



Project Summary

Isolation or Concentration of Organic Substances from Water — An Evaluation of Reverse Osmosis Concentration

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This study describes the development and evaluation of a reverse osmosis (RO)/Donnan dialysis system for preparing drinking water concentrates for biological testing. Commercially available RO and Donnan membranes were surveyed for applicability to the RO concentration method and to prepare organic concentrates. Two RO membranes, cellulose acetate (Osmonics, Inc.)* and FT-30 (Film Tec, Inc.)*, were selected for laboratory evaluation, primarily because of their purported chlorine tolerance. Two Donnan membranes, Nafion® (Dupont)* and MA 3475 (IONAC)*, were chosen for further study based upon their chemical resistance characteristics (chlorine, caustic, and acid tolerance). The FT-30 membrane, a thin-film composite, demonstrated a substantially greater rejection efficiency than the cellulose acetate membrane. The effect of humic acid, a natural constituent of potable water sources, and inorganic salts on the rejection of model compounds by FT-30 and cellulose acetate RO membranes was also evaluated and found not to be significant under the test conditions.

As expected from the rejection data, the recoveries of model solutes were much better for the FT-30 membrane system than the cellulose acetate

system. Overall the recovery values (2-74%) were disappointing for the majority of model compounds in both RO systems and substantially less than anticipated based on the rejection data.

This Project Summary was developed by EPA's Health Effects Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In recent years, the trace organic content of potable water supplies has been identified as a potential health hazard. Epidemiological studies have suggested a relationship between the ingestion of these pollutants in drinking water and carcinogenic and teratogenic effects. Although hundreds of organic compounds have been detected and quantified in drinking water, the majority of organic material, i.e., the nonvolatile fraction, cannot be identified using currently available technology. Therefore, the direct concentration/isolation of organic contaminants in aqueous samples for biological testing offers a practical solution to the determination of health risks associated with trace organic contaminants.

The Health Effects Research Laboratory - Cincinnati of the U.S. Environmental Protection Agency (EPA) has

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

funded several independent studies to determine the effectiveness of different isolation/concentration techniques. Systems or techniques investigated include reverse osmosis (RO), vacuum distillation, solid adsorbents, and supercritical fluid CO₂ extraction. The necessity of concentrating aqueous samples prior to biological testing stems from the trace levels of contaminants and the lack of sensitivity associated with existing *in vitro* and *in vivo* biological test systems.

The RO concentration method has been used previously to prepare concentrates under several EPA tasks (EPA Contract Nos. 68-03-2090, 68-03-2194, 68-03-2367, 68-03-2464, 68-03-2550, and 68-03-2713). The method basically involves repetitive batch concentrations using a RO membrane to retain organics and reduce the sample volume (with an accompanying increase in concentration) by discarding water that permeates the membrane. The Donnan dialysis process has been used in several of the concentrations to minimize solids precipitation resulting from the increase in inorganic salt concentrations.

Previous studies utilized total organic carbon (TOC) measurements as a surrogate to monitor the progress or efficiency of the concentration. Although TOC is a convenient tool, it is a nonspecific measurement and provides little insight about either the rejection or recovery of specific chemicals. Therefore, a standard set of model compounds with differing functionalities, solubilities and sorption properties were selected to evaluate this and the other isolation/concentration techniques.

Experimental Procedures

Preparation of Model Compound Test Solutions

Test solutions of model compounds used in the membrane screening runs and in the membrane concentration runs were prepared by simply diluting the required volume(s) of stock solution with organic-free water containing an inorganic salt matrix. The membrane concentration runs utilized a "1X" salt matrix consisting of 70 ppm NaHCO₃, 120 ppm CaSO₄ and 47 ppm CaCl₂·2H₂O. In the membrane screening runs, a "5X" salt matrix representing a 5-fold increase in salt concentration was employed. Table 1 lists the final concentration at which each model solute was tested and the solvent used in the preparation of individual stock solutions.

Membrane Screening Tests

Four membranes were ultimately selected for screening tests based on commercial availability, salt rejection, stability at pH 5, and the ability to tolerate a low to moderate free chlorine residual (<5 ppm) which is commonly encountered in drinking water. The four considered to be the most promising were the cellulose acetate and FT-30 (thin-film composite) RO membranes, the Nafion® cation exchange membrane, and the IONAC MA 3475 anion exchange membrane. Initial objectives of the screening tests were:

- To determine specific membrane rejections with selected model organic solutes.
- To determine whether levels of humic acid typical of those experienced in drinking water significantly affected the organic solute rejections.
- To determine what trace organic compounds might leach from the membranes and to determine what effect a free chlorine residual might have on the types of substance(s) leached from the membranes.
- To determine whether flushing regimes typical of those used in previous RO concentrations were

adequate to eliminate contamination from leachate compounds.

- To provide sufficient data to estimate solute losses to the membranes and other system components.

A three-stage screening protocol was developed to evaluate the selected RO and Donnan membranes and to address the stated objectives. The three stages were *flushing*, *system blank determinations* and *membrane solute screening*. Figures 1 and 2 show the basic components of the RO concentration/Donnan dialysis system used for the preliminary screening of RO and ion exchanges membranes.

Because all the test runs were performed using the same basic membrane screening procedure, data on the adequacy of the flush procedure were obtained from each of the runs on leaching, chlorine exposure, organic model compound retention and humic exposure.

One important aspect to be considered in any system designed to concentrate organic chemicals from water is the possible leaching of organic compounds from components of the system. While nearly all the elements of the RO system are fabricated from glass, Teflon, or

Table 1. Model Compounds and the Conditions Used in the Evaluation of the Reverse Osmosis Concentration System

Model Compound	Concentration µg/L		Stock Solution Solvent	Method of Detection
	Membrane Screening Runs	Concentration Membrane Runs		
Isophorone	2500	50	Acetone	GC, GC/MS
2,4-Dichlorophenol	2500	50	Acetone	GC, GC/MS
Quinoline	2500	50	Acetone	GC, GC/MS
1-Chlorododecane	250	5	Acetone	GC, GC/MS
Biphenyl	2500	50	Acetone	GC, GC/MS
2,4-Dichlorobiphenyl	250	5	Acetone	GC, GC/MS
2,2',5,5'-Tetra-chlorobiphenyl	250	5	Acetone	GC, GC/MS
2,6-di-tert-butyl-4-methylphenol	2500	50	Acetone	GC, GC/MS
Caffeine	2500	50	Acetone	GC, GC/MS
Anthraquinone	2500	50	Acetone	GC, GC/MS
Stearic Acid	2500	50	Acetone	GC, GC/MS
bis(2-Ethylhexyl)-phthalate	2500	50	Acetone	GC, GC/MS
Trimesic Acid	2500	50	Acetone	HPLC
Furfural	2500	50	Acetone	HPLC
5-Chlorouracil	2500	50	H ₂ O	HPLC
Glycine	2500	50	H ₂ O	Fluorescence
Glucose	N.T.	50	H ₂ O	Liquid Scintillation
Chloroform	2500	50	Acetone	GC
Methylisobutyl ketone	2500	50	Acetone	GC, GC/MS
Humic Acid	2000	2000	NaOH	HPLC

N.T. = Not Tested

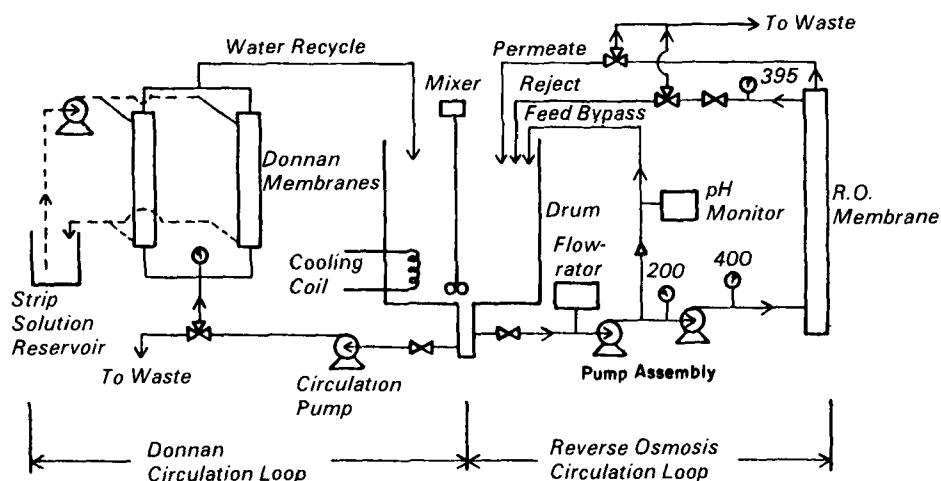


Figure 1. Major components of a reverse osmosis (RO) concentration/Donnan dialysis organic recovery system.

stainless steel, other components of the concentration system such as membranes, adhesives and seals are made from synthetic organic materials. Chemical analyses for organic leachables included examination for low molecular weight halogenated compounds (primarily trihalomethanes), semivolatile priority pollutants by GC/MS (EPA Method 625), as well as the model solutes.

It was necessary to evaluate the effect that low levels of disinfectant would have on the membranes and other system components because they are exposed to residual disinfectant during the preparation of drinking water concentrates. The effect of the chlorine exposure was determined by dosing the system blank water with sodium

hypochlorite and examining the recirculated water after 4 hours.

Experiments designed to measure the ability of the membrane system to concentrate the model solutes were also conducted and represented the single most important aspect of the project. The two primary objectives of these experiments were to determine the membrane's ability to retain the model compounds (i.e., its solute rejection) and to determine the extent of losses via mechanisms such as volatilization, adsorption, or solubility limitations. Each of the four membranes (cellulose acetate, FT-30, Nafion®, and MA 3475) were evaluated in a series of membrane/solute screening tests. Three samples were routinely collected during each run. The recirculating water or feed was sampled

at 5 min (0.08 hr) and at the end of a 4-hr period of total recirculation (i.e., where both the permeate and concentrate are returned to the process reservoir) to allow the calculation of solute losses to the environment and system components (adsorption, volatilization). A third sample, taken from the permeate stream, was collected after 4 hr. By utilizing this type of sampling program it was possible to determine solute rejections for each membrane using Equation 1 and to estimate system losses by comparing the initial and final concentrations of solutes in the recirculating feed solution.

$$\% \text{ Rejection} = 100 \frac{(1 - C_p/C_f)}{(Eq. 1)}$$

where

C_p = permeate conc. of solute
 C_f = feed conc. of solute.

Since very little water is transported across the Donnan (ion exchange) membranes a permeate sample is not relevant. Instead, the Donnan membranes were dialyzed against a salt, acid, or base solution, and this "strip" or "pump" solution was sampled at the same time (4 hr) as the last sample from the process reservoir. This allowed an estimation of the amount of solute lost to the chemical pump solution.

Because humic acid comprises a major portion of the dissolved organic material in drinking water, its effect on the membrane systems and model solute rejection was surveyed. The concentration of humic acid varies from source to source but it is not uncommon to find 1-5 mg/L of humic material present in surface sources. A concentration of 2 mg/L was selected for this study.

Membrane Concentration Tests

The primary objective of the membrane concentration tests was to evaluate the efficiency of the RO/Donnan dialysis concentration system for concentrating trace levels of model solutes (1-50 ppb) in 500L of water.

Figure 3 illustrates the major processing steps in the concentration of 500 liters of organically spiked water. The concentration was designed to reduce 500 liters to 10 liters and incorporates two major types of membrane processes, RO concentration and Donnan dialysis. First, an RO system was used to reduce (and concentrate) three 167-liter batches to 13.5 liters each. RO concentration was temporarily interrupted at 12.6X volumetric concentration as this level of concentration was found to approach the in-

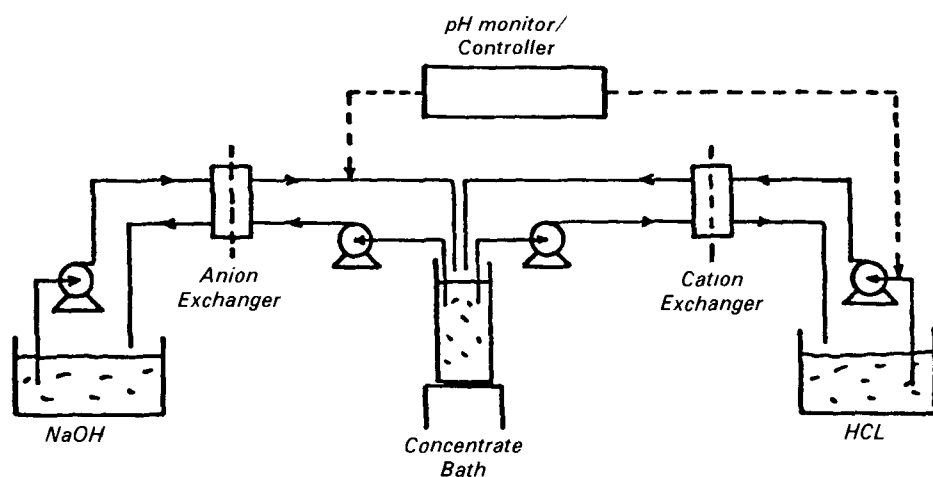


Figure 2. Simplified drawing of a Donnan dialysis test apparatus.

organic solubility threshold. At this time, the second membrane process, Donnan softening, was used to reduce the concentration of calcium ions and thereby avoid any inorganic salt preparation.

Following the 4-hr Donnan softening treatment, the RO concentration was resumed until a 50-fold concentrate was obtained. A slight volumetric decrease (with an accompanying increase in concentration factor) was experienced during Donnan softening due to osmotic pumping of water from the concentrate into the salt "pump" solution.

In Figure 3, the asterisks indicate the samples that were collected at various points during the concentration run to monitor its progress. Three streams were sampled during each concentration run: the concentrate (also termed "feed" and designated F); the RO permeate, designated P; and the salt pump solution, designated S.

Results and Discussion

Leaching Studies

Leaching of organic compounds from the membranes and system components was studied in two series of tests. In the first series, the samples were only examined for model solutes. The existence of model solutes in the system blanks was sporadic and at trace levels and probably represents slow, reversible adsorption and desorption of spike organic solutes from earlier exposures to the membrane.

Potential leaching of organic compounds from the membrane systems was examined in more detail in the second level of tests where gas chromatography (GC)/mass spectrometry (MS) was used in addition to the routine GC/flame ionization detector, GC/electron capture detector, and high performance liquid chromatography methodologies. In this series of tests, the effect of chlorine exposure on the types of leachable organics recovered in the blanks was also examined. Low levels of a limited number of solutes occurred sporadically for all the membrane types (in the absence of chlorine) with no strong trends or consistency of results evident. In tests with chlorine present, the analysis for model solutes did not reveal any significant variations from the prior tests, but a greater number and variety of compounds were detected by GC/MS. While tentative identifications could be made only for some of the compounds, it was important to note that none of them were obvious chlorination by-products. Several of the compounds detected in the FT-30 membrane blank before and after chlorine exposure were

nitrogen-containing compounds which may have originated from the barrier coating of the thin-film composite, FT-30 membrane.

Membrane Screening and Concentration Studies

Membrane rejection values from both the screening and concentration runs are presented in the full report for the cellulose acetate and FT-30 RO membranes. Rejection values indicating the effect of humic acid are also provided.

Several items that require further explanation are the negative rejection values and rejections listed as indeterminate values. Negative values result whenever the organic solute concentration is higher in the permeate stream than in the corresponding feed solution. Rejections listed as indeterminate values resulted whenever the sample concentrations were below the analytical detection limits.

While membrane rejection may be the most important single factor in any RO concentration system, the success or efficiency is nonetheless measured by the overall recovery of as many different types of compounds as possible. Tables in the full report list the percent mass recoveries for the three concentration runs where:

$$\text{Percent recovery} = 100 (C_f^i V_f^i / C_f^f V_f^f) \text{ (Eq. 2)}$$

and C_f^i , C_f^f represents the initial and final concentration of the solute in the feed, respectively.

V_f^i , V_f^f represents the initial and final volume of the feed, respectively.

Upon inspection, the recovery values for many of the solutes are extremely low, especially for the cellulose acetate membrane. Under the experimental conditions, losses due to adsorption were considerable.

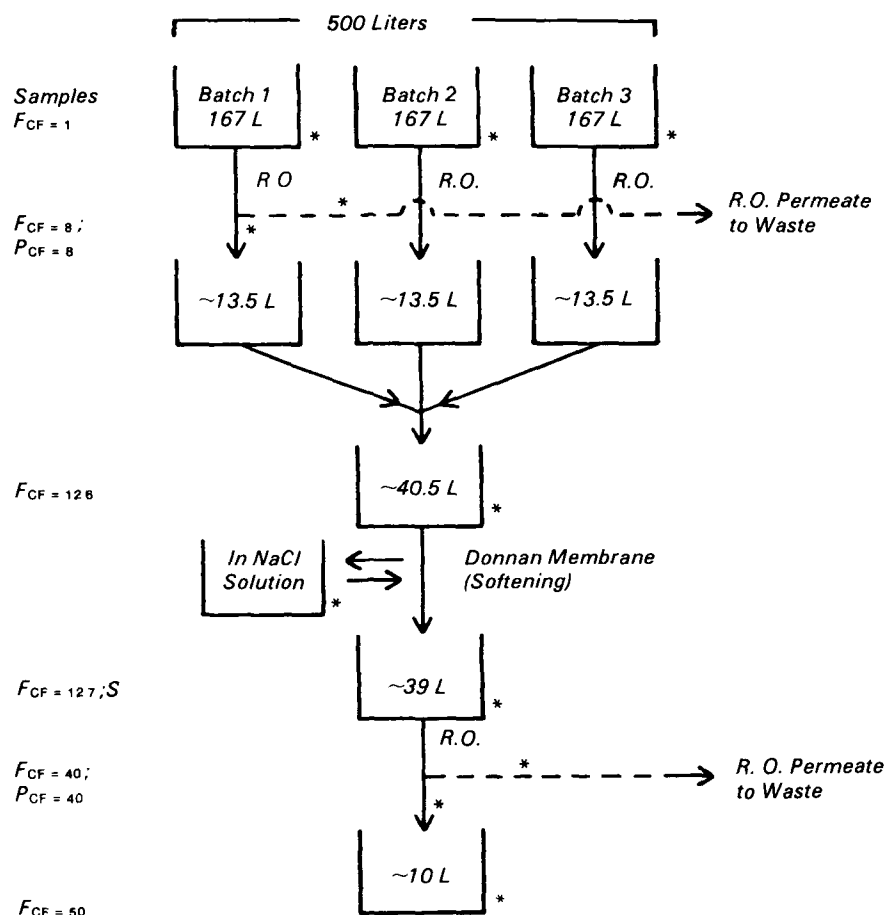


Figure 3. General experimental design and sampling regime for the reverse osmosis concentration runs.

Two major comparisons can be made from the recovery data listed in the full report. First, a comparison of the recoveries of the cellulose acetate membrane (Run 618-41) and the FT-30 membrane (Run 618-51) indicated that in practically all cases, organic solute recovery by the FT-30 membrane equaled or more often far exceeded the recovery demonstrated by the cellulose acetate membrane. This was not unexpected since membrane rejections determined for the two membranes in the screening tests and the concentration runs reflected this same trend.

The second comparison was between the FT-30 tests with (618-57) and without (618-51) humic acid in the water matrix. There are 12 pairs of data that can be compared directly. For comparison, three categories were defined: 1) higher recovery with humic acid present, 2) lower recovery with humic acid present, and 3) no difference. It was stipulated that the differences were to exceed 10 percent to qualify as significant.

The results of this comparison showed that higher recovery was exhibited for two compounds, 1-chlorododecane and 2,2',5,5'-tetrachlorobiphenyl, with humic acid present; and that lower recovery was exhibited for two compounds, 5-chlorouracil and methylisobutyl ketone, in the presence of humic acid. Eight compounds showed no change when humic acid was present in the test matrix.

Adsorption Studies

The mechanism implicated in the disappearance of most of the solute material was adsorption, even though limited solubility, biodegradation, and chemical decomposition of some solutes may be complicating factors. Estimates of solute losses due to adsorption on the system components were provided by examination of the extent of model solute loss during the 4 hr of total solution recirculation.

Adsorption losses of greater than 70 percent were observed for biphenyl; 2,6-di-tert-butyl-4-methylphenol; anthraquinone, stearic acid and bis(2-ethylhexyl) phthalate in the presence of humic acid. In addition to determining the actual adsorption losses, it was possible to make comparisons between: 1) the two RO systems, 2) the RO systems and the Nafion® membrane system, and 3) solute solutions with and without humic acid present. The data indicated no significant differences in solute losses between RO membranes; however, the Nafion® system exhibited significantly less adsorption than either RO system. Comparisons

of the effect of humic acid in the water matrix on solute losses to adsorption in the three membrane systems revealed appreciable changes in only four instances for the 12 solutes for which data were available. Because of the magnitude of scatter and the fact that none of the changes were greater than 50 percent, these changes may not be significant.

Recommendations

- The FT-30 membrane should be used in future concentration studies because of better solute rejection, recovery, and chemical resistance as compared to the cellulose acetate membrane.

- Steps should be taken to satisfy adsorptive demands during sample collections using the reverse osmosis concentration method. Preconditioning of this nature could involve exposing the membranes and other system components to water (both at ambient and concentrated levels) being sampled. This type treatment should help maximize recovery of organics in any stream where significant adsorption may occur.

- The apparent losses to adsorption should be investigated in further detail under conditions more favorable to analytical chemistry. By removing some of the major analytical complications (i.e., mixed salts, acetone, and humic acid) and spiking at higher solute levels, better accuracy will be provided. Extended test periods and expanded sampling schedules should be instituted to better determine the attainment of steady-state conditions and characterize the solute sorption phenomena. It is expected that more benefit will be gained from these modifications than will be lost in deviating from "real world" modeling. Answers to these questions should be sought.

1. Is the adsorption phenomenon associated with the membrane or other system components?
2. Is the phenomenon reversible?
3. Can the "demand" for solute be satisfied?
4. Is the adsorption a function of the solute concentration?

- The search should continue for a better anion exchange membrane. This membrane is needed whenever concentration procedures require the concurrent removal of inorganic burden. Research is being conducted to develop improved membranes with polyolefin backbone structures in the laboratories of several major membrane manufacturers. These membranes should possess better chemical resistance than the styrene/divinylbenzene based membranes currently in

production. The apparent chlorine sensitivity of the MA 3475 membrane indicates manufacturers' claims may be adequate for electrodialysis applications, but are less than optimum for organic sampling.

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H. P. Ringhand is the EPA Project Officer (see below).

The complete report, entitled "Isolation or Concentration of Organic Substances from Water—An Evaluation of Reverse Osmosis Concentration," (Order No. PB 85-124 147; Cost: \$19.00, subject to change) will be available only from:

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