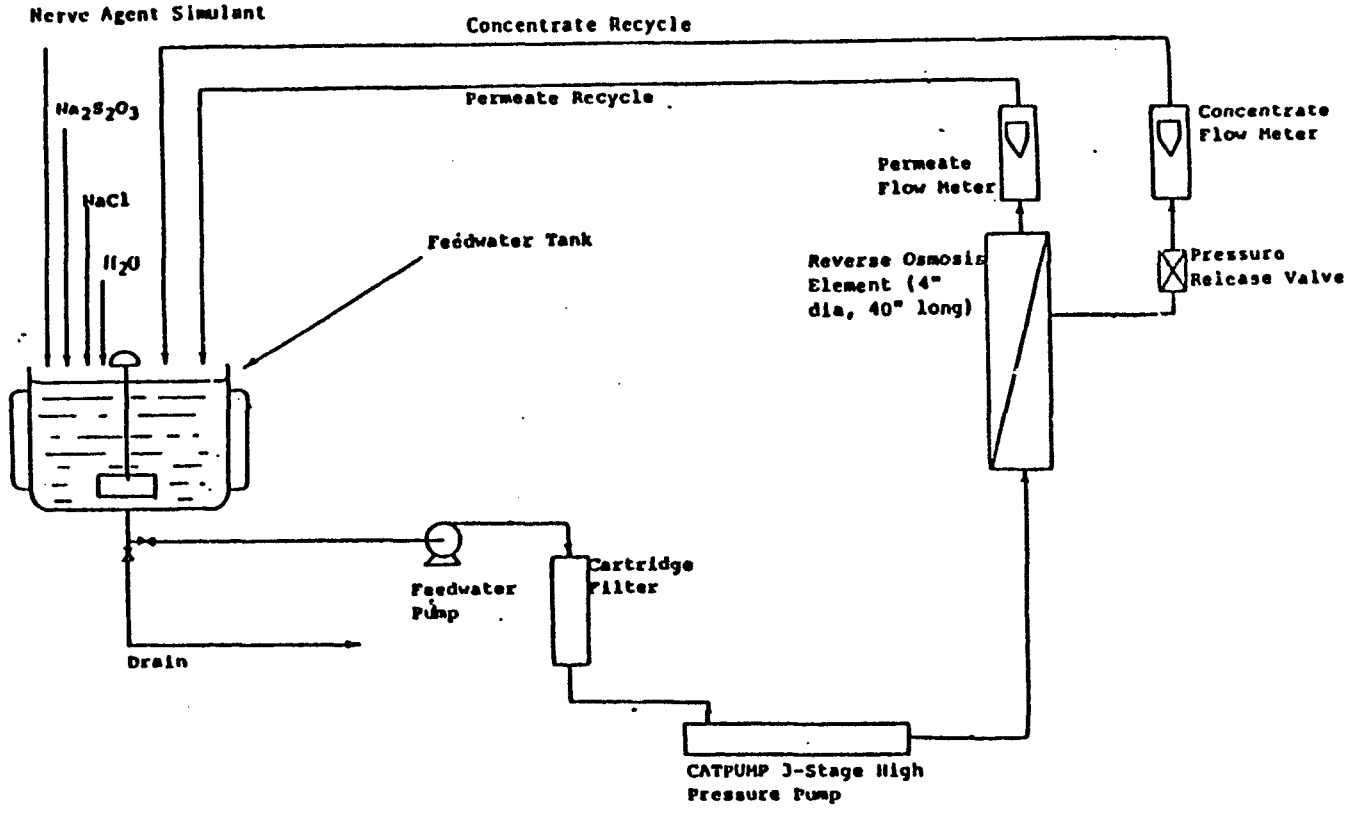


Figure 6. Schematic of the reverse osmosis test stand supplied by Ft. Belvoir Research and Development Command

from Fort Belvoir Research and Development Center and after each sample run. The water used for each run was tap water filtered through a 10 micron cotton filter wound cartridge (Filterite # C10A10A). The tap water was dechlorinated and the residual was measured as described in the previous section. Upon addition of the solute and required level of sodium chloride to the feed water, two Lightning heavy-duty stirrers operating at 1750 rpm were engaged. The mixing action coupled with the flow from the high pressure discharge line provided the blending of the return of product and waste streams. The return product line was fixed eighteen inches above the surface of the tank to avoid solute contamination of the product sample. At the start of a test run, the feed pump operated for approximately 1 minute before the high pressure pump was engaged. The system temperatures could not be controlled but were measured to ensure that the membrane was not exposed to temperatures greater than 34°C. Three 4 inch UOP spiral wound elements were provided, one with previous use and two new.

The module with previous operational use was employed for tests to bring the system on line and for personnel training. Of the two remaining modules, one was flawed in some manner as shown by very high product water flow rate (in excess of three gallons per minute). The only remaining module proved satisfactory and was used for all testing.

RESULTS

STABILITY OF pH

Three samples of dechlorinated tap water containing 35,000 mg/l NaCl, 5,000 mg/l NaCl and no salt were tested for pH stability over time at pH values of 5, 7 and 9. Plots of pH versus time are shown in Figures 7, 8, and 9. The samples were kept at room temperature and sample temperature was recorded when pH determinations were made. The temperatures ranged from 23 to 25°C. Five pH measurements were made over 24 hours. Although small fluctuations occurred, no trends were observed over this period.

ANALYSIS OF DIMP

Characteristics of the Nitrogen-Phosphorous (N-P) Detector

The level of sensitivity of the N-P detector can be varied by applying different voltages to the ceramic bead in the collector. The offset can be measured from a trace on the chart and provides a measure of this sensitivity. It is desirable to maintain a constant offset over the course of an analysis in order to avoid distortion of the results due to variations in sensitivity. The manufacturer's literature on this detector indicated that it should be stable over an eight hour period, but that variations from day to day and from one collector to another can be expected. No quantitative description of the relationship between offset variations and sensitivity were provided by the manufacturer however. Prior to analysis of samples in this study, an attempt was made to characterize the variation in offset with time and the effect of changing offset on the detector response. In the course of the study, variations in

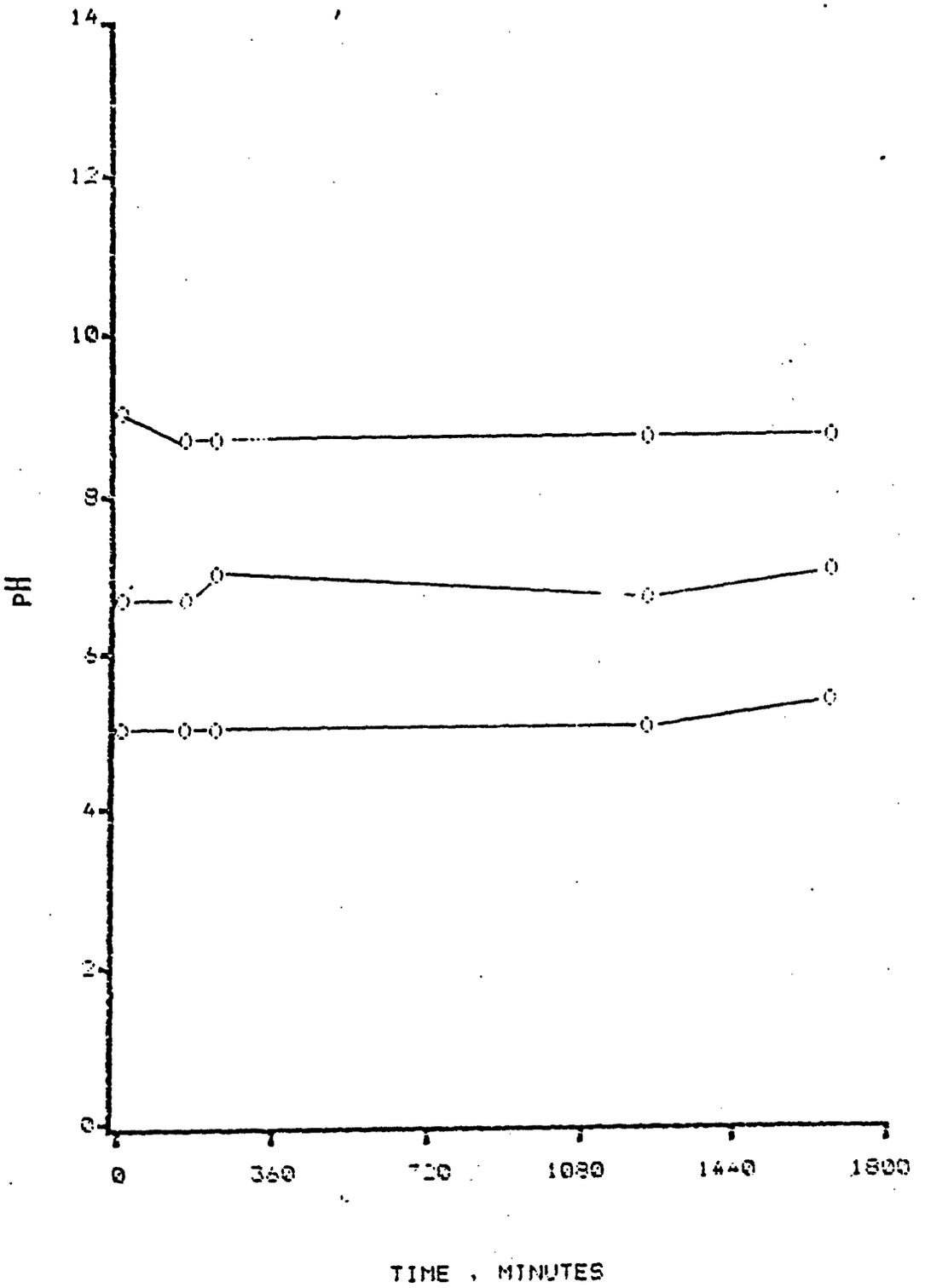


Figure 7. Stability of pH over time for dechlorinated Edgewood Arsenal tap water with 35,000 mg/l NaCl.

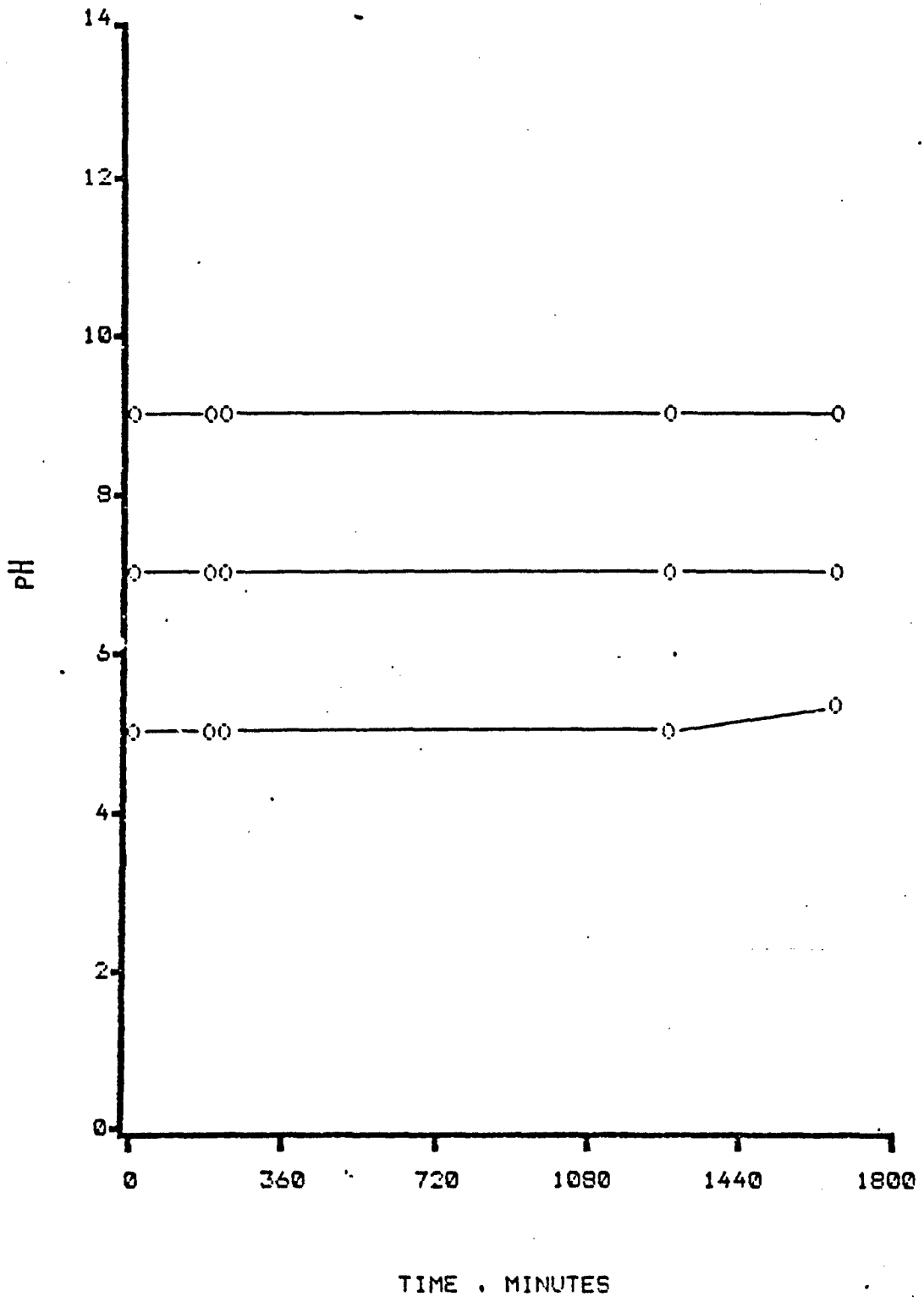


Figure 8. Stability of pH over time for dechlorinated Edgewood Arsenal tap water with 5,000 mg/1 NaCl.

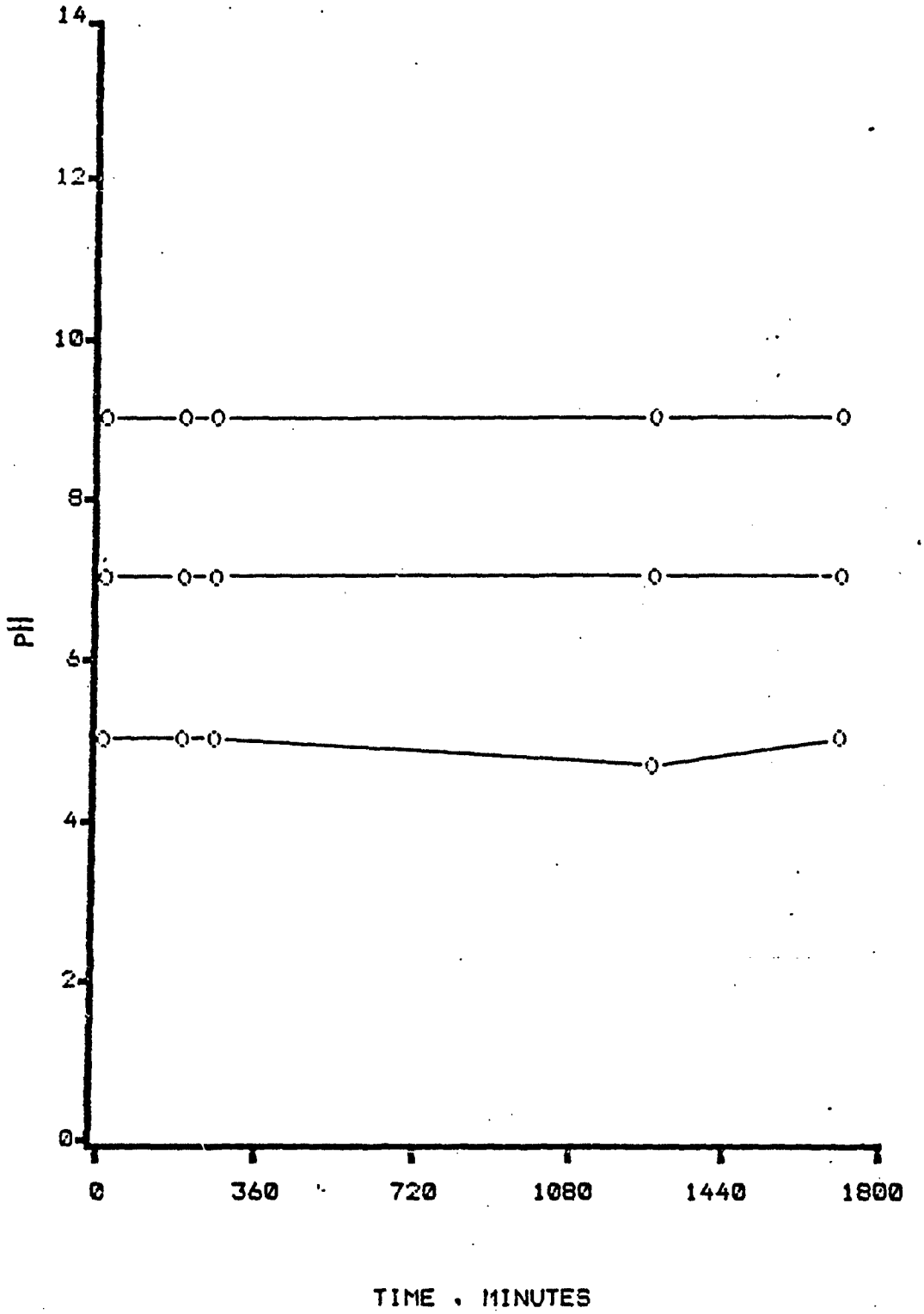


Figure 9. Stability of pH over time for dechlorinated Edgewood Arsenal tap water.

detector response independent of offset were observed and considerable differences in behavior between two collectors were noted.

Offset and Detector Response--

To observe the variation in offset over time, the offset was monitored continuously for a twelve hour period without injecting any samples. Smooth peaks and valleys were seen in the resulting trace. Figure 10 shows the offset at high and low points over the period starting with the first measured value. The maximum value was 90.5 mm at 0.42 hr and the minimum was 66.5 mm at 11.53 hr, a difference of 27%. Overall, the plot showed a downward trend with irregular fluctuations.

In order to assess the significance of offset variations with respect to the response of the detector, three replicate injections of 1.00 mg/l DIMP in acetone were made at offset values ranging from 74.0 mm to 123.0 mm. After each injection, the offset was higher than it had been before the injection. Time was allowed for the offset to restabilize at the original setting before the next injection. At offsets over 100 mm, this was not always possible to accomplish in a reasonable period. A plot of the detector response (area per microliter) versus offset is shown in Figure 11 with the least squares line of best fit. The response varied from about 21,000 to 25,000, that is, by 19% for a 66% increase in offset over the range tested.

Variation of Response Independent of Offset--

The variation in the response is the result of numerous factors other than the offset. These include irregularities in gas flows, uncertainty of of injection volume, fluctuations in temperature at the injection port, in

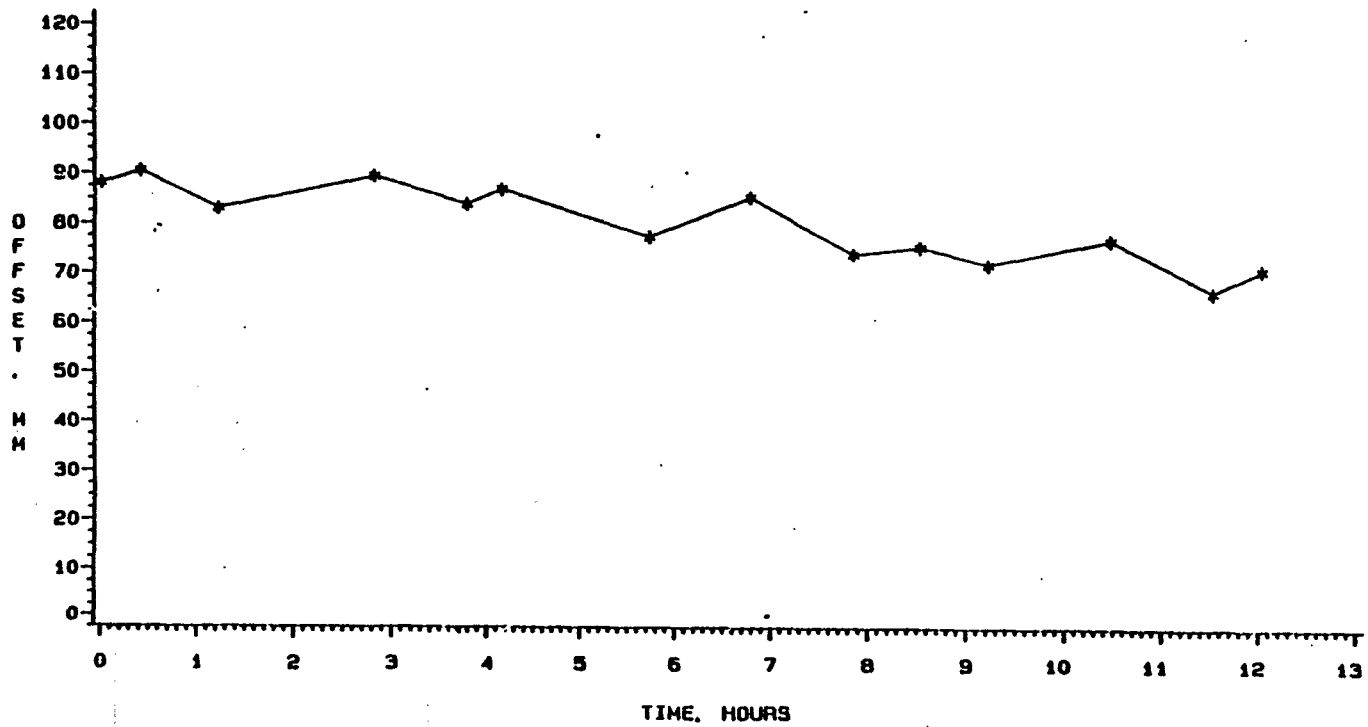


Figure 10. Variation in offset for the nitrogen-phosphorous detector with time (no sample injections). Column: 10% Carbowax 20M on 80/100 chromosorb W-HP, 2 m x 2 mm ID glass. Flow rates: 30 ml/min helium, 3 ml/min hydrogen, 60 ml/min air. Temperatures: column 165°C (isothermal), injection port 220°C, detector 300°C.

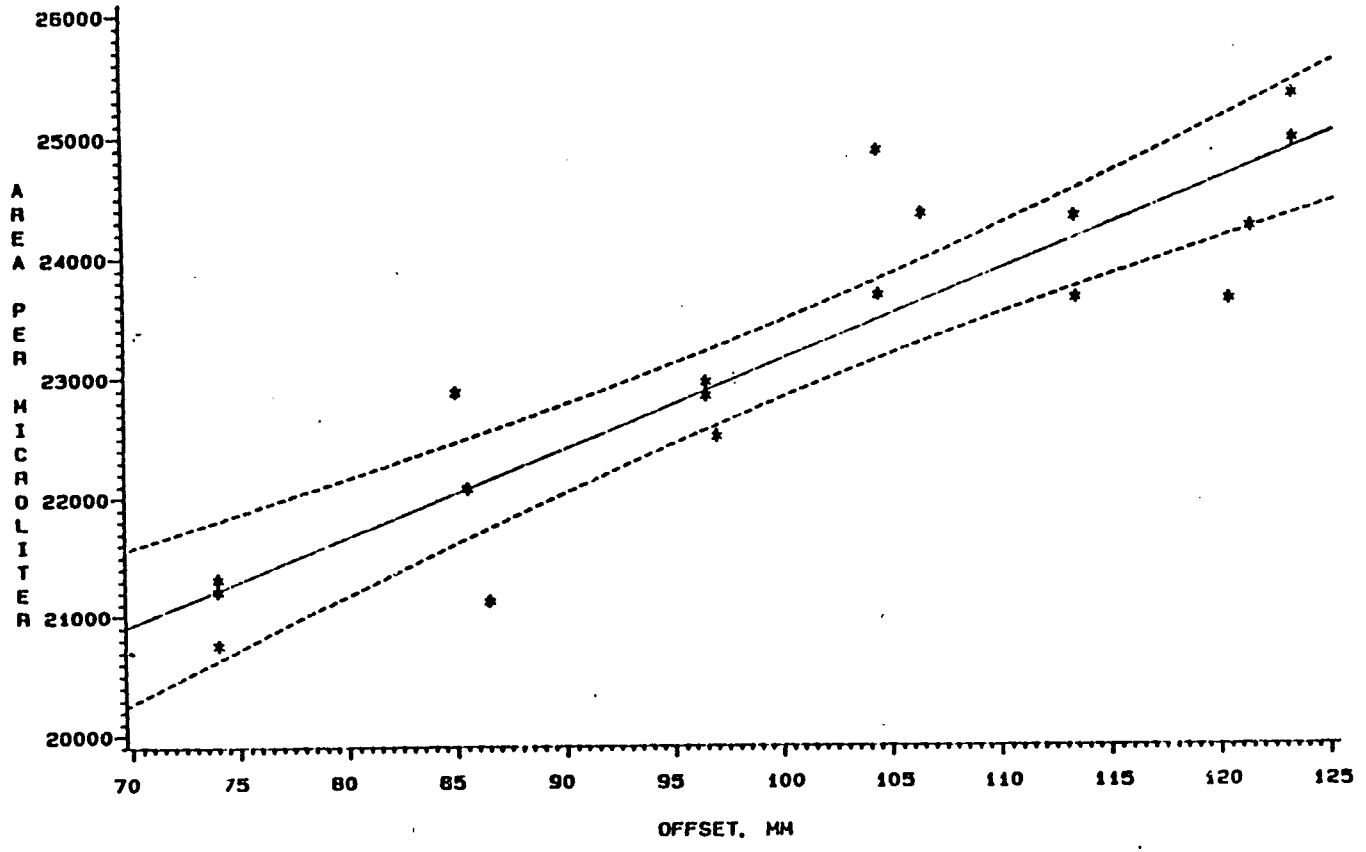


Figure 11. Effect of intentional change in offset on the response of the nitrogen-phosphorous detector to replicate injections of 1.00 mg/l DIMP in acetone. The solid line is the least squares line of best fit with a correlation coefficient r = 0.900. The dashed lines are the 95% confidence interval around the line of best fit. Column: 10% Carbowax 20M on 80/100 chromosorb W-HP, 2 m x 2 mm ID glass. Flow rates: 30 ml/min helium, 3 ml/min hydrogen, 60 ml/min air. Temperatures: column 165°C (isothermal), injection port 220°C, detector 300°C.

the oven and at the detector, condition of the column and age of the collector. In addition, variations due to the extraction procedure can be expected.

Two collectors were used in the course of the study; the first was expended after three months of use. The observations reported above in relation to the offset were obtained with the first collector. The same type of variation may be expected with any collector. No effort was made to characterize the second so extensively, but important differences were seen. The first collector gave higher responses than the second. Typical responses to DIMP in acetone are shown in Table 3. The second appeared to be more stable since there was considerably less change in offset following injections and a more rapid recovery to pre-injection levels.

Table 4 shows the initial offset values and the response (area per microliter) for the analysis of 0.100 mg/l DIMP in acetone performed on different days. Although the offset values were all approximately the same, the average responses on different days showed considerable variation. The minimum and maximum average responses were 1,410 and 1,690 respectively, corresponding to offsets of 101.5 and 100.0 mm. The overall mean response was 1,550 with standard deviation of 111.

The variation between injections on a single day for a series of DIMP concentrations was observed by performing ten to twenty replicate injections for each concentration. Table 5 shows the response (area per microliter) for DIMP concentrations from 0.025 to 20.0 mg/l. The coefficient of variation was highest for the 0.025 mg/l concentration at about 7%. For concentrations of 0.050, 0.100 and 20.0 mg/l, the

TABLE 3. RESPONSE OF THE N-P DETECTOR WITH DIFFERENT COLLECTORS FOR A RANGE OF DIMP CONCENTRATIONS. COLUMN: 10% CARBOWAX 20 M ON 80/100 CHROMOSORB W-HP, 2 M x 2 MM ID GLASS. FLOW RATES: 30 ML/MIN HELIUM, 3 ML/MIN HYDROGEN, 60 ML/MIN AIR. TEMPERATURES: COLUMN 165°C (ISOTHERMAL), INJECTION PORT 220°C, DETECTOR 300°C

		Response (area/microliter)		
DIMP Concentration (mg/l)		0.100	1.00	10.0
Collector	1	2,200	23,000	220,000
	2	1,500	16,000	163,000

TABLE 4. RESPONSE TO 0.100 MG/L DIMP IN ACETONE FROM DAY TO DAY WITH INITIAL OFFSET APPROXIMATELY 100 MM. COLUMN: 10% CARBOWAX 20 M ON 80/100 CHROMOSORB W-HP, 2 M x 2 MM ID GLASS. FLOW RATES: 30 ML/MIN HELIUM, 3 ML/MIN HYDROGEN, 60 ML/MIN AIR. TEMPERATURES: COLUMN 165°C (ISOTHERMAL), INJECTION PORT 220°C, DETECTOR 300°C

Date	Initial Offset (mm)	Response (area/microliter)	Average Response (area/microliter)
2/2/84	101.5	1,465 1,412 1,345	1,407
2/3/84	99.5		1,476
8:50 to 9:15 am		1,545 1,434 1,449	
11:10 to 12:15		1,418 1,426 1,443 1,391	1,420
2/9/84	102.0	1,634 1,505 1,584 1,538 1,540	1,560
2/23/84	109.0	1,666 1,701 1,672 1,591 1,607	1,647
2/25/84	100.0	1,713 1,649 1,672 1,715	1,687
2/29/84	103.0	1,686 1,725 1,564 1,497	1,618

TABLE 4. continued

Date	Initial Offset (mm)	Response (area/microliter)	Average Response (area/microliter)
3/1/84	101.5	1,634	1,658
		1,734	
		1,667	
		1,549	
		1,696	
		1,669	
3/8/84	102.0	1,407	1,441
		1,416	
		1,430	
		1,483	
		1,524	
		1,481	
		1,495	
		1,377	
		1,388	
		1,407	
Mean		1,550	
Standard Deviation		111	

TABLE 5. RESPONSE OF THE N-P DETECTOR FOR REPLICATE INJECTIONS OF DIMP IN ACETONE. COLUMN: 10% CARBOWAX 20 M ON 80/100 CHROMOSORB W-HP, 2 M x 2 MM ID GLASS. FLOW RATES: 30 ML/MIN HELIUM, 3 ML/MIN HYDROGEN, 60 ML/MIN AIR. TEMPERATURES: COLUMN 165°C (ISOTHERMAL), INJECTION PORT 220°C, DETECTOR 300°C

	Concentration			
Injection	0.025	0.050	0.100	20.0
1	255	638	1473	338842
2	284	657	1397	312105
3	246	633	1419	319282
4	246	641	1407	335282
5	231	689	1416	321179
6	246	624	1430	339800
7	263	624	1483	322513
8	239	638	1524	321000
9	287	640	1481	338316
10	260	637	1495	329100
11	ND	ND	1377	347282
12	ND	ND	1388	341474
13	ND	ND	1407	327700
14	ND	ND	ND	330051
15	ND	ND	ND	338256
16	ND	ND	ND	340718
17	ND	ND	ND	345744
18	ND	ND	ND	327333
19	ND	ND	ND	333053
20	ND	ND	ND	319590
Mean	255	642	1438	331481
Standard Deviation	18.3	18.9	47.0	9826
Coefficient of Variation (%)	7.18	2.94	3.27	2.96

ND = Not done.

coefficients of variation were substantially the same at about 3%. The mean response for 0.025 mg/l DIMP was 255. Greater variation is to be expected at such low levels.

The assay of DIMP in water by gas chromatography requires the extraction of DIMP from the water by adsorption on treated silica gel and elution with acetone. To assess the variability associated with the extraction procedure, six extractions each of a single product water and a single feed water sample were made. Five replicate injections of each extraction were performed. The data appear in Table 6. Mean values for the response (area per microliter) obtained with the product water extractions ranged from 323 to 419. Standard deviations ranged from 14 to 91. The mean of all responses was 376 and the overall standard deviation was 55. The coefficient of variation was 14.6%. For the feed water extractions, mean responses ranged from 292,000 to 306,000 with standard deviations from 5,100 to 9,210. The mean of all responses was 297,000, and the overall standard deviation was 7,810. The coefficent of variation was 2.6%.

Calibration of Response to DIMP in Acetone Standards

Before the reverse osmosis testing began, it was anticipated that concentrations of DIMP in the extractions would range from 0.10 to 20 mg/l. Figure 12 presents a calibration curve over this range with collector #2 installed. The response over the range of concentration tested was linear. The least squares line of best fit is given by the equation:

$$\text{Response} = 18{,}900 \times \text{Concentration} + 1{,}080$$

The correlation coefficient, r, was 0.997. It was subsequently found that

TABLE 6. RESPONSE OF THE N-P DETECTOR FOR SIX REPLICATE EXTRACTIONS OF A PRODUCT SAMPLE AND A FEED SAMPLE. COLUMN: 10% CARBOWAX 20 M ON 80/100 CHROMOSORB W-HP, 2 M x 2 MM ID GLASS. FLOW RATES: 30 ML/MIN HELIUM, 3 ML/MIN HYDROGEN, 60 ML/MIN AIR. TEMPERATURES: COLUMN 165°C (ISOTHERMAL), INJECTION PORT 220°C, DETECTOR 300°C

	Response (area per microliter)					
	Extraction Number					
Product Water	1	2	3	4	5	6
	444	398	405	348	423	332
	476	460	377	356	335	318
	554	389	367	365	324	295
	373	344	378	352	408	301
	296	409	403	384	351	352
Mean	419	400	386	361	368	323
Standard Deviation	91	41	17	14	44	27
Overall Mean	376					
Overall Standard Deviation	55					
Coefficient of Variation (%)	14.6					
Feed Water						
	306263	300895	302368	305526	299895	294579
	297179	286500	285421	305892	298900	294684
	296769	304051	279282	306923	293282	307316
	295026	301026	294632	299210	284950	292211
	292308	300821	296526	313250	290667	285684
Mean	297504	298658	291645	305760	291558	294894
Standard Deviation	5256	6931	9210	5096	7687	7849
Overall Mean	297000					
Overall Standard Deviation	7810					
Coefficient of Variation (%)	2.6					

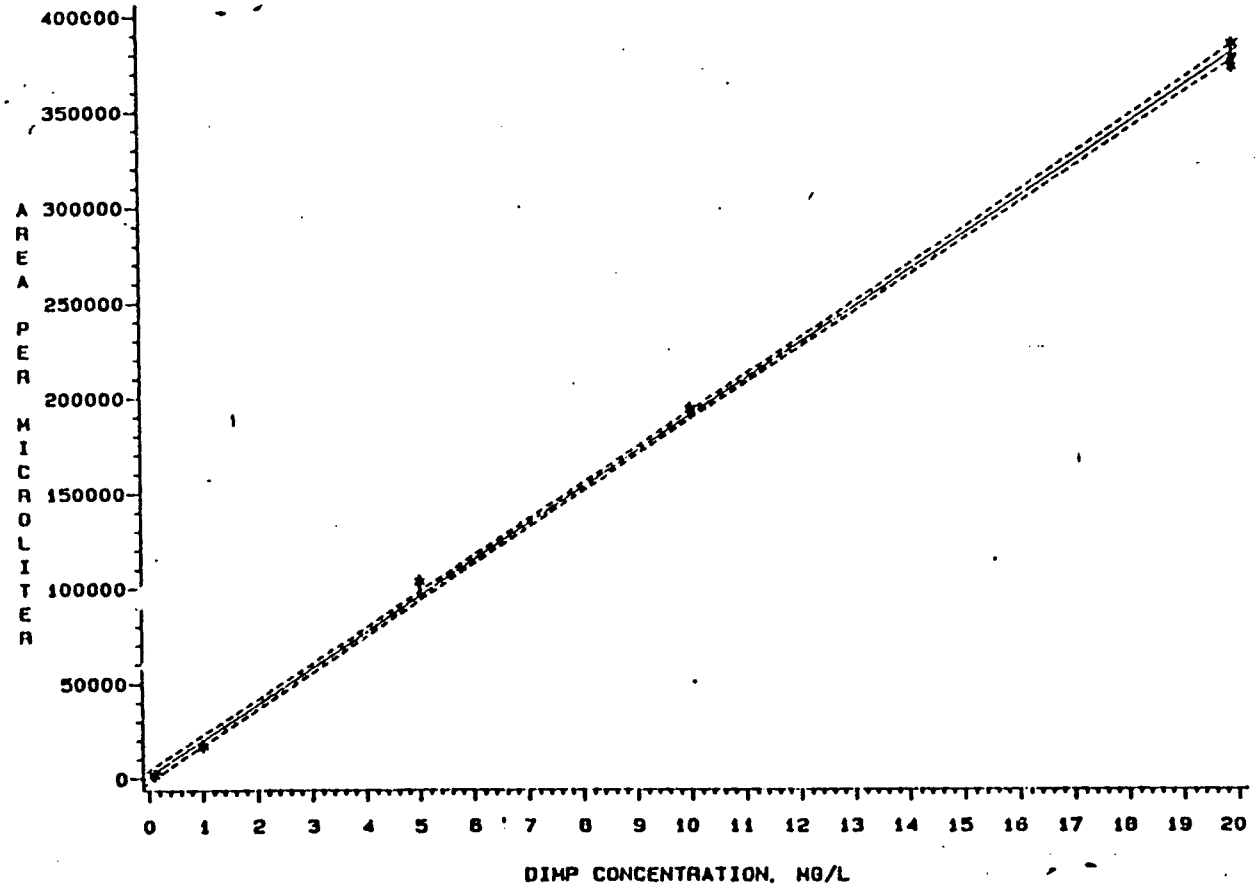


Figure 12. Selected calibration curve for expected concentrations of DIMP in acetone. The solid line is the least squares line of best fit, with a correlation coefficient r = 0.999. The dashed lines represent the 95% confidence interval around the line of best fit. Column: 10% Carbowax 20M on 80/100 chromosorb W-HP, 2 m x 2 mm ID glass. Flow rates: 30 ml/min helium, 3 ml/min hydrogen, 60 ml/min air. Temperatures: column 165°C (isothermal), injection port 220°C, detector 300°C.

the product water extracts gave results below this range. Figure 13 gives a calibration curve for the range of 0.025 to 0.100 mg/l. The response was again linear; the equation of this line was:

$$\text{Response} = 15{,}000 \times \text{Concentration} - 143$$

with $r = 0.9980$. No attempt was made to force the curve through the origin or extrapolate below the data, since it seemed likely that some threshold amount of DIMP would be required to produce a response. Calculations of concentrations on the basis of response utilized these equations.

Figure 14 shows four calibration curves generated by a single set of DIMP in acetone standards on four different days with collector #1 installed. As discussed above, variation was to be expected from day to day. In order to relate the response of an unknown sample to a concentration it was therefore necessary to incorporate calibration samples in each analysis. Such variation may have accounted for the difference in slope between the low range and high range calibration curves.

Evaluation of Extraction Procedure

The recovery efficiency of the extraction procedure was evaluated by comparing responses to DIMP in acetone standards and to extracted DIMP in water standards. The aqueous systems included brackish (5000 mg/l NaCl) and dechlorinated tap water at pH values of 5, 7 and 9. Responses and percent recoveries are given in Table 7. Overall, recoveries ranged from 86.0 to 100%. It appeared that recoveries were higher for 1.00 mg/l than for 10.0 mg/l and that for the 10.0 mg/l standards recovery increased with increasing pH. The results must be treated with caution, however, since in the course of analyzing the 10.0 mg/l samples, a significant drop in the

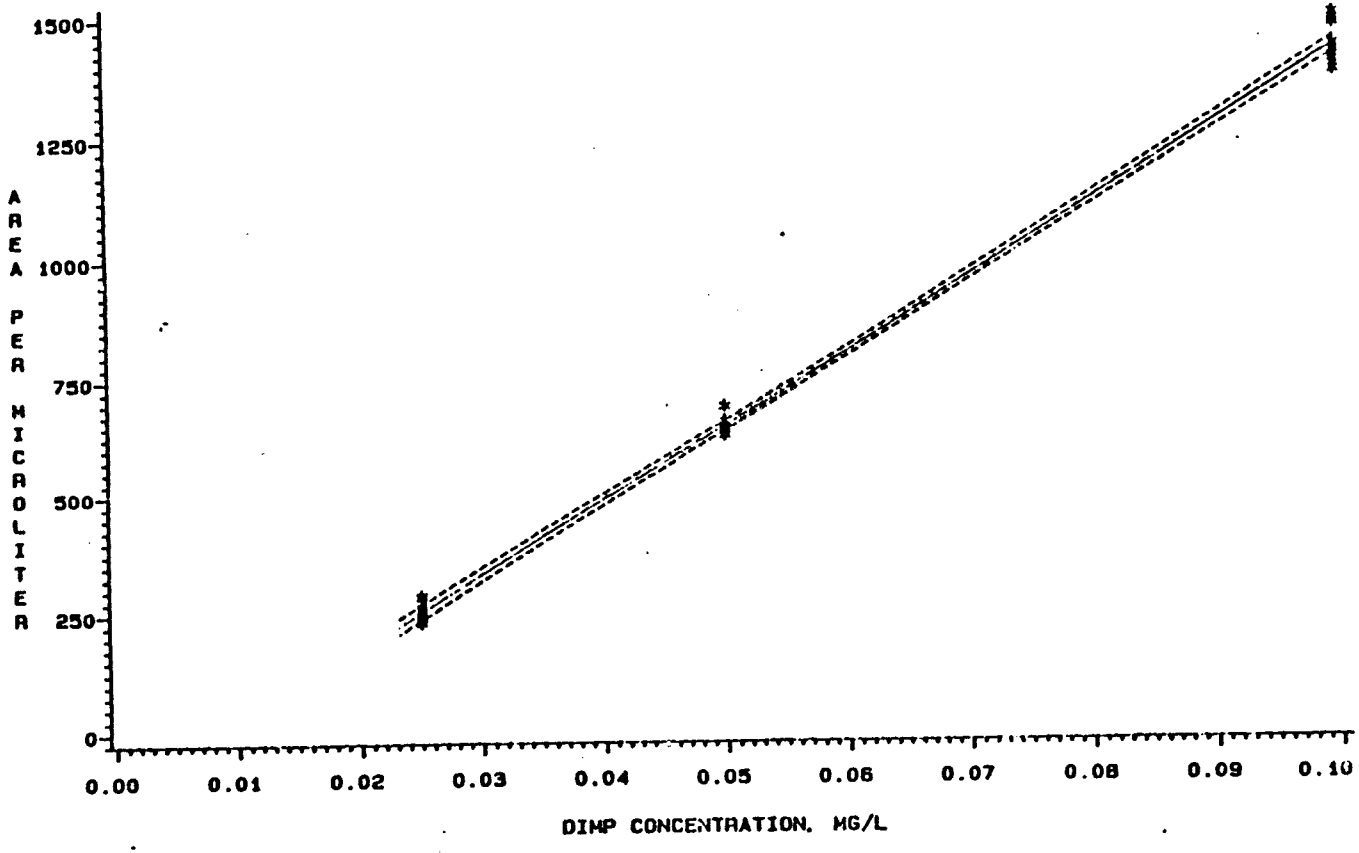


Figure 13. Calibration curve for low concentrations of DIMP in acetone. The solid line is the least squares line of best fit, with a correlation coefficient r = 0.9980. The dashed lines represent the 95% confidence interval around the line of best fit. Column: 10% Carbowax 20M on 80/100 chromosorb W-HP, 2 m x 2 mm ID glass. Flow rates: 30 ml/min helium, 3 ml/min hydrogen, 60 ml/min air. Temperatures: column 165°C (isothermal), injection port 220°C, detector 300°C.

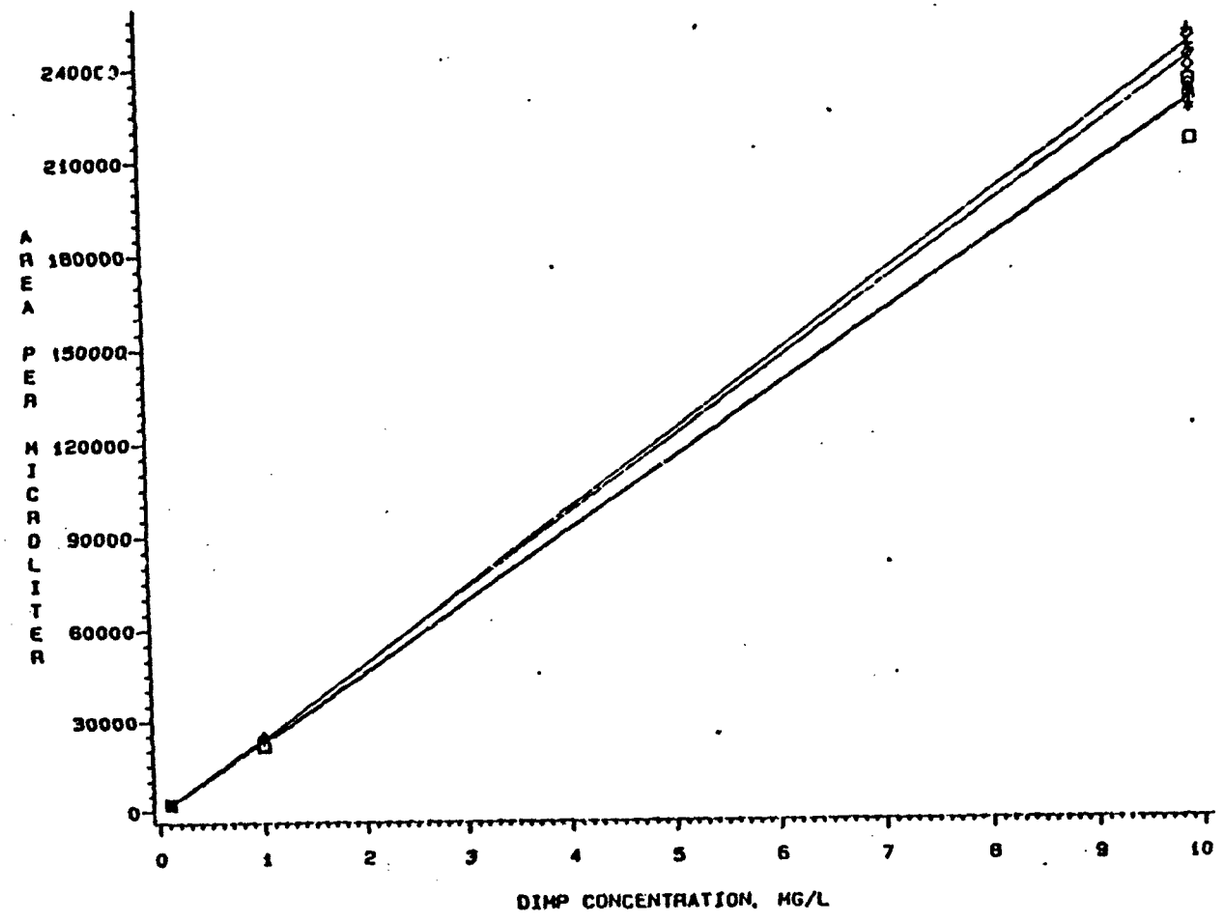


Figure 14. Example calibration curves of DIMP in acetone prepared on different days. Each symbol corresponds to standard analyzed on different days. Column: 10% Carbowax 20M on 80/100 chromosorb W-HP, 2 m x 2 mm ID glass. Flow rates: 30 ml/min helium, 3 ml/min hydrogen, 60 ml/min air. Temperatures: column 165°C (isothermal), injection port 220°C, detector 300°C.

TABLE 7. RECOVERY OF DIMP FROM AQUEOUS SOLUTIONS WITH AND WITHOUT 5000 MG/L NaCl at pH 5, 7, AND 9. COLUMN: 10% CARBOWAX 20 M ON 80/100 CHROMOSORB W-HP, 2 M x 2 MM ID GLASS. FLOW RATES: 30 ML/MIN HELIUM, 3 ML/MIN HYDROGEN, 60 ML/MIN AIR. TEMPERATURES: COLUMN 165°C (ISOTHERMAL), INJECTION PORT 220°C, DETECTOR 300°C

	Response area per microliter (percent recovery)	
Sample	1.00 mg/l	10.0 mg/l
DIMP in Acetone Standard	21,400	218,000
DIMP in Dechlorinated Tap Water		
pH 5	21,400 (99.9)	187,000 (86.0)
pH 7	20,900 (97.4)	194,000 (89.2)
pH 9	21,000 (98.0)	211,000 (96.9)
DIMP in Dechlorinated Tap Water with 5000 mg/l NaCl		
pH 5	21,000 (98.2)	193,000 (88.8)
pH 7	21,600 (100)	200,000 (92.0)
pH 9	20,200 (94.1)	209,000 (96.0)

offset occurred. It was readjusted, but whether the sensitivity returned to the same level as when the DIMP in acetone standards were analyzed was uncertain. There was also the possibility that the extraction columns were overloaded for the 10.0 mg/l aqueous standards since relatively large volumes of 15 and 25 ml were passed through. In extracting feed water samples during the reverse osmosis tests, only 2 ml of sample were extracted.

Variation between extractions was discussed above. As expected, the relative variation was lower for the feed water extractions which yielded responses nearly 1,000 times greater than those of the product water extractions.

STABILITY OF DIMP

In Acetone

The stability of DIMP in acetone was evaluated under three different storage conditions over a period of twenty days. The conditions were 1) room temperature (23-25^{o}C), with normal diurnal variations in light, 2) room temperature with no light and 3) 4^{o}C with no light. For no light storage, the vials were wrapped in foil and kept in the dark except during analysis. Figures 15 through 17 present the results for the different storage conditions for the three concentrations of DIMP tested: 0.100, 1.00 and 10.0 mg/l. No degradation in the response with time was observed. One of the more useful implications of this result was that once extracted, samples could be stored before analysis. Also, the same standards could be kept and reused over long periods, obviating the burden of preparing fresh standards for each analysis.

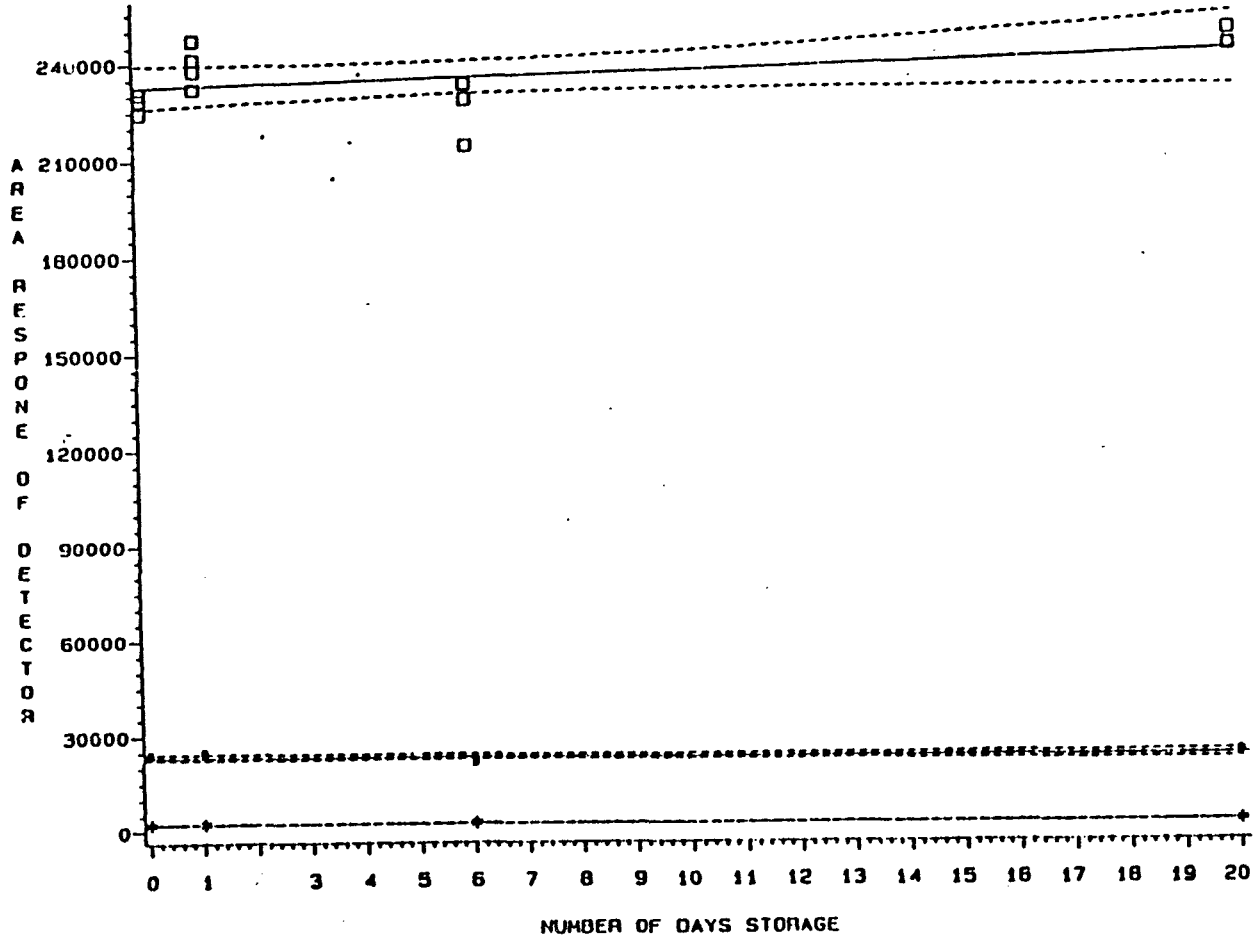


Figure 15. Stability of DIMP in acetone at 25°C for 10 mg/l (□), 1.0 mg/l (D) and 0.1 mg/l (*). Each sample was exposed to normal diurnal variations in light. Column: 10% Carbowax 20M on 80/100 chromosorb W-HP, 2 m x 2 mm ID glass. Flow rates: 30 ml/min helium, 3 ml/min hydrogen, 60 ml/min air. Temperatures: column 165°C (isothermal), injection port 220°C, detector 300°C.

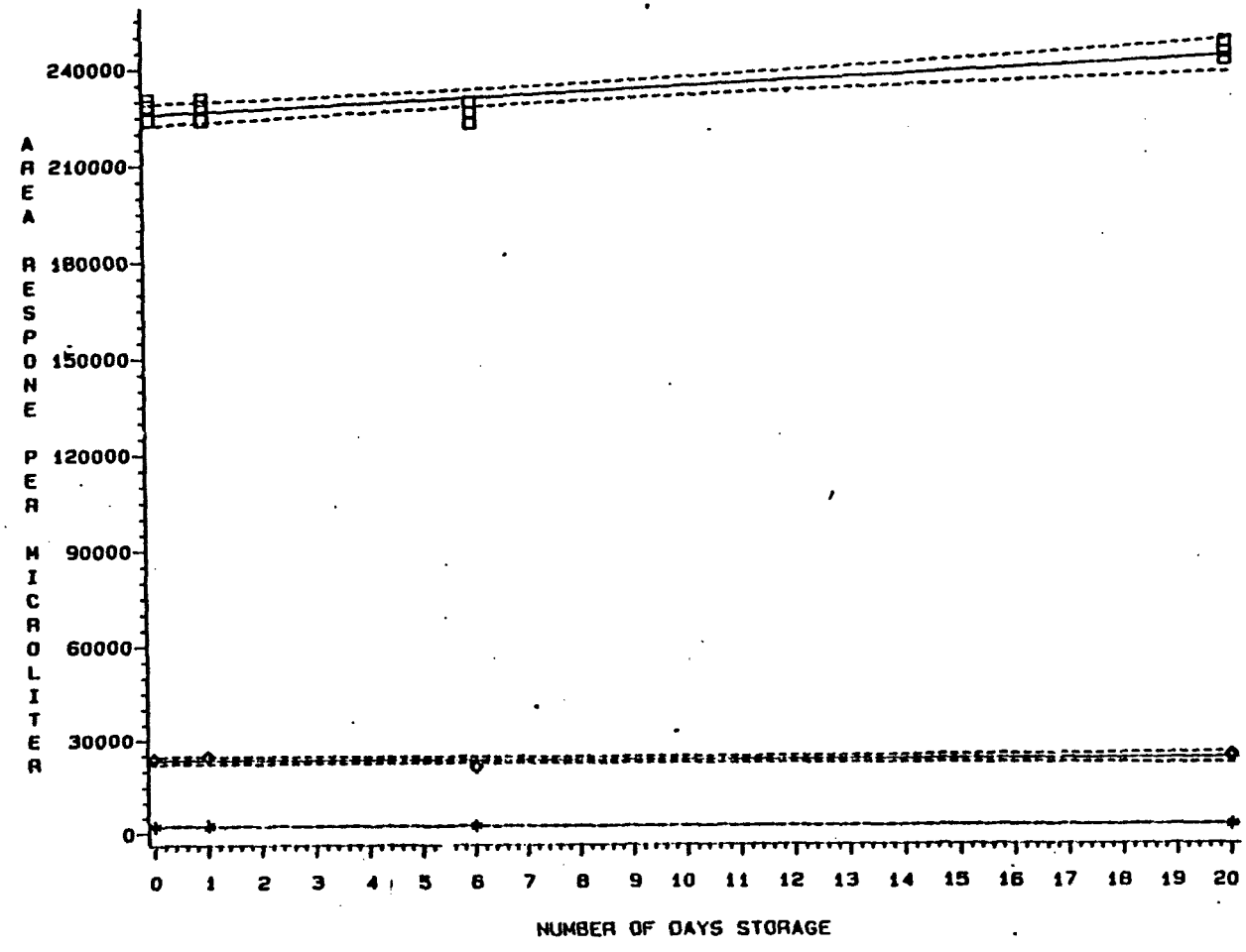


Figure 16. Stability of DIMP in acetone at 25°C for 10 mg/l (□), 1.0 mg/l (◇) and 0.1 mg/l (*). Each sample was stored in the dark. Column: 10% Carbowax 20M on 80/100 chromosorb W-HP, 2 m x 2 mm ID glass. Flow rates: 30 ml/min helium, 3 ml/min hydrogen, 60 ml/min air. Temperatures: column 165°C (isothermal), injection port 220°C, detector 300°C.

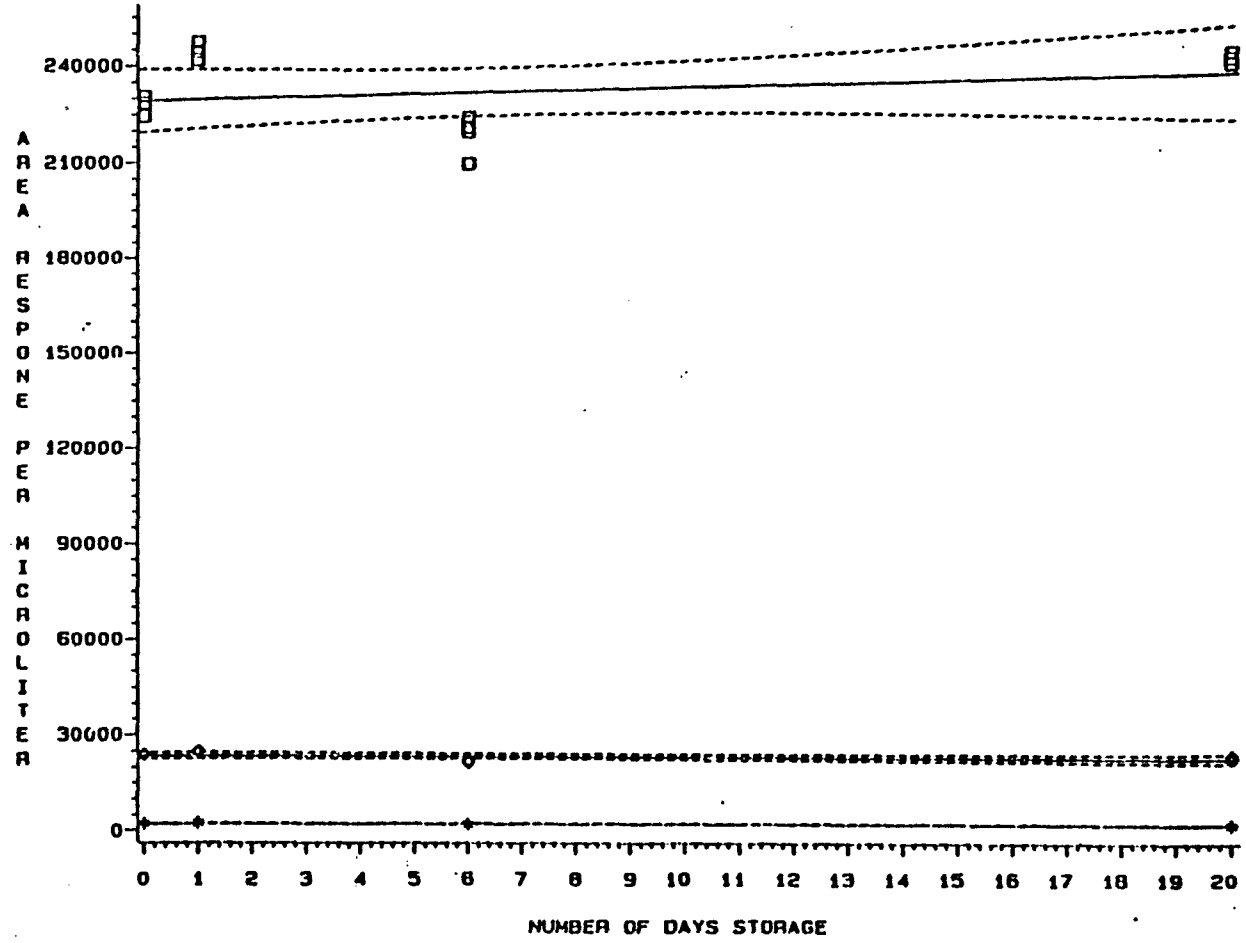


Figure 17. Stability of DIMP in acetone at 4°C for 10 mg/l (□), 1.0 mg/l (◇) and 0.1 mg/l (*). Each sample was stored in the dark. Column: 10% Carbowax 20M on 80/100 chromosorb W-HP, 2 m x 2 mm ID glass. Flow rates: 30 ml/min helium, 3 ml/min hydrogen, 60 ml/min air. Temperatures: column 165°C (isothermal), injection port 220°C, detector 300°C.

In Aqueous Solution

The stability of DIMP in aqueous solution was tested for brackish water and dechlorinated tap water at pH values of 5, 7 and 9 over a 14 day period. The tap water results appear in Table 8. The brackish water results are presented in Table 9. Overall, average responses (area per microliter) decreased from 1.5% to 19% between day 0 and day 14 for the 0.100 and 1.00 mg/l DIMP concentrations. No consistent trends related to pH, salt or concentration were seen. A significant portion of the variation in these results was probably due to sources discussed above. The responses for day 14 extractions of the 10.0 mg/l DIMP samples were higher than the day 0 values by 9% to 34.4% for all but one sample which showed a decrease of 1.62%. The same precautions in interpretation of the results for the 10.0 mg/l solutions discussed in relation to extraction efficiency apply here as well. During the reverse osmosis trials, samples were generally extracted within 24 hours and all were extracted within 48 hours.

REJECTION OF DIMP BY REVERSE OSMOSIS

Johns Hopkins University Trials

Preliminary trials of DIMP rejection by reverse osmosis were conducted with the bench scale test cell. The results for both brackish (2,404 mg/l NaCl) water and salt (33,540 mg/l NaCl) water trials are presented in Table 10. The salt water rejection was 75% with a corresponding 88.7% DIMP rejection in the salt water test. For the brackish water test, the salt rejection was 81.0% with a DIMP rejection of 98%.

TABLE 8. STABILITY OF DIMP IN DECHLORINATED TAP WATER AT 35°C AT pH 5.0, 7.0, AND 9.0 OVER A 14 DAY PERIOD. COLUMN: 10% CARBOWAX 20 M ON 80/100 CHROMOSORB W-HP, 2 M x 2 MM ID GLASS. FLOW RATES: 30 ML/MIN HELIUM, 3 ML/MIN HYDROGEN, 60 ML/MIN AIR. TEMPERATURES: COLUMN 165°C (ISOTHERMAL), INJECTION PORT 220°C, DETECTOR 300°C

pH	Nominal DIMP Concentration (mg/l)	Average Response (area per microliter) Day 0	Day 14	% Change
5	0.100	2820	2630	-6.74
	1.00	20400	19000	-6.91
	10.00	324000	385000	+18.6
7	0.100	2750	2260	-17.9
	1.00	20900	16900	-19.3
	10.0	308706	349673	+13.3
9	0.100	2580	2140	-16.9
	1.00	20500	19300	-5.77
	10.00	323000	352000	+8.96

TABLE 9. STABILITY OF DIMP IN DECHLORINATED TAP WATER WITH 5000 mg/l NaCl AT 35°C AT pH 5.0, 7.0, AND 9.0 OVER A 14 DAY PERIOD COLUMN: 10% CARBOWAX 20 M ON 80/100 CHROMOSORB W-HP, 2 M x 2 MM ID GLASS. FLOW RATES: 30 ML/MIN HELIUM, 3 ML/MIN HYDROGEN, 60 ML/MIN AIR. TEMPERATURES: COLUMN 165°C (ISOTHERMAL), INJECTION PORT 220°C, DETECTOR 300°C

pH	Nominal DIMP Concentration (mg/l)	Average Response (area per microliter) Day 0	Day 14	% Change
5	0.100	3100	2670	-13.9
	1.00	19700	19000	-3.48
	10.0	307000	302000	-1.62
7	0.100	2910	2470	-15.2
	1.00	19700	19400	-1.53
	10.0	301000	350000	+16.5
9	0.100	2970	2710	-8.98
	1.00	19800	19200	-3.31
	10.0	325000	437000	+34.4

TABLE 10. REJECTION OF DIMP AND SALT IN BRACKISH AND SALT WATER BY BENCH SCALE REVERSE OSMOSIS TEST CELLS

	Salt Water	Brackish Water
Temp	24°C ± 1°C	24°C ± 1°C
pH	7.5 ± 0.2	7.4 ± 0.2
Flow	80 ml/min.	85 ml/min.
Pressure	800 PSI ± 50 PSI	200 PSI ± 20 PSI
Feed		
NaCl mg/l	33,540 mg/l	2404 mg/l
DIMP mg/l	19.5 mg/l	25.0 mg/l
Product		
NaCl mg/l	8,430 mg/l	445 mg/l
DIMP mg/l	2.2 mg/l	2.5 mg/l
% Reduction		
NaCl	75.0	81.0
DIMP	88.7	98.0

The rejection of DIMP by reverse osmosis was evaluated for DIMP in dechlorinated tap water at pH 7 and in brackish water (5000 mg/l NaCl) at pH 7. Two trials were performed for each. The tap water results are presented in Tables 11 and 12. Product water concentrations ranged from 0.041 to 0.091 mg/l for feed water concentrations ranging from 14.6 to 17.8 mg/l. The percent removal varied from 99.5% to 99.7%. Results for the brackish water are in Tables 13 and 14. For the two trials, product water concentrations ranged from 0.023 to 0.063 mg/l for feed concentrations from 16.2 to 18.7 mg/l. Percent removals ranged from 99.6% to 99.8%, with most of the samples resulting in the latter value.

Figure 18 shows a plot of the logarithm of the percent DIMP remaining against cumulative flow through the membrane for the tap water trials. There is little difference between the two trials with the rejection remaining essentially constant over the course of a run. Figure 19 is the same plot for the brackish water trials. The same pattern was observed.

CRDC Trials

The trials performed at CRDC comprised two with DIMP in dechlorinated tap water and one with brackish water. The tap water results appear in Tables 15 and 16. Product water concentrations ranged from 0.080 to 0.223 mg/l with feed water concentrations from 22.0 to 22.9 mg/l. Rejection ranged from 99.0% to 99.6%. Results for the brackish water trials are in Table 17. The product water concentration ranged from 0.057 to 0.143 mg/l with the feed water concentration from 21.3 to 22.5 mg/l. The percent removal was from 99.4% to 99.7%.

TABLE 11. REJECTION OF DIMP IN DECHLORINATED TAP WATER BY REVERSE OSMOSIS IN THE JOHNS HOPKINS UNIVERSITY TEST STAND (TRIAL 1) MEMBRANE

Time	Temperature (°C)	pH	Pressure (psi)	DIMP (mg/l) Feed	Product	% Removed
0.25	23	7.1	580	15.6	0.0756	99.5
1.25	24	7.1	550	15.8	0.0625	99.6
2.25	25	7.1	510	15.6	0.0622	99.6
3:25	26	7.1	500	15.3	0.0558	99.6
10:25	33	7.1	500	14.6	0.0413	99.7

TABLE 12. REJECTION OF DIMP IN DECHLORINATED TAP WATER BY REVERSE OSMOSIS IN THE JOHNS HOPKINS UNIVERSITY TEST STAND (TRIAL 2) MEMBRANE

Time	Temperature (°C)	pH	Pressure (psi)	DIMP (mg/l) Feed	Product	% Removed
0.25	20	7.2	600	17.0	0.0912	99.5
1.92	22	7.2	550	17.0	0.0488	99.7
2.42	23	7.2	550	17.6	0.0493	99.7
2.92	24	7.2	525	16.9	0.0472	99.7
3.42	25	7.2	500	17.4	0.0432	99.7
3.92	25.5	7.2	500	17.8	0.0456	99.7

TABLE 13. REJECTION OF DIMP IN BRACKISH WATER (5000 mg/1) BY REVERSE OSMOSIS IN THE JOHNS HOPKINS UNIVERSITY TEST STAND (TRIAL 1)

Time	Temperature (°C)	pH	Pressure (psi)	DIMP (mg/1) Feed	Product	% Removed	% Salt Removed
0.25	21	7.2	680	17.0	0.0538	99.7	99.0
1.75	24	7.2	650	17.1	0.0353	99.8	99.3
2.75	25	7.2	600	16.2	0.0376	99.8	99.4
3.75	26	7.2	575	18.7	0.0337	99.8	99.3
4.75	27	7.2	575	16.5	0.0330	99.8	99.2
5.75	28	7.2	550	18.7	0.0316	99.8	99.3

TABLE 14. REJECTION OF DIMP IN BRACKISH WATER (5000 mg/l) BY REVERSE OSMOSIS IN THE JOHNS HOPKINS UNIVERSITY TEST STAND (TRIAL 2)

Time	Temperature (°C)	pH	Pressure (psi)	DIMP (mg/l) Feed	Product	% Removed	% Salt Removed
0.25	18	7.3	750	18.4	0.0634	99.6	98.7
1.25	20	7.3	700	18.0	0.0437	99.7	99.1
2.25	21	7.3	720	18.2	0.0353	99.8	99.2
2.75	22	7.3	650	17.8	0.0383	99.8	99.3
3.25	23	7.3	650	17.9	0.0327	99.8	99.2
3.75	24	7.3	625	18.3	0.0266	99.8	99.4
4.25	25	7.3	625	17.9	0.0318	99.8	99.3
4.75	25.5	7.3	600	18.3	0.0327	99.8	99.5

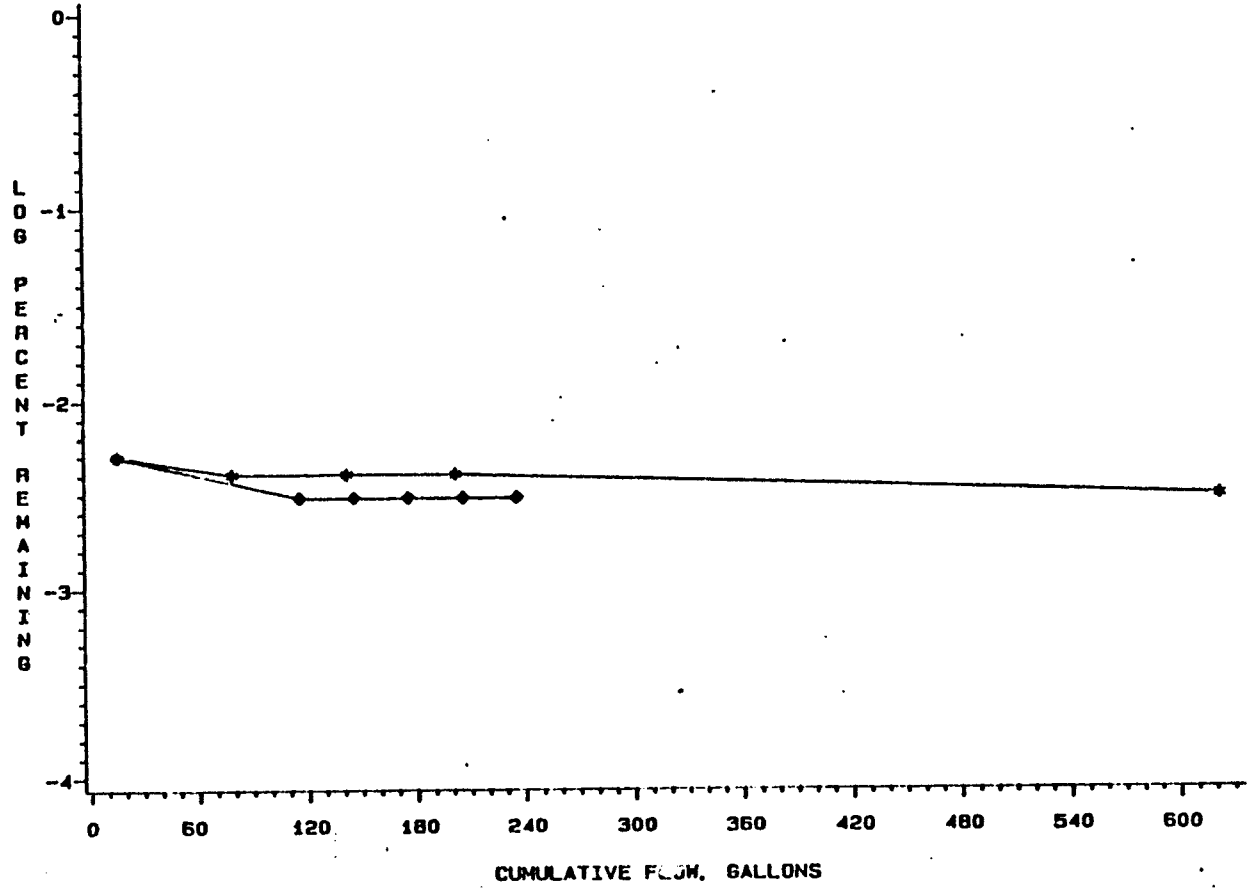


Figure 18. Logarithm of the % DIMP remaining in dechlorinated tap water after treatment by reverse osmosis in the Johns Hopkins University test stand. Average feed concentration 15.4 to 17.3 mg/l DIMP. Trial 1 (*) and trial 2 (◇).

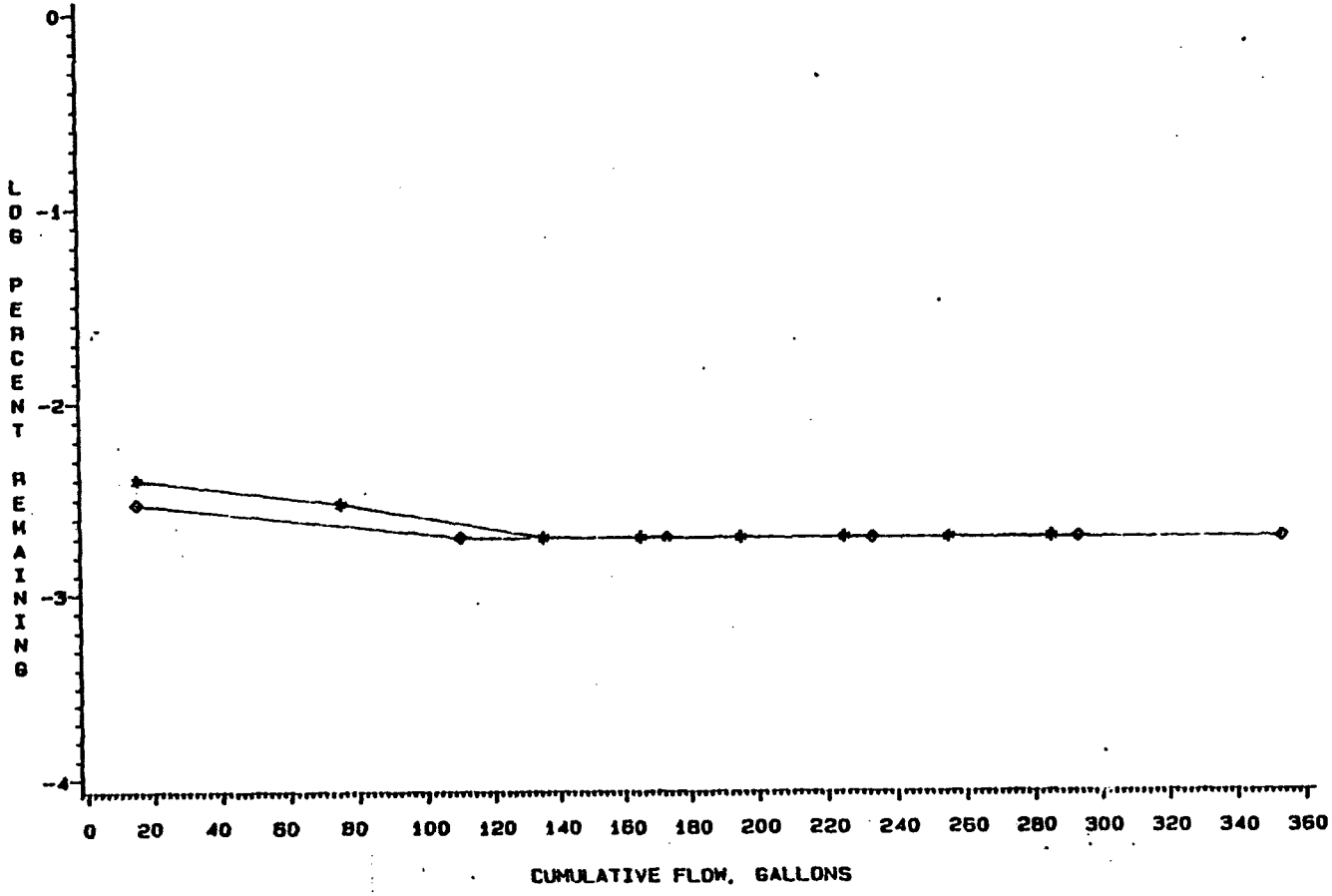


Figure 19. Logarithm of the % DIMP remaining in brackish (5000 mg/1 NaCl) water after treatment by reverse osmosis in the Johns Hopkins University test stand. Average feed concentration 17.3 to 17.4 mg/1 DIMP. Trial 1 (◇) and trial 2 (*). Average salt rejection 99.2%.

TABLE 15. REJECTION OF DIMP IN DECHLORINATED TAP WATER BY REVERSE OSMOSIS IN THE CRDC TEST STAND (TRIAL 1)

	DIMP Concentration, (mg/l)			
Time	Feed	Product	Waste	% Removed
1030	22.6	0.101	24.3	99.6
1200	22.9	0.0952	25.0	99.6
1330	22.0	0.103	24.7	99.5
1500	22.6	0.0849	24.2	99.6

TABLE 16. REJECTION OF DIMP IN DECHLORINATED TAP WATER BY REVERSE OSMOSIS IN THE CRDC TEST STAND (TRIAL 2)

	DIMP Concentration, (mg/l)			
Time	Feed	Product	Waste	% Removed
1015	22.8	0.223	25.3	99.0
1215	22.5	0.0928	24.8	99.6
1415	22.5	0.0796	26.3	99.6
1615	22.5	0.0819	25.5	99.6

TABLE 17. REJECTION OF DIMP IN BRACKISH WATER (5000 mg/NaCl) BY REVERSE OSMOSIS IN THE CRDC TEST STAND

	DIMP Concentration, (mg/l)			
Time	Feed	Product	Waste	% Removed
1015	22.5	0.143	25.4	99.4
1215	22.0	0.0582	25.8	99.7
1415	21.3	0.0572	23.8	99.7
1615	22.3	0.0624	26.1	99.7

Figure 20 shows a plot of the logarithm of the percent DIMP remaining against time for the tap water trials. Figure 21 is the same plot for the brackish water trial. The pattern is quite similar to that observed in the JHU tests with little change in the percent remaining over the course of a run.

It should be noted that in both the JHU and the CRDC trials the removal for the first sample was lower than for subsequent samples. This is illustrated in Figure 22 which shows the percent removal of DIMP on an expanded scale against time from the first sample. One CRDC run was an exception. The time between start-up of the reverse osmosis unit and the first sampling in the CRDC trials was not known, however. It appears from these results that a warm-up period should be provided in order to obtain optimum removal of the chemical.

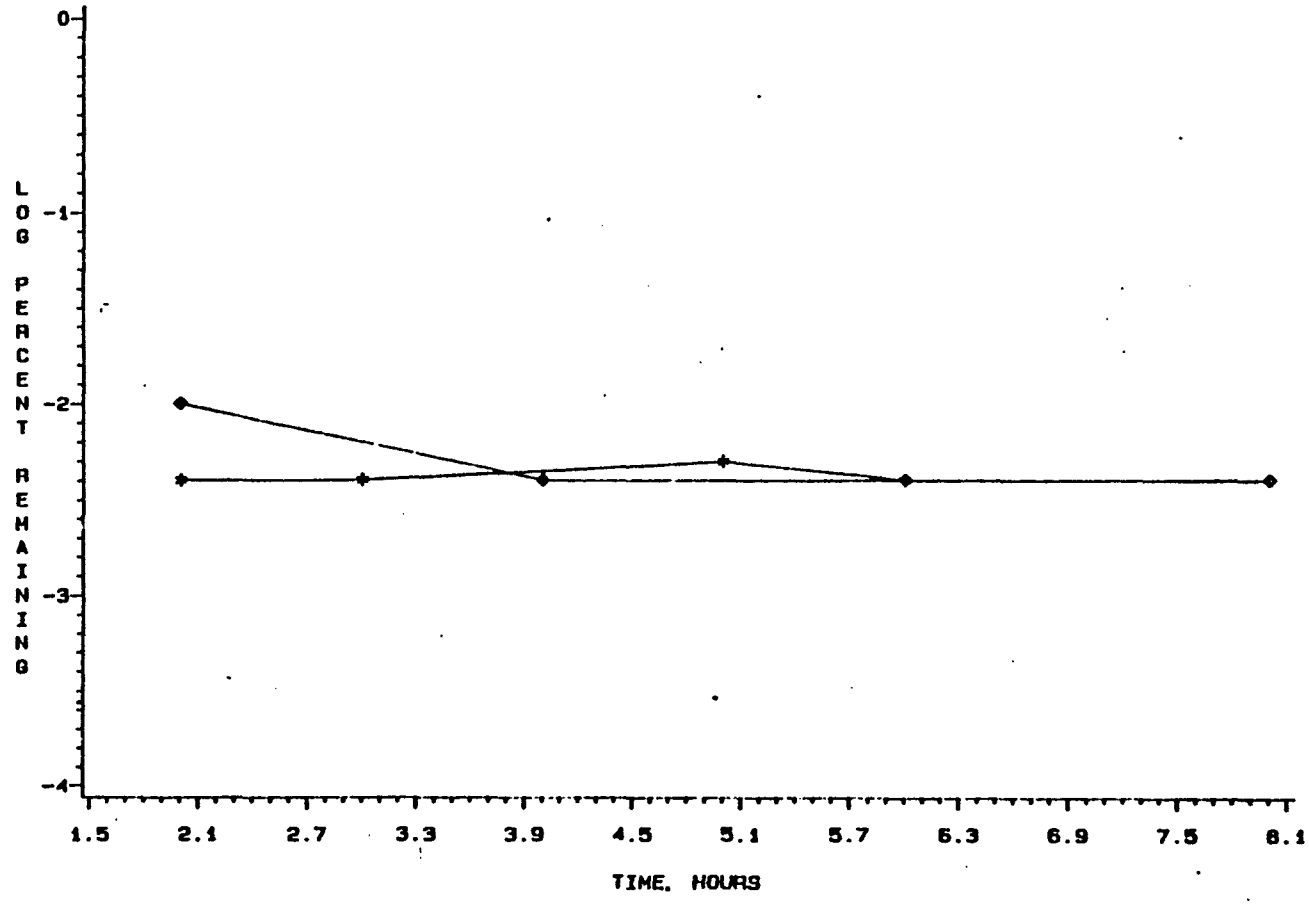


Figure 20. Logarithm of the % DIMP remaining in dechlorinated tap water after treatment by reverse osmosis in the CRDC test stand. Average feed concentration 22.5 mg/l DIMP. Trial 1 (*) and trial 2 (◊).

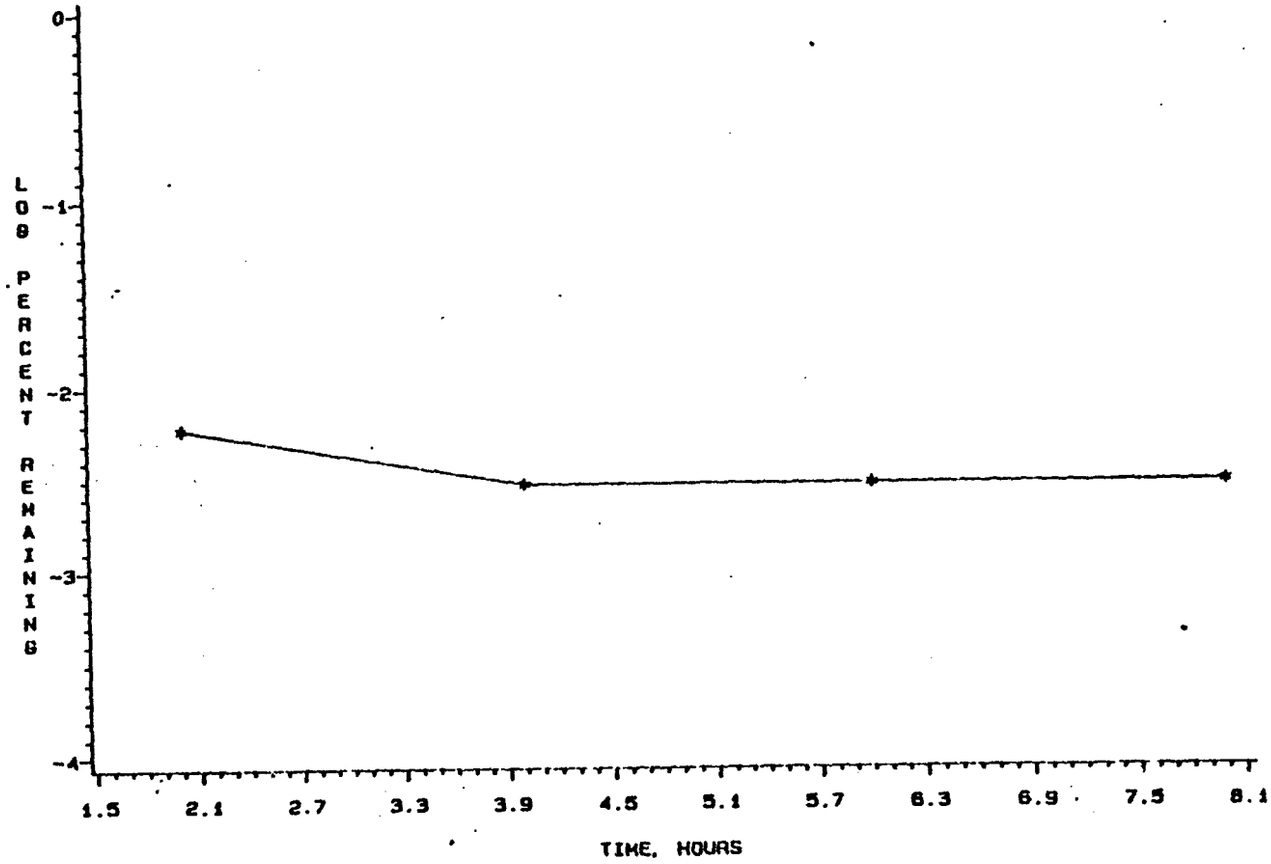


Figure 21. Logarithm of the % DIMP remaining in brackish (5000 mg/l NaCl) water after treatment by reverse osmosis in the CRDC test stand. Average feed concentration 22.0 mg/l.

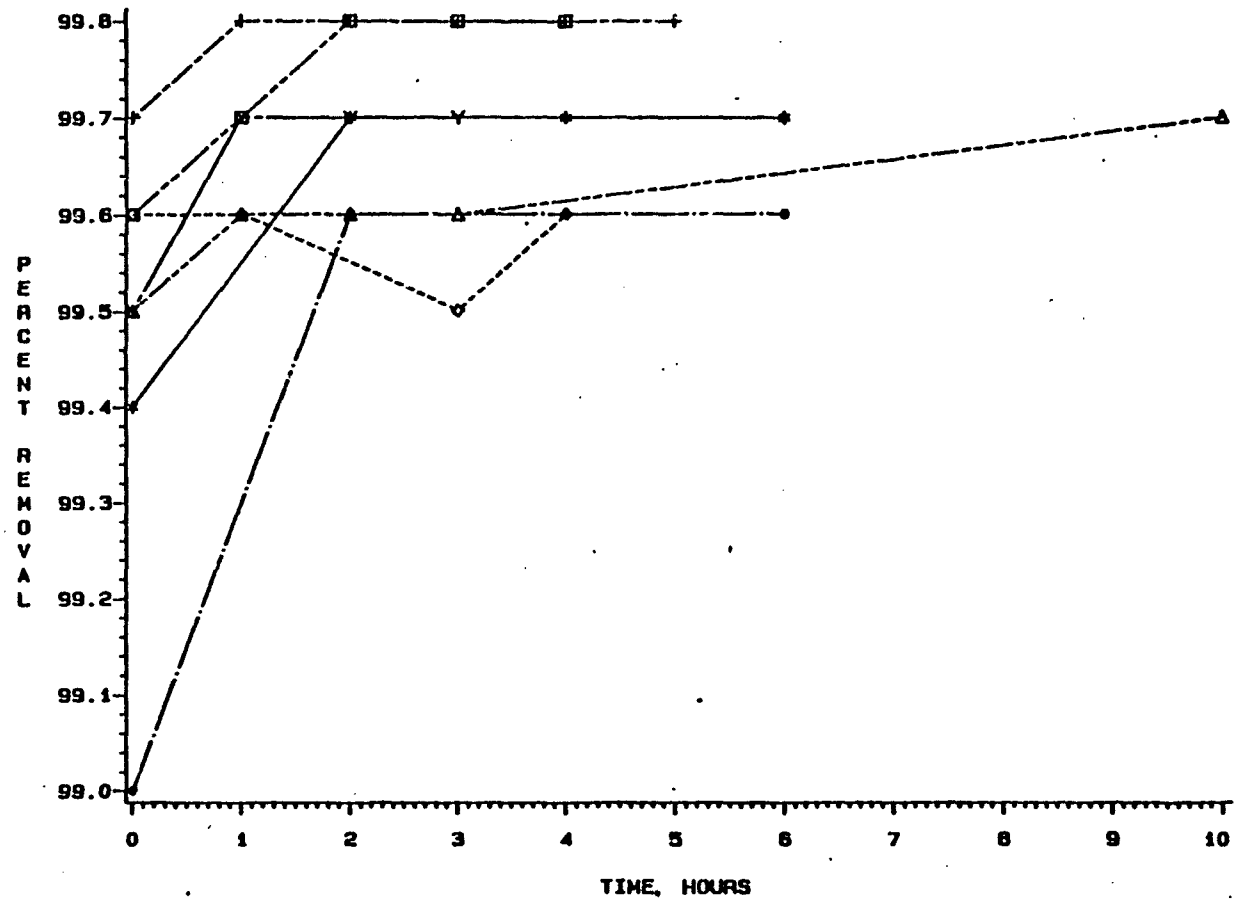


Figure 22. Percent DIMP removal by reverse osmosis on expanded scale versus time for all runs. Time 0 corresponds to time of first sample. The Johns Hopkins University tap water trial 1 (*) trial 2 (◇); CRDC tap water trial 1 (o), trial 2 ( ); Johns Hopkins University brackish (5000 mg/l NaCl) water trial 1 (+), trial 2 (□); CRDC brackish (5000 mg/l NaCl) water (Y).

DISCUSSION

SIMULANT CRITERIA

The choice of candidate simulants was based on the desirable characteristics of an ideal simulant and a comparison of chemical properties that might influence the rejection of compounds by membranes. The primary purpose of the simulant was to develop a system that could be used to provide a preliminary evaluation of the ability of membranes to reject important toxic organics. Such a system could also be used to develop operational and evaluation procedures under field conditions. Consequently, the toxicity, stability, analytical methodology and membrane rejection were prime criteria. Unfortunately, information for these parameters was limited and a more pragmatic approach was employed to make the initial selection of the compounds to be tested. After the compounds were chosen for chemical, physical and operational characteristics, the short list was subjected to further review. The initial list of simulants developed in the literature search and additional selected criteria are shown in Table 18. The list was quickly reduced based on molecular weight, presence of phosphorous, and solubility in water. Bis (2-ethyl hexyl) phosphonate was rejected because the molecular weight was near the exclusion limit suggested for RO membranes (Reid, 1966). Diethyl phthalate was insoluble in water. Most agents of concern contain the phosphorous. The presence of phosphorous would be a useful characteristic for the simulant and provide a common characteristic that could be used to develop analytical methods. Diethyl glycol dimethyl ether, dietyl phthalate,

TABLE 16. SELECTED PROPERTIES FOR CANDIDATE NERVE AGENT SIMULANTS

		Molecular Weight	Phosphorous	Water Solubility
1.	Bis (2-ethyl hexyl) phosphonate	306.4	+	NL
2.	Diethyl glycol dimethyl ether	134.2	-	S
3.	Diethyl phosphonate (DEMP)	138.2	+	S
4.	Diethyl phthalate	222.2	-	-
5.	Diethyl sebacate	255.4	-	NL
6.	Diethyl sulfite	138.2	-	S
7.	Diisopropyl methyl phosphonate (DIMP)	181.1	+	S
8.	Dimethoxy methyl phosphonate (DMMP)	129.1	+	S
9.	Ethyl dimethyl phosphite	138.1	+	S

NL = Not listed.

diethyl sebacate and diethyl sulfite did not contain phosphorous and were not considered further. Of the remaining compounds DIMP, dimethoxy methyl phosphonate (DMMP) and diethyl phosphonate (DEMP) were commercially available. A detailed description of the chemical properties, chemical reactivity, and toxicity for DIMP and DMMP compiled by the U.S. Army CRDC Environmental Technical Division on Current Chemical Agent Simulants can be found in APPENDIX 2.

DIMP was chosen for the initial evaluation because of the ancillary information available and previous experience with this compound in related situations. While DIMP did not match within 20% of the selected chemical and physical properties, the other attributes were considered important for initial trials. Except for a minor inhalation hazard, little evidence of acute or chronic toxicity has been reported and at present a threshold limit value has not been established. DIMP is a hydrolysis product of the agent GB and contains phosphorous. Outterson and Prociv (1980) reported the applicability of DIMP as a simulant. The compound was stable in water and believed to be non toxic. The U.S. Army at Rocky Mountain Arsenal found DIMP to be a useful indicator of groundwater contamination and exhaustion of activated carbon used to treat wastes before recharging to the groundwater (Civil Engineering, 1981). As a result of the use of DIMP for these investigations, analytical methods have been investigated for the determination of DIMP in water (Fasime, 1982; Broaders, 1982).

DEVELOPMENT OF ANALYTICAL METHODS

A major task of the present project was to develop a method of analysis for the assay of the simulants. Conventional colorimetric methods,

while easy and simple to perform, may suffer from interferences in actual systems, may not be flexible enough to evaluate different simulants and may not possess the necessary sensitivity to be of value in detecting the low concentrations of materials expected in the reverse osmosis product water. The methods employed for the assay of the simulants were selected by the criteria listed below:

1. SENSITIVITY
2. FLEXIBILITY
3. SPECIFICITY
4. ADAPTABILITY
5. SIMPLICITY
6. COST

Considerable effort was expended to develop a basic analytical approach that would provide a workable, flexible, adaptable technique that could be applied to a variety of simulants. DIMP was used as a prototype simulant to develop the analytical methodology.

The method for the analysis of DIMP involved the quantitative adsorption of the DIMP on octasilized silica gel cartridges, the quantitative elution with acetone, and subsequent analysis by gas liquid chromatography.

The adsorption on the silica gel was performed with commercially available cartridges and served to remove the compound. The material could then be eluted, seperated by gas liquid chromatography and analyzed by a specific detector sensitive for the elements nitrogen, phosphorous and sulfur. The adsorption step also provides a practical technique to

concentrate the simulant to increase the sensitivity of the assay. In this study, small volumes of water were passed through the cartridge since the increased sensitivity was not needed. For other simulants, the sensitivity could be increased by several orders of magnitude by simply increasing the volume of sample applied to the cartridge. The volume of sample applied would not be unlimited. It would be a function of the adsorbant employed and the compound to be adsorbed. A large number of adsorbants are available and can be chosen to increase or decrease the specificity and selectivity of the determination.

The elution step can be carried out with a variety of solvents. The choice of solvent will be influenced by the efficiency of elution of the simulant from the adsorptive agent, the column and detector used on the gas chromatograph and the stability of the simulant in the solvent. The solvent employed can also add specificity and selectivity to the determination.

Gas chromatography is becoming the standard method for the analysis of volatile organics in water and a considerable body of literature is available on specific procedures, methods and techniques. It separates and provides quantitative information on complex mixtures that would be found in any trials conducted under field conditions. The column may be selected to provide the capability of a wide variety of separations. The detector may be chosen to yield the necessary selectivity and sensitivity.

Gas Chromatographic Analysis of DIMP

A considerable amount of time was spent establishing satisfactory operation of the gas chromatograph (GC) and the nitrogen-phosphorous

detector. As discussed in the Results section, the offset provides a measure of the detector sensitivity. Wide variations in the offset were a major point of concern. Variations may be symptomatic of several problems, including detector performance, column performance and more banal difficulties such as column and septum leakage. A discussion concerning the nitrogen-phosphorous detector and various columns based on experience and technical information from Hewlett-Packard (HP) follows.

Nitrogen-Phosphorous Detector

The nitrogen-phosphorous detector is a thermionic emission detector, also known as an alkali flame ionization detector. It employs a rubidium silicate bead positioned above the flame tip by the collector assembly. The bead is heated by an adjustable current and the sensitivity of the detector is a function of the bead temperature. When the bead has been consumed or damaged, the collector must be replaced.

The beads are highly hygroscopic. New collectors must therefore be conditioned according to the instructions provided by HP. This procedure drives out moisture slowly and avoids cracking or chipping of the bead. Likewise, if the GC has been left on standby, the bead may have had an opportunity to take up moisture. When starting up, the voltage should be increased slowly until the desired offset is reached. None of the HP literature was explicit on this point. It was possible that some collectors suffered damage from rapid heating.

Too rapid application of the appropriate voltage for the desired sensitivity can also burn the bead. This resulted in the loss of one new

collector. The voltage should be increased slowly to allow the temperature of the bead to equilibrate slowly.

Moisture in the injected sample can have a depressing effect on the detector's response. This can be compensated by increasing the voltage to the bead; at some level the response will remain stable at a constant, although depressed value. This will accelerate deterioration of the bead, however, perhaps through a combination of the effects of higher voltage and exposure to moisture. If the collector is in good condition, the detector will recover to its normal operating state when injections of the moisture laden sample cease.

The response of the detector is susceptible to fluctuations in ambient temperature. It was observed that opening and closing the cover over the detector resulted in a transient rise in an otherwise stable offset. The existing insulation over the oven and around the detector was then supplemented with glass wool and the GC was subsequently operated with the cover in place.

The HP manual recommends a collector height of 0.075" (Hewlett-Packard, 1974), but the Operating Note, "Evaluating and Optimizing the Performance of the Nitrogen-Phosphorous Detector," (Hewlett-Packard, 1978), indicates that the height can be anywhere from 0.015" to 0.15". HP reported that they usually obtain best results with settings between 0.025" and 0.050". All analyses of DIMP presented in this report were performed with a collector height of 0.075", but some experimentation was done. With the 2% OV 101 HP test column installed, injections of the performance evaluation sample (PES) were made with a setting of 0.075". The average

phosphorous response (area per microliter) for 7 injections was 1370. The setting was then lowered to between 0.050" and 0.060". The average phosphorous response for four injections was 2600, an increase of about 100%. The neight was then lowered to between 0.025" and 0.050". A single injection of PES dropped the offset from 91 to 14 mm. It appears from HP's Operating Note that the optimum setting may vary from one collector to the next. It is probably not necessary to go through the relatively cumbersome procedure of optimizing the setting each time a new collector is installed; unless the sensitivity is unacceptably low, recalibration with standard solutions should be sufficient.

Replacement of the chimney assembly of the detector apparently resolved certain problems. The offset had been highly erratic, eventually decaying to zero despite voltage increases. Spiking also occurred when there was any movement in the area around the detector. With a new chimney, the problem was eliminated. It is conceivable that earlier difficulties in obtaining a stable offset were attributable to deteriorating performance of this component.

Performance Evaluation--

The 2% OV 101 test column was installed in order to check the overall operation of the GC. The collector was not changed initially. The performance evaluation sample supplied with the test column contains azobenzene, octadecane and malathion in 2,2,4-trimethylpentane. Evaluation of performance is based on the ratios of azobenzene and malathion peak areas to the octadecane peak area and the ratios of these areas to peak to peak noise measured in millimeters. According to HP, "The response of the

[N-P detector] to the evaluation sample will vary from instrument to instrument, from collector to collector, and even from day to day." As long as the ratio of peak area to octadecane area is greater than or equal to 3.5 for azobenzene and 7.5 for malathion, and the ratio of peak area to noise is greater than or equal to 1000 for azobenzene and 2000 for malathion, the collector is performing acceptably. It is also noted, however, that for a given analysis, acceptable performance is that which allows the analysis to be accomplished and that this might be quite different from their definition of acceptable (Hewlett-Packard, 1978). There are therefore no precisely defined criteria for acceptable performance.

A stable offset was obtained for the evaluation and the chromatograms resulting from injections of PES appeared reasonable; that is, the relative retention times were correct, the peak areas were reproducible, the peaks were well defined and the factory performance criteria based on area ratios were met. The malathion response was consistently lower than the azobenzene response, however. According to HP this "can almost always be traced to a bad column," since the malathion is the most readily adsorbed compound in the sample (Hewlett-Packard, 1978). Other observations were consistent with this possibility. For example, successive injections produced increasing malathion peak areas which according to Supelco can be caused by "adsorption of components and saturation of active sites with sample (priming the column)" (Supelco, 1983). The offset also increased slightly after each injection which may be attributable to a response to residual malathion. With a new collector in place, essentially the same

pattern was observed, although the malathion peak areas were about 250% greater and the azobenzene areas were about 50% greater. Some experimentation with collector height was also done as described above.

HP's Operating Note mentions that most collectors seem to have some "steady state" offset at which they are most stable. This is usually 25% to 50% less than the checkout procedure offset of 75 to 100 mm. If the offset is higher, it will slowly return to the steady state value, resulting in a change of sensitivity (Hewlett-Packard, 1978). Monitoring the offset over a 12 hour period revealed a decline to about 80% of the initial value (88.5 mm). According to HP, the offset should be stable over an eight hour period. In the first eight hours of observation the offset had declined to 75 mm or 85% of the initial value. This may have been a manifestation of the detector's tendency to approach some steady state offset value. The significance of offset variation was tested as described in the Results section. Between offset values of 75 and 88.5 mm, the response for 1.0 mg/l DIMP in acetone increased by 4.5%. Although intentional changes in the voltage applied to the bead are not necessarily equivalent to uncontrolled factors influencing the offset, this result suggested that offset variations may have a significant impact on the response. In general, however, on the basis of the performance evaluation it appeared that the detector was functioning normally.

Columns

Several different columns were tried in conjunction with the simulant DIMP, including both solid and liquid phase types. Because of the multiplicity of factors affecting the response, it was difficult to assign

particular causes to observed aberrations. It was clear that in many instances, the detector was not functioning properly. On the other hand, column and septum leaks were occasionally responsible. Despite the uncertainties, it was possible to differentiate the performances of various columns. These are summarized in Appendix 3. The best results were obtained with the 10% Carbowax 20M on 80/100 chromosorb W-HP glass column. The operating conditions that were finally established after investigation of the detector and columns were reported in the Methods section.

The data collected for DIMP demonstrates the applicability of the procedure. The gas chromatograph provided a rapid, selective, sensitive technique. The standard curves prepared were reproducible and provided a linear response with high correlation coefficients. Typical correlation coefficients greater than 0.99 were observed. Replicate injections of DIMP in acetone had a coefficient of variation of about 7% for the poorest conditions tested at low concentrations approaching the sensitivity limits of the detector. At concentrations of 0.05, 0.10 and 20.0 mg/l the coefficient of variation was only 3%. The observed variations are well within the variations observed for this type of analysis.

DIMP was found to be stable in acetone, the elution solvent. The stability of DIMP in acetone has important implications for the mundane manipulations and processing of samples. The levels of DIMP in acetone showed little change over a period of 20 days for a range of 0.1 to 10.0 mg/l at $4^{\circ}C$ and 23-$25^{\circ}C$ under dark and natural light conditions. For DIMP this means that samples may be collected, adsorbed and eluted in the field, and shipped to a laboratory for subsequent quantitative analysis

without any special handling. Determinations in the field may be conducted without any special precautions concerning the sample.

The adsorption and elution of the DIMP on the octylsilane bonded silica gel cartridge was quantitative and overall recoveries in tap water and tap water with 5000 mg/l of salt at neutral and slightly alkaline pH were 94.1% or greater for samples of 1.0 mg/l DIMP and greater than 89.2% for samples of 10.0 mg/l DIMP. There appeared to be decreased recovery for water samples at acidic pH at the 10.0 mg/l level. Only 86.0% and 88.8% of the DIMP was recovered under these conditions. These results must be treated with caution since variation in detector sensitivity was encountered during the analysis. It is also possible that the extraction columns were overloaded for the 10.0 mg/l samples. Relatively large volumes of 15 and 25 ml were passed through the adsorption columns for these samples. During reverse osmosis trials, only 2 ml were extracted for the feed water samples.

The addition of the extraction step increased the variability associated with the overall measurement. The coefficient of variation for replicate extraction and analysis was 14.6% for low concentrations found in the product water. It should be noted that the levels approached the lower sensitivity limit. For the higher concentrations observed in the feed water the coefficient of variation was only 2.6% The data suggested the overall recovery of the DIMP was sufficient for concentrations to be expected in this study. The data also suggested that variation may be decreased by increasing the sample size . The adsorption step could be used to concentrate the low level samples and increase the quantity of material analyzed by the gas chromatograph.

Once worked out, the procedure was found to be simple, easy, rapid and relatively inexpensive. The sample collection, extraction and gas chromatographic procedures could all be automated and large numbers of samples could be processed efficiently. The procedure may be interupted at several points allowing transport to places where the analysis may be continued more efficiently and economically. The analytical approach is sufficiently developed to test other simulants developed in the literature search. Preliminary trials have been conducted with DMMP and DEHP. These compounds may be analyzed under chromatographic conditions similar to DIMP.

STABILITY IN AQUEOUS SOLUTIONS

To be of value as a simulant for the agents to be removed by reverse osmosis the simulant should be stable in aqueous solution to facilitate testing. Information in the literature suggested that DIMP was stable in water. At the temperatures of 4-40^{o}C and pH values of 5 - 10 expected to be encountered in the aquatic environment, the hydrolysis of DIMP would be slow (Bel'skii et al., 1975). Studies were conducted in our laboratories to determine the stability of DIMP under conditions closer to field conditions. DIMP was added to tap water and tap water with 5000 mg/l NaCl at pH 5.0, 7.0 and 9.0. The latter conditions with salt were intended to approximate brackish waters. Each test was conducted over the range of concentrations of DIMP expected to be encountered in the test system (0.10, 1.00, and 10.0 mg/l). For each concentration of DIMP and aquatic conditions, the simulant appeared to be stable for a 14 day period. While the stability of DIMP was expected, the data collected covered the conditions to be used in subsequent experiments. In addition, the DIMP

stability trials in aqueous solutions served to establish workable experimental protocols for future studies.

REMOVAL OF DIMP BY REVERSE OSMOSIS

Trials were conducted in the reverse osmosis test stand supplied by Ft. Belvoir Research and Development Center at the JHU field station at Edgewood Area. DIMP was added to dechlorinated tap water at about 20 mg/l and the reverse osmosis unit was operated as a closed loop system. The temperature range over the course of the test was 23-33°C and the pH was 7.1. DIMP was rejected at better than 99% for the conditions tested. The level of DIMP was reduced from 15 mg/l in the feed water to 0.04-0.08 mg/l in the product water. The addition of 5000 mg/l of salt had little demonstrable effect on the rejection of DIMP in the reverse osmosis test system . Similar rejections were found for the trials conducted by the CRDC group with their reverse osmosis test stand and assayed in our laboratory. The average level of DIMP in the feed water was 22.6 mg/l and the average concentration in the product water was 0.12 mg/l in tap water trials. The average level of DIMP in the feed water was 22.0 mg/l and the average level in the product water was 0.08 mg/l in the brackish water trial. Again slightly better removal was observed for the brackish water.

Unfortunately no data is available at this time for the anticholinesterase agents from CRDC to permit a comparison with the rejection rates observed for DIMP. The suitability of DIMP as a simulant therefore cannot be judged with respect to removal by reverse osmosis. Some data for the removal of anticholinesterase agents by reverse osmosis was reported by Lindsten (1978). Removals of 99.9 and 99.1 were reported

CONCLUSIONS

1. DIMP and DMMP were chosen as possible simulants for acetyl choline esterase inhibitors for testing reverse osmosis membranes.

2. The system developed for the extraction and analysis of DIMP was sensitive enough to permit assay down to the 0.02 mg/l range presently established by the Surgeon General for acetyl choline esterase inhibitors.

3. The extraction, elution, and assay steps provide a method that may be adapted to other simulants and lower levels of detection.

4. DIMP was stable in acetone for at least 20 days and allows for a flexible sample processing schedule.

5. DIMP was stable in water and will not require special consideration for development of membrane test protocols.

6. The levels of DIMP in the product water was 0.04 to 0.09 mg/l in tap water and 0.03 to 0.06 in the brackish water trials. This corresponded to about 99.7% and 99.8% rejection, respectively. The salt rejection for the brackish water trials was approximately 99%. Similar DIMP rejection was observed for trials conducted by CRDC.

7. A comparison between removal of the DIMP and the acetyl choline esterase inhibitors by reverse osmosis cannot be made. Information on the rejection of nerve agents by the membrane used in this study is not yet available.

RECOMMENDATIONS

1. The current project has set up general operational methods and procedures that allow for the assay and application of simulants for the testing of reverse osmosis membranes and reverse osmosis systems. A good deal of time and effort was directed toward the development of an analytical methodology and procedures that would be applicable to a broad range of possible simulants and have the necessary sensitivity and specificity. The studies should be continued and expanded to evaluate additional simulants and other membranes.

2. The ultimate test for the simulants would be a thorough comparison of the simulant with the agent under conditions as close to "in use" conditions as possible. Unfortunately, open testing of the nerve agents is not possible but after preliminary comparative testing under controlled conditions, the functional simulants can be tested in the field. This would allow a thorough evaluation of the effects of different water quality parameters on the rejection rates under realistic conditions.

3. The analytical method used in this study employed a gas chromatograph with a nitrogen-phosphorous detector. The gas chromatograph performed well, but considerable time was spent with the detector. The advantages of the gas chromatographic method for analysis warrants further work to evaluate other detectors.

LITERATURE CITED

Bagley, F.D. et al. 1977. Simulant Review and Selection DPG Document No. DPG-1R-T-125A U.S. Army Dugway Proving Ground, Dugway, Utah 84022.

Banks, W., Sharples, F. 1964. Arthur D. Little Research Institute, Final Report to Office of Saline Water.

Bel'skii, U.E., et al. 1975. Kinetics of Dialkyl Methylphosphonate Hydrolysis Izu. Akad. Maus SSSR, Ser Kuin, 72:78155.

Blais, P. 1977. Polyamide Membranes. In: Reverse Osmosis and Synthetic Membranes. Edited by S. Sourirajan, National Research Council, Canada Publications.

Breton, E.J., Jr. 1957. Water and Ion Flow Through Imperfect Osmotic Membranes. Office of Saline Water Research and Development Progress Report No. 16 PB 161341.

Broadus, J. 1982. DIMP and DMMP in Water. Chemical Analysis Method, Rocky Mountain Arsenal, Commerce City, CO 80022.

Chian, E.S., et al. 1975. Removal of Pesticides by Reverse Osmosis. Environmental Science and Technology, 9(1):52.

Coon, P.A., et al. 1982 (Draft) Simulant Users Handbook. Chemical Systems Laboratory Special Publication, Chemical Systems Laboratory, Aberdeen Proving Ground, Maryland 21010

Fasamo, R. et al. 1982. Analytical Methods Development for Dimethyl Methylphosphonate Diisopropyl Methylphosphonate and Trimethylphosphate. Report DRXTH-TE-Cr. Final Task Report prepared for U.S. Army Toxic and Thazorcloric Material Agency, Aberdeen Proving Ground, Maryland. Arthur D. Little Inc., Cambridge, Massachusetts.

Hewlett Packard, Inc. 1974. Gas Chromatograph Instrument Manual Series 5830A, Avondale, PA.

Hewlett Packard, Inc. 1978. Operating Note: Evaluating and Optimizing the Performance of the Nitrogen-Phosphorous Detector.

Lindsten, Don C. 1972. Memorandum Report, 600 Gallon Per Hour Reverse Osmosis Water Purification Unit. Project Officer U.S. Army Material Development and Readiness Command.

Lonsdale, H.K. et al. 1965. J. of Appl. Polymer Sci. 9:1341

Nusbaum, I. 1981. Membrane Process—Design and Application. In: Proceedings Twenty-Third Annual Public Water Supply Engineer Conference. Champaign, Illinois.

Pusch, W. 1977. Determination of Transport Parameters of Synthetic Membrane by Hyperfiltration Experiments.

Sherwood, T.K. et al. 1967. Desalination by Reverse Osmosis 9 & EC Fundamentals 6:1.

Sourirajan, S. 1970. Reverse Osmosis. Academic Press, New York.

Spiegler, K.S., and Lavial, A.D.K. 1980. Principles of Desalination. Academic Press, New York.

Standard Methods for the Examination of Water and Wastewater. 1980. APHA-AWWA-WPCF.

Supelco, Inc. 1983. Troubleshooting Guide, Bellefonte, PA.

BIBLIOGRAPHY

Anderson, J.E., et al. 1972. Factors Influencing Reverse Osmosis Rejection of Organic Solutes From Aqueous Solutions. The Journal of Physical Chemistry. 76(26):4006 .

Ford, A., et al. 1974. Removal of f2 Virus from Water by Army Water Purification Units. NTIS AD-A-005557.

Gregg, S.J. 1961. The Surface Chemistry of Solids. The Whiterfriars Press Ltd., London, England.

Lacey, R.E. 1972. Membrane Separation Processes. Chemical Engr., 79:56-74.

Lindsten, D.C. and Schmitt. 1976. Decontamination of Water Containing Chemical Warfare Agents. Report 2125, U.S. Army Mobility Equipment Research and Development Center, Fort Belvoir, Virginia.

Loeb, S. 1966. High Flux Cellulose Acetate Membranes. In: Merten (ed) Desalination by Reverse Osmosis, The MIT Press, Boston, Massachusetts.

Lonsdale, H.K. 1982. The Growth of Membrane Technology. J. of Membr. Sci. 10:81-181.

Merten, U., and Bray, D.T. 1966. Reverse Osmosis for Water Reclamation. Third Inter. Conf. on Water Pollut. Res., Munich, Germany.

Michaels, A.S. and Porter, M.C. 1971. Membrane Ultrafiltration. Chem. Tech. 57.

Outterson, G.C. and Prociv T.M. 1980. Ed. Proceeding of Toxic Substance Control: Decontamination Symposium Sponsored by Chemical Systems Laboratory, Aberdeen Proving Ground, Maryland 21010.

Porter, M.C. 1975. Selecting the Right Membrane. Chem. Eng. Prog. 71:55,

Reid, C.E. 1966. Principles of Reverse Osmosis. In: Merten (ed.), Desalination by Reverse Osmosis. The MIT Press, Boston, Massachusetts, pp. 1-15.

Reid, C.E. and Breton, E.J. 1959. Water and Ion Flow Across Cellulosic Membranes. J. Appl. Polymer Sci. 1:133.

Riley, R.L. et al. 1971. Preparation Morphology and Transport of Composite Reverse Osmosis Membranes for Seawater Desalination. Office of Saline Water Symposium on Membrane Transport.

Saltonstall, C.W., Jr. 1976. Practical Aspects of Sea Water Desalination by Reverse Osmosis. Principles and Desalination 18:315-320.

Sliger, H.B. and Quinn, R. 1976. Application of Membrane Processes Desalination 19.

Tang, T.L. Don, et al. 1981. Application of Membrane Technology. Ind. Water Eng., 18-26.

APPENDIX 1

SIMULANT DATA SHEETS FROM CRDC

RECORD NUMBER

1	ENTRY	= 20
2	TYPE	= COMPOUND
3	CONTAINS AGENT	= NO
4	COMMON NAME	= BIS(2-METHOXYETHYL)ETHER OR BME
5	TECH NAME	= DIETHYL GLYCOL DIMETHYL ETHER
6	MOLEC WT	= 134.17
20	FORMULA	= C6H14O3
21	LOGTEN VPR PRESS MMHG	= .465
22	X21 TEMP DEGC	= 25
24	LIQ DENS GM/CC	= .9554
25	X23-24 DENS TEMP DEGC	= 25
26	VAPOR DENS ATM	= 4.6300
27	X26 TEMP DEGC	= 25
28	BOILING POINT DEGC	= 162
29	X28 PRESS MMHG	= 760
31	WLN	= 1O2O2O1
32	MELTING PT DEGC	= -68
34	SURFACE TENSION DYNES/CM	= 29.30
35	X34 TEMP DEGC	= 25
38	LOGTEN CENTISTOKE VISCOSITY	= .009
39	X38 TEMP DEGC	= 25
40	LOGTEN VOLATILITY MG/METER3	= 4.324
41	X40 TEMP DEGC	= 25
42	MOLEC DIFFUS COEFF CM2/SEC	= .061
43	X42 TEMP DEGC	= 25
44	LOGTEN HEAT OF VAPORIZATION KCAL/KG	= 1.868
47	REFRACTIVE INDEX	= 1.4097
48	X47 TEMP DEGC	= 20
49	SOL IN WATER	= MISCIBLE
67	LOGTEN ETV KCAL/KG	= 2.150
68	SPEC HEAT CP KCAL/(KG DEGC)	= .5000
74	FLASH POINT DEGC	= 70
75	HILDEBRAND SOL PARA	= 3.0

RECORD NUMBER 3

1	ENTRY	= 44
2	TYPE	= COMPOUND
3	CONTAINS AGENT	= NO
4	COMMON NAME	= DIETHYL SULFITE OR DIS
5	MOLEC WT	= 138.19
20	FORMULA	= C4H10O3S
21	LOGTEN VPR PRESS MMHG	= .533
22	X21 TEMP DEGC	= 25
24	LIQ DENS GM/CC	= 1.0789
25	X23-24 DENS TEMP DEGC	= 25
28	BOILING POINT DEGC	= 120
29	X28 PRESS MMHG	= 760
71	WLN	= 2O 2SO
74	SURFACE TENSION DYNES/CM	= 29.70
75	X34 TEMP DEGC	= 25
78	LOGTEN CENTISTOKE VISCOSITY	= -.108
79	X38 TEMP DEGC	= 25
40	LOGTEN VOLATILITY MG/METER3	= 4.405
41	X40 TEMP DEGC	= 25
42	MOLEC DIFFUS COEFF CM2/SEC	= .064
48	LOGTEN HEAT OF VAPORIZATION KCAL/KG	= 1.832
57	LOGTEN ETV KCAL/KG	= 2.053
75	HILDEBRAND SOL PARA	= 8.9
81	QUOTE SOURCE	= MCB

RECORD NUMBER 6

1	ENTRY	= 67
2	TYPE	= COMPOUND
3	CONTAINS AGENT	= NO
4	COMMON NAME	= ETHYL DIMETHYL PHOSPHITE
5	MOLEC WT	= 138.11
20	FORMULA	= C4H11O3P
21	LOGTEN VPR PRESS MMHG	= .531
22	X21 TEMP DEGC	= 25
24	LIQ. DENS GM/CC	= 1.0040
25	X23-24 DENS TEMP DEGC	= 25
28	BOILING POINT DEGC	= 124
31	WLN	= 10 2PO2
34	SURFACE TENSION DYNES/CM	= 31.20
35	X34 TEMP DEGC	= 25
38	LOGTEN CENTISTOKE VISCOSITY	= -.237
39	X38 TEMP DEGC	= 25
40	LOGTEN VOLATILITY MG/METER3	= 4.403
41	X40 TEMP DEGC	= 25
42	MOLEC DIFFUS COEFF CM2/SEC	= .067
43	X42 TEMP DEGC	= 25
44	LOGTEN HEAT OF VAPORIZATION KCAL/KG	= 1.350
57	LOGTEN ETV KCAL/KG	= 2.437
75	HILDEBRAND SOL PARA	= 7.3

RECORD NUMBER 1

1	ENTRY	= 19
2	TYPE	= COMPOUND
3	CONTAINS AGENT	= NO
4	COMMON NAME	= BIS
5	TECH NAME	= BIS(2-ETHYLHEXYL)PHOSPHONATE
6	MOLEC WT	= 306.42
10	FORMULA	= C16H35OP
21	LOGTEN VPR PRESS MMHG	= -3.194
24	LIQ DENS GM/CC	= .9300
25	X23-24 DENS TEMP DEGC	= 25
28	BOILING POINT DEGC	= 290
29	X28 PRESS MMHG	= 760
31	WLN	= 4Y2810 2PHO
34	SURFACE TENSION DYNES/CM	= 29.60
35	X34 TEMP DEGC	= 25
36	LOGTEN CENTIPOISE VISCOSITY	= .785
37	X36 TEMP DEGC	= 25
38	LOGTEN CENTISTOKE VISCOSITY	= .794
39	X38 TEMP DEGC	= 25
40	LOGTEN VOLATILITY MG/METER3	= 1.025
41	X40 TEMP DEGC	= 25
42	MOLEC DIFFUS COEFF CM2/SEC	= .038
43	X42 TEMP DEGC	= 25
44	LOGTEN HEAT OF VAPORIZATION KCAL/KG	= 1.633
45	LOGTEN HEAT OF COMBUSTION KCAL/KG	= 3.868
47	REFRACTIVE INDEX	= 1.4416
48	X47 TEMP DEGC	= 25
67	LOGTEN ETV KCAL/KG	= 2.559
68	SPEC HEAT CP KCAL/(KG DEGC)	= .4000
72	LOGTEN SATN VAPOR CONC MG/M3	= 1.025
74	FLASH POINT DEGC	= 165
75	HILDEBRAND SOL PARA	= 6.2

RECORD NUMBER 7

1 ENTRY	= 39
2 TYPE	= COMPOUND
3 CONTAINS AGENT	= NO
4 COMMON NAME	= DIETHYL PHOSPHONATE OR DEHP
5 TECH NAME	= DIETHYL PHOSPHITE OR DIETHYL HYDROGEN P
6 MOLEC WT	= 138.11
20 FORMULA	= C4H11O3P
21 LOGTEN VPR PRESS MMHG	= .505
22 X21 TEMP DEGC	= 25
24 LIQ DENS GM/CC	= 1.0578
28 BOILING POINT DEGC	= 183
29 X28 PRESS MMHG	= 760
31 WLN	= 20 2PHO
34 SURFACE TENSION DYNES/CM	= 30.35
35 X34 TEMP DEGC	= 25
36 LOGTEN CENTIPOISE VISCOSITY	= .068
37 X36 TEMP DEGC	= 25
38 LOGTEN CENTISTOKE VISCOSITY	= .053
39 X38 TEMP DEGC	= 25
40 LOGTEN VOLATILITY MG/METER3	= 4.373
41 X40 TEMP DEGC	= 25
42 MOLEC DIFFUS COEFF CM2/SEC	= .069
43 X42 TEMP DEGC	= 25
44 LOGTEN HEAT OF VAPORIZATION KCAL/KG	= 1.820
47 REFRACTIVE INDEX	= 1.4073
48 X47 TEMP DEGC	= 20
49 SOL IN WATER	= SOL
67 LOGTEN ETV KCAL/KG	= 2.170
68 SPEC HEAT CP KCAL/CKG DEGC)	= .5350
69 X68 TEMP DEGC	= 55
71 AUTOIGNITION TEMP DEGC	= 224
74 FLASH POINT DEGC	= 32
75 HILDEBRAND SOL PARA	= 8.1

RECORD NUMBER 4

1	ENTRY	= 42
2	TYPE	= COMPOUND
3	CONTAINS AGENT	= NG
4	COMMON NAME	= DIETHYL SEBACATE OR DES
6	MOLEC WT	= 258.36
20	FORMULA	= C14H26O4
21	LOGTEN VPR PRESS MMHG	= -3.252
22	X21 TEMP DEGC	= 25
24	LIQ DENS GM/CC	= .9597
25	X23-24 DENS TEMP DEGC	= 25
28	BOILING POINT DEGC	= 307
31	WLN	= 20V8V02
34	SURFACE TENSION DYNES/CM	= 32.30
35	X34 TEMP DEGC	= 25
36	LOGTEN CENTIPOISE VISCOSITY	= .708
37	X36 TEMP DEGC	= 25
38	LOGTEN CENTISTOKE VISCOSITY	= .732
39	X38 TEMP DEGC	= 25
40	LOGTEN VOLATILITY MG/METER3	= .892
41	X40 TEMP DEGC	= 25
42	MOLEC DIFFUS COEFF CM2/SEC	= .043
43	X42 TEMP DEGC	= 25
44	LOGTEN HEAT OF VAPORIZATION KCAL/MO	= 1.814
47	REFRACTIVE INDEX	= 1.4369
48	X47 TEMP DEGC	= 20
75	HILDEBRAND SOL PARA	= 7.8

RECORD NUMBER 5

1	ENTRY	= 41
2	TYPE	= COMPOUND
3	CONTAINS AGENT	= NO
4	COMMON NAME	= DIETHYL PHTHALATE OR DEP
5	TECH NAME	= ETHYL PHTHALATE
6	MOLEC WT	= 222.23
20	FORMULA	= C12H14O4
21	LOGTEN VPR PRESS MMHG	= -3.180
22	X21 TEMP DEGC	= 25
24	LIQ DENS GM/CC	= 1.1230
25	X23-24 DENS TEMP DEGC	= 25
26	VAPOR DENS ATM	= 7.6500
28	BOILING POINT DEGC	= 296
29	X28 PRESS MMHG	= 760
31	WLN	= 2OVR BV02
32	MELTING PT DEGC	= -40
34	SURFACE TENSION DYNES/CM	= 36.10
35	X34 TEMP DEGC	= 25
36	LOGTEN CENTIPOISE VISCOSITY	= 1.049
37	X36 TEMP DEGC	= 25
38	LOGTEN CENTISTOKE VISCOSITY	= 1.000
39	X38 TEMP DEGC	= 25
40	LOGTEN VOLATILITY MG/METER3	= 1.556
41	X40 TEMP DEGC	= 25
42	MOLEC DIFFUS COEFF CM2/SEC	= .049
43	X42 TEMP DEGC	= 25
44	LOGTEN HEAT OF VAPORIZATION KCAL/KG	= 1.780
45	LOGTEN HEAT OF COMBUSTION KCAL/KG	= 3.783

47 REFRACTIVE INDEX	= 1.5062
48 X47 TEMP DEGC	= 25
49 SOL IN WATER	=/INSOL
68 SPEC HEAT CP KCAL/[KG DEG C]	= .4500
71 AUTOIGNITION TEMP DEGC	= 457
72 LOGTEN SATN VAPOR CONC MG/M3	= .897
73 X72 TEMP DEGC	= 25
74 FLASH POINT DEGC	= 152
75 HILDEBRAND SOL PARA	= 8.0
77 COST UNITS	= POUND
78 COST QUOTE	= .50
81 QUOTE SOURCE	= MATHESON-COLE-BELL

APPENDIX 2

DETAILED CHEMICAL PROPERTIES AND REACTIVITY
OF CHEMICAL AGENT SIMULANT COMPILED BY
ENVIRONMENTAL TECHNICAL DIVISION CRDC

DRAFT

IDENTIFIER	CHEMICAL NAME	CAS REG NO
DIMP	Diisopropyl methylphosphonate	1445-75-6

CHEMICAL FORMULA: $C_7H_{17}O_3P$

SYNONYMS: Phosphonic acid, methyl-, diisopropyl ester; phosphonic acid, methyl-, bis (1-methylethy ester; diisopropyl methylphosphonate; methanephosphonic acid, diisopropyl ester.

DISCRIPTORS: DIMP belongs to a group of compounds known as organophosphates.

CHEMICAL AND PHYSICAL PROPERTIES:

Property	Value (Ref)	Property	Value (Ref)
Molecular weight	180 (1)	Specific gravity	0.98 g/ml (1)
Boiling point	174°C (1)	Solubility	0.1 - 0.2% (1)
Flash point	71°C (2)		

MILITARY APPLICATION: DIMP is used as a simulant for the G-agents. The compound has spectral characteristics similar to those of the G-agents, and is therefore used in general remote detection.

INDUSTRIAL APPLICATION: DIMP has no industrial application.

STORAGE, SHIPPING, AND HANDLING: DIMP is classified as a combustible liquid as defined in the US Department of Transportation 49 CFR 173.115 (b).[3] The compound is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA), (40 CFR 261.33), and its high flash point (71°C) does not qualify it as a hazardous waste on the basis of ignitability, as defined in 40 CFR 261.21.[4]

FROM COMPILATION BY ENVION TECH DIV ON CURRENT CHEM AGENT SIMULANTS

TOXICOLOGY: Acute toxicity of DIMP.

ROUTE	SPECIES	DOSE	EFFECTS/REMARKS (Ref)
Intravenous	Rabbit	224 mm^3/kg undiluted	caused local irritation (5)
Percutaneous	Rabbit	> 200 mm^3/kg undiluted	no irritation at the site of application (5)
Ocular (eye)	Rabbit	0.25 mm^3/eye undiluted	inflammation, mild to severe, neg in 24 hours, lacrimation, edema - slight, neg in 24 - 48 hrs. (5)
Intraperitoneal	Mice	> 250 mg/kg undiluted	LD_{50} (5)
Inhalation (total exposure)	Mice	Ct = 24,811 mg min/m^3 (t=43 min)	0/10 died in 14 days after exposure in a 386 liter chamber. The average chamber concentration was 577 mg/m^3. No toxic signs. (5)
Subcutaneous	Rat	> 200 mg/kg undiluted	LD_{50} (5)
Oral	Duck	1490 mg/kg	LD_{50} (6)
	Bird	1000 mg/kg	LD_{50} (6)
	Mammal	503 mg/kg	LD_{50} (6)
	Cattle	750 mg/kg	LD_{50} (7)

Carcinogenicity: An extensive search of the literature did not present any data on the carcinogenity of DIMP.

Mutagenicity: Hart[8] has reported that specially purified samples of DIMP proved to be non-mutagenic when administered to mice, rats, and dogs.

Teratogenicity: Hart[8] also reported that no teratogenic effects were observed in rats given dietary levels of 80, 250, or 750 ppm on days 6 through 15 of gestation. He observed that the compound produced no teratogenic effects in rats when dietary levels of 300-3000 ppm was given on days 6 through 15 of gestation. Dietary incorporation of DIMP at 300-3000 ppm produced no dose-related reproductive response in the rat over 3 successive generations with 2 matings per generation.

Health Hazards: DIMP imposes a minor acute inhalation hazard. The compound is slightly irritating to the eyes, nose, skin, and respiratory tract. Presently, no threshold limit value (TLV) has been established for DIMP.

Plant Data: No data was found on this subject.

CHEMICAL REACTIVITY:[9]

Alkali and Alkaline Earth Metals: An exothermic reaction may occur upon mixing DIMP with alkali and alkaline earth metals.
Azo Compounds: Azo compounds may react with DIMP to produce hazardous conditions.
Caustics: The hydrolysis of DIMP under alkaline conditions yields isopropyl alcohol and metal salt of methylphosphonic acid.
Epoxides: The reaction between DIMP and epoxides may produce hazardous conditions.
Mineral Acids: Excessive strong mineral acids can cause decomposition of DIMP to yield primarily alcohol and methylphosphonic acid.[10]
Organic Peroxides: There is very little available information on the reaction of DIMP with organic peroxides. The reaction between the organic peroxides and DIMP may produce hazardous conditions.
Oxidizing Agents: The exhaustive oxidation of DIMP can yield toxic and corrosive fumes of oxides of phosphorus, sulfur, nitrogen, and heat.
Oxidizing Mineral Acids: Excessive oxidizing acids can decompose DIMP to yield heat and toxic fumes of nitrogen oxides, sulfur oxides and phosphorus oxides.
Reducing Agents: For information on the reducing agents, see alkali and alkaline earth metals above.
Water Reactives: The water reactive materials may react with DIMP to produce highly unstable mixtures, heat and toxic and/or flammable gases.

ENVIRONMENTAL FATE: Organophosphorus compounds such as DIMP are subject to biological and chemical degradation upon entering the natural environment.[11(a)] The ultimate degradation product is orthophosphoric acid (H_3PO_4) or orthophosphate salts. Chemical degradation occurs primarily through hydrolysis. The hydrolytic behavior of phosphate diesters such as DIMP is similar to that of the corresponding phosphate triesters[11(b)] while the hydrolytic behavior of the phosphonate monoester parallels that of the equivalent phosphate diester.[10] Under alkaline conditions, DIMP hydrolyzes much more rapidly to produce the monoisopropyl ester than the monoester does to produce methylphosphonic acid. DIMP and the monoester hydrolyze at approximately the same rates under acid conditions. Isopropyl methylphosphonate is very stable under neutral conditions. The primary products anticipated upon complete hydrolysis of DIMP are isopropyl alcohol (flammable, low boiling liquid), methylphosphonic acid, and various amounts of isopropyl methylphosphonate, depending on environmental conditions and the length of time. The rate of chemical hydrolysis of isopropyl methylphosphonate to produce methylphosphonic acid and ultimately phosphoric acid or its salts may be very slow, especially under alkaline conditions. However, hydrolysis rate can be greatly accelerated by the presence of microorganisms, enzymes, and other factors in the environment. DIMP's hydrolysis product, methyl phosphonic acid, is a very stable compound. The compound can be recrystallized from fairly strong hydrochloric acid or heated in boiling sodium hydroxide for several hours without change.[12] Methyl phosphonic acid and other phosphate derivatives are susceptible to further degradation by photolysis with sunlight and ultraviolet radiation to yield phosphonic acid derivatives.[13] Phosphonates may be assimulated and subsequently serve as a sole source of phosphorus for aquatic plants.[11(c)] Methyl phosphonic acid is also very slowly oxidized by ozone to orthophosphonic acid, carbon dioxide, and water. DIMP[14] and its hydrolysis products are water soluble and isopropyl alcohol is highly volatile. These factors would facilitate their disposition in the environment.

CONCLUSIONS: DIMP is an irritant of the eyes, nose, skin, and repiratory tract, and prlonged inhalation and skin contact should be avoided. Since it is not known whether DIMP is a carcinogen, personnel should take extra precautionary measures, and wear protective clothing, rubber gloves, and an approved respirator. It is suggested that the data gaps concerning the phytotoxicity and carcinogenicy of DIMP be investigated in the future.

REFERENCES:

1. Rosenblatt, David H. et. al., Problem Definition Studies on Potential Environmental Pollutants: Physical, Chemical, Toxicological, and Biological Properties of 16 Substances, US Army Medical Research and Development Command, Forrestal Building, 1975.

2. Allen, Craig R., The Relationship Between Oxygen Index and the Flashing Propensity of Explosively Disseminated Liquids, October 1977.

3. Code of Federal Regulations, Vol. 49, Parts 100-177, US Government Printing Office, Washington, DC, 1981.

4. Code of Federal Regulations, Vol. 40, Parts 190-399, US Government Printing Office, Washington, DC, 1981.

5. Jacobson, Keith, H., The Acute Toxicity of Some Intermediates in GB Manufacture, Chemical Corps Medical Laboratories Special Report, February 1953.

6. Aulerich, R. J., Coleman, T. H., Polin, D., Ringer, R. K., Howell, K. S., Toxicology Study of Diisopropyl Methylphosphonate and Dicyclopentadiene in Mallard Ducks, Bobwhite Quail and Mink, Michigan State University East Lansing Department of Poultry Science, DAMD17-76-C-6054, April 76 - June 79.

7. Palmer, J. S. et. al., Toxicologic Evaluation and Fate of Diisopropyl Methylphosphonate (DIMP) and Dicyclopentadiene (DCPD) in Cattle, Science and Education Administration College Station TX Veterinary Toxicology and Entomology Research Laboratory, March 77-Sep 79.

8. Hart, E. R., Mammalian Toxicological Evaluation of DIMP and DCPD, Government Reports Announcements and Index (GRA + I), Issue 15, 1980.

9. A Method for Determining the Compatibility of Hazardous Wastes, April 1980.

10. Keary, Leonard, Canadian Journal of Chemistry, Vol 43, pg 2637, 1965.

11. Griffith, E. J., et. al., Environmental Phosphorus Handbook, John Wiley and Sons, New York, (a) pg 250; (b) pg. 259; (c) pg 242, 1973.

12. Corbridge, D. E. C., Phosphorus, An Outline of its Chemistry, Biochemistry and Technology; Elsevier Scientific Publishing Co., New York, pg. 204, 1978.

13. Libby, R. A., Inorganic Chemistry, Vol 10, No. 2, pg. 386, 1971.

14. Coon, Phillip, Research Division, Chemical Research and Development Center, Aberdeen Proving Ground (APG), MD, July 1983.

DRAFT

IDENTIFIER	CHEMICAL NAME	CAS REG NO.
DMMP	Dimethyl methylphosphonate	756-79-6

CHEMICAL FORMULA: $(CH_3O)_2P(O)CH_3$

SYNONYMS: Methanephosphonic acid, dimethyl ester; dimethyl methane-phosphonate; dimethoxymethylphosphine

DISCRIPTORS: DMMP belongs to a group of stable organophosphorus esters known as the dialkyl alkylphosphonates. It is classified as a diester of methylphosphonic acid.

CHEMICAL AND PHYSICAL PROPERTIES: DMMP is a clear, colorless, mobile liquid with a very mild characteristic odor. The compound is miscible with water, alcohols, esters and aromatic solvents, but immiscible in aliphatic hydrocarbons. Selected chemical and physical parameters are listed below:

Property	Value (Ref)	Property	Value (Ref)
Molecular weight	124.1 (1)	Flash point	104.4°C; Open Cup (Cleveland) (1)
Boiling point	181°C, 54 mm Hg (4)	Viscosity (Centistokes)	1.81, 25°C (1)
Melting point	below -50°C (2)	Vapor pressure	*0.61 mm Hg, 20°C (3)
Specific gravity	1.174, 20°C (1)	Volatility	4100 mg/m^3 (3)
Vapor specific gravity	*4.3 (3)	Solubility	miscible

note: *estimated values

MILITARY APPLICATION: DMMP is extensively used as the simulant for simulating non-persistent chemical agents. The compound is a volatile agent simulant, and is used in vehicle penetration/vulnerability studies, protective mask filter element quality assurance tests, freon decontamination tests, chemical units, and teams decontamination capabilities studies (with K125 thickener), aircraft spray tank dissemination tests (with K125 thickener), and the shelter vulnerability tests.

INDUSTRIAL APPLICATION: DMMP is used quite extensively in industry as a flame retardant additive and viscosity depressant in resins, such as unsaturated polyesters and epoxies. It is also used in heavy metal extraction, solvent separation, preignition additive for gasoline, as an antifoam agent, plasticizer and stabilizer, textile conditioner and antistatic agent, and as an additive in solvents and low temperature hydraulic fluids.

STORAGE, SHIPPING, AND HANDLING: DMMP is classified as a combustible liquid as defined in the US Department of Transportation (DOT) 49 CFR 173.115 (b),[5] and all storage, shipping, and handling procedures must be in accordance with the regulations therein. DMMP is not specifically listed as a hazardous substance, and its flash point (104.4°C) and oral toxicity value (150 mg/kg) do not qualify it as a hazardous waste as defined in 40 CFR 261.21.[6] The compound has been reported in the Environmental Protection Agency (EPA) Toxic Substances Control Act (TSCA) inventory since 1980.[7]

TOXICOLOGY: Acute toxicity of DMMP.

ROUTE	SPECIES	DOSE	EFFECTS/REMARKS/(Ref)
Oral	Rat	150 mg/kg (in corn oil)	LD_{50} (8)
	Rat	>4640 mg/kg	LD_{50} (9)
Intragastric	Rat	>3000 mg/kg	LD_{50} (1)
Intraperitoneal	White Leghorn Hen	50 mg/kg	lowest dose that produced visible detectable ataxia, produced no delayed neurotoxic activity (8)
Intraperitoneal	Mouse	250 µl/kg	0/10 died in 24 hr, 2/10 died in 7 days, weakness ataxia, prostration (10)
Inhalation (total exposure)	Mouse	3900 mg min/m^3 (Time = 10) (norminal concn. 77 ppm)	0/10 died in 10 days (Benesh machine) (11)
Percutaneous	Rabbit	> 4740 mg/kg	LD_{50} (9)
Subcutaneous	Mouse	50 mg/kg 300 mg/kg 100 mg/kg	0/2 died in 10 days (12) 0/2 died in 10 days (12) 0/2 died in 10 days (12)
Eye Irritation	Rabbits	4740 mg/kg	nonirritant (9)
Skin Effects	Human	240 l/kg	no effect (11)

Carcinogenicity: Little[13] reported that DMMP had no effect in asays which were indicative of dioxyribonucleic acid (DNA) damage or measured neoplastic transformation.

Mutagenicity: According to Little,[13] DMMP produced no mutagenic responses in the Ames Salmonella mutagenicity assays.

Teratogenicity: DMMP is currently being tested for teratogenic acitivity in a study conducted under the auspices of the National Toxicology Program, National Institute of Health. No official data has been released on the teratogenicity of DMMP.

Health Hazards: DMMP causes irritation of the eyes, skin, and respiratory tract. According to Dunnik,[14] the compound was toxic to the reproductive system of male rats. The author reported that with increasing doses of DMMP, the number of pregnancies decreased, the mean litter size decreased, and the percent of resorptions increased. The male rats showed some weight decrease, and at high doses DMMP showed an increase in the number of abnormal sperms.[14] Presently, no Threshold Limit Value (TLV) has been established for DMMP in humans.

Plant Data: Libby,[15] indicated in a recent publication that phosphonates will undergo photolytic reactions with sunlight to produce orthophosphates. The orthophosphates tend to serve as a sole phosphorus source to aquatic plants.

CHEMICAL REACTIVITY:[16]

Alkali and Alkaline Earth Metals: When DMMP is mixed with these metals, an exothermic reaction may occur.

Azo Compounds: DMMP may react with azo compounds to produce hazardous conditions. However, little information is available on these conditions.

Caustics: DMMP is slowly hydrolyzed under alkaline conditions to produce an alkali salt of methylphosphonic acid and methyl alcohol.[18]

Non-oxidizing Mineral Acids: The non-oxidizing mineral acids can hydrolyze DMMP to highly flammable methyl alcohol (flash point: 11°C) and methylphosphonic acid, a fairly strong acid (first ionization constant (pk_1) 2.3 at 20 - 25°C.[17]

Organic Peroxides: Mixing DMMP with organic peroxides may create hazardous conditions; however, little information is available.

Oxidizing Agents: Exhaustive oxidation of DMMP can yield toxic and corrosive fumes of oxides of phosphorus and other toxic compounds.

Oxidizing Mineral Acids: Excess oxidizing mineral acids can decompose DMMP to yield toxic fumes such as nitrogen oxides, sulfur oxides, and phosphorus oxides.

Reducing Agents: Dialkyl alkylphosphonates in general are resistant to reducing agents. Materials such as sodium or aluminum amalgam have little effect. Stronger reducing agents do react, but information is scant. An exothermic reaction may occur especially if the DMMP contains some water.

Water Reactives: DMMP can react with water reactive materials to yield heat along with toxic and/or flammable gases.

ENVIRONMENTAL FATE: "Having entered the natural environment, organophosphorus compounds are degraded by biological and/or chemical reactions to orthophosphate, the ultimate degradation product."[18] Hydrolysis is the primary chemical procedure for degrading organophosphorus compounds entering the environment. Phosphonate diesters (such as DMMP) are similar to phosphate triesters in their hydrolytic behavior.[18] The lower molecular weight dialkyl alkylphosphonates are moderately resistant to hydrolysis; however, hydrolysis will occur both under acidic, and less rapidly, under alkaline conditions. The primary products anticipated upon exhaustive hydrolysis are methyl alcohol and methylphosphonic acid or its salts (alkaline hydrolysis). Methyl alcohol is very volatile (boiling point: 64.5°C), and completely miscible with water; therefore, it would have little tendency to accumulate in the environment. The lower alkyl phosphonic acids such as methyl phosphonic acid are hygroscopic (absorbs water from the atmosphere) white crystalline solids. Methyl phosphonic acid melts at 105°C.[17,19] Methyl phosphonic acid is a fairly strong acid (pk_1: 2.3 at 20 to 25°C), and it would tend to form water soluble salts in an alkaline environment. Therefore, both the free methyl phosphonic acid and its salts would be washed away over a period of time. Dialkyl alkylphosphonates in general are resistant to reaction with oxygen and oxidizing agents.[9]

CONCLUSIONS: DMMP has been reported as an irritant of the eyes, skin, and possibly a nonspecific irritant of the upper respiratory tract. In addition, the compound causes sterility of the reproductive system in male rats. The compound has been reported to produce no mutagenic responses in the ames Salmonella Assays, and had no effect in assays which were indicative of DNA damage or measured neoplastic transformation. However, personnel should avoid contact by wearing protective clothing, rubber gloves, and an approved respirator since the compound produces sterility in male rats, and the teratogenic effects are not available.

REFERENCES:

1. Mobile Chemical Company, Product Information Bulletin, Dialkyl Alkylphosphonates, Industrial Chemicals Division, page 3.
2. Toxicology Laboratory Report T-4125, Stauffer Chemical Company, Western Research Center, Westport Connecticut, 06880.
3. Lyman, W. J.; et. al., eds., Handbook of Chemical Property Estimation Methods, New York: McGraw-Hill Book Company, 1982.
4. Tomlinson, G. J., and A. H. Samuel, Literature Survey of Physical and Chemical Properties of Agents VX, GD, HD, and HL, Vol 1, Final Report, July 1980. Chemical Systems Laboratory Contractor Report, ARCSL-CR 80051 (Battelle).
5. Code of Federal Regulations, Vol 49, Parts 100-177, US Government Printing Office, Washington, DC, 1981.
6. Code of Federal Regulations, Vol 40, Parts 190-399, US Government Printing Office, Washington, DC, 1981.
7. Lewis, Richard J., and Rodger L. Tatken, Registry of Toxic Effects of Chemical Substances, US Department of Health and Human Services, February, 1982.
8. Hollingshaus, J. G.; et., al., Delayed Toxicity and Delayed Neurotoxicity of Phosphorothioate and Phosphorothioate Esters, Journal of Toxicol. Environ. Health 8: 619-627, 1981.
9. Morey, H. W. Jr., "Toxicology Data on Fryol DMMP," Letter, Stauffer Chemical Company, Specialty Division, Westport, Connecticut, 6 Aug 1980.
10. Jones, Jr., H. W., et. al. The Relationship of Cholinesterase Inhibiting Activity to the Toxicity of Some Organic Phosphorus Compounds, Medical Division Reports no. 134, p. 11, April 1948.
11. Geiling, E. M. K. et al., (Compiled by HD Young) Division 9, National Defense Research Committee Office of Scientific Research and Development, OSRD No. 4176, Status Report on Toxicity and Vesicant Test of Compounds Referred to the University of Chicago Toxicity Laboratory Aug 1, 1944, Oct 3, 1944. Unclassified Report.
12. The University of Chicago Toxicity Laboratory, Informal Monthly Progress Report on Toxicity and Irritancy of Chemical Agents, Informal Report No. N.S. 1, p. 39, april 15, 1945.
13. Little, Arthur D., Evaluation of Dimethyl Methylphosphonate and Exo-Tetrahydrodi-(Cyclopentadiene) in a Battery of in Vitro Short-Term Assays, Air Force Aerospace Medical Research Laboratory, 1983.
14. Dunnick, June, Personal Communication, NIEHS, North Carolina, 1982.
15. Libby, Robert A., The Photolysis of Two Diphosphonates, Inorganic Chemistry, Vol 10, No. 2, 1971.
16. A Method for Determining the Compatibility of Hazardous Wastes, EPA-600/2-80-076, April 1980.
17. Van Wazer, J. R., Phosphorus and Its Compounds, Vol I, Interscience, New York, 1958.
18. Griffith, E. Jr., et al., Environmental Phoshporus Handbook, John Wiley and Sons, New York, 1973.
19. Corbridge, D. E. C.; Phosphorus, An Outline of the Chemistry, Biochemistry and Technology; Elsevier Scientific; New York; 1978.

APPENDIX 3

PERFORMANCE OF SELECTED COLUMNS FOR GAS CHROMATOGRAPHIC ANALYSIS

Performance of Selected Columns for Gas Chromatographic Analysis

1. 15% DEGS on 80/100 chromosorb WAW, 6' x 0.125" O.D., 0.085" I.D., stainless steel; Date: 4/29/77; max. temp. 200 C.

Prior use: unknown.

Most recent period of use: from ? to 9/23/83.

This column was replaced after difficulties had been encountered in obtaining a stable offset. Looking at the chromatograms in retrospect, it may be that the collector was the actual source of the problem, although deterioration of the column cannot be ruled out entirely. The column was operated at oven temperatures from 150 to 175°C.

2. HP test column: 2% OV 101 on 100/120 chromosorb W HP, 4' x 2 mm I.D., 1/4" O.D., glass; no date; max. temp. 350°C.

Prior use: Received with the N-P detector and used during initial checkout.

Most recent period of use: from 11/3/83 to 11/10/83.

This column was conditioned at 250°C overnight. The peak areas for DIMP were not reproducible. When operated with an oven temperature of 150 C, peaks showed unacceptable tailing. This was eliminated by raising the temperature to 175°C, but at this temperature, the separation between the negative acetone peak and the DIMP peak was insufficient. Integration of the DIMP peak therefore started before the response had returned to baseline. Reduction of the slope sensitivity lead to good positioning of the end integration mark, but did not ameliorate the peak separation problem at the start.

3. 10% Carbowax 20M on 80/100 chromosorb W HP, 6' x 0.125" O.D., 0.085" I.D., stainless steel; Date: 4/29/77; max. temp. 225°C.

Prior use: not known precisely. Reasonable results were obtained in the past with this column.

Most recent period of use: 9/28/83 to 11/1/83 (from 9/29 to 10/12, the GC was not used because the oven heating element had burned out).

Initially, the system seemed to perform acceptably with this column. However, subsequent difficulty in obtaining a stable offset resurfaced. In addition, injection of acetone resulted in dramatic drops in the offset. There was no substantial reason to doubt the integrity of the collector and a test comparing demoisturized acetone to untreated acetone yielded no indication that the solvent was the source of the problem. Column bleed with no other changes in the system was a possible explanation. Subsequent installation of solid phase columns resulted in a quite stable offset, which suggests that this column was not in good condition. It was operated at 150°C throughout this installation period.

4. 10% Carbowax 20M on 80/100 chromosorb W-HP, 2 m x 0.25" O.D., 2 mm I.D., glass; Date: 11/8/83; max. temp. 225°C.

Prior use: none.

Because the Carbowax column described above had performed adequately in the past, a new column was employed. Use of the glass column allowed on column injection. Operating with a column temperature of 165°C and carrier gas flow of 30 ml/min, the DIMP retention time was about 1.8 min. Peaks were reproducible and well formed. Satisfactory performance of this column resulted in its use for all gas chromatographic analysis of DIMP samples.

5. 80/100 Porapak QS, 6' x 0.125" O.D., stainless steel; Date: 10/24/83; max. temp. 250°C.

Prior use: none

Most recent period of use: 11/1/83 to 11/2/83

This solid phase column was tried since it would eliminate the possibility of column bleed. A stable offset was obtained. With injections of 0.2 and 10 mg/l DIMP in acetone, the acetone peak spread from 3 to 6 minutes and no other peaks were observed after a 20 minute wait. Rather than spend time experimenting with various temperatures a second solid phase column containing Tenax was installed.

6. 80/100 Tenax GC, 6' x 0.125 O.D., stainless steel; Date: 10/24/83, max. temp. 375°C.

Prior use: none

Most recent period of use: 11/2/83 to 11/3/83

The column was conditioned at 300°C. The acetone peak appeared at about 0.75 minutes with an oven temperature of 200°C. No DIMP peak was evident, but after 20 minutes and oven temperature increases to 290°C, a low bump did appear which may have represented the DIMP.

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