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MOLECULAR SIZE DISTRIBUTIONS OF HEAVY
METALS IN LAKE WASHINGTON

BY

WILLIAM B. ANDREWS
B.S., Civil Engineering, Auburn University, 1972

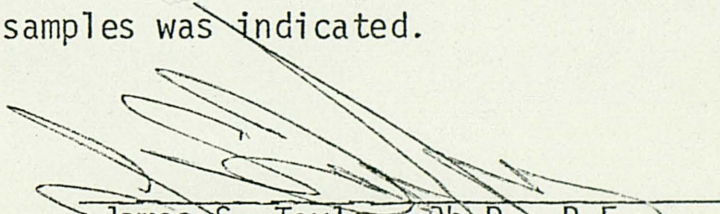
RESEARCH REPORT

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Engineering
in the Graduate Studies Program of the College of Engineering
at the University of Central Florida; Orlando, Florida

Summer Quarter
1979

ABSTRACT

Four untreated and one magnesium treated water samples from Lake Washington, the potable water source for the city of Melbourne, Florida, were collected and analyzed for As, Cd, Cr, Cu, Fe, Pb, Ni, Zn, Mg, Ca, and color on the basis of molecular weight distribution. Molecular weight distributions of the samples were obtained using a Millipore ultrafiltration system and filters in the following sizes: 10^6 , 10^5 , 2.5×10^4 , 10^4 , and 10^3 nominal molecular weight limits (nmwl). Color causing materials in the untreated samples were found to be located in the molecular weight fraction greater than 2.5×10^4 nmwl. The majority of the metals concentrations (approximately greater than 80%) were also found to be located in the molecular weight fraction greater than 2.5×10^4 nmwl. Analysis of the magnesium treated (for maximum color removal) sample showed higher concentrations of metals passing the respective filter sizes as opposed to the untreated samples indicating less complexation or smaller molecular complexes of the metals. Thus, a fairly strong correlation between heavy metals concentrations and color in the Lake Washington samples was indicated.



James S. Taylor, Ph.D., P.E.
Director of Research Report

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TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vi
LIST OF FIGURES	vii

Chapter

I	INTRODUCTION	1
	General Discussion	1
	Scope and Objectives	8
II	LITERATURE REVIEW	10
	Sources of Heavy Metals	10
	Complexation of Heavy Metals by Other Materials	11
	Health Effects	14
III	EXPERIMENT	19
	Sample Collection and Preparation	19
	Ultrafiltration	19
	Heavy Metals Analysis	25
	Color Analysis	26
IV	RESULTS AND DISCUSSION	28
	Results	28
	Discussion	29
	Arsenic	31
	Cadmium	33
	Chromium	34
	Copper	34

TABLE OF CONTENTS (Continued)

<u>Chapter</u>		<u>Page</u>
	Iron.	35
	Lead.	35
	Nickel.	36
	Zinc.	36
	Magnesium	37
	Calcium	38
	Magnesium Treated Sample.	38
	Distilled Water Sample.	39
	Color	39
	Correlations Between Heavy Metals and Color.	40
V	CONCLUSIONS	71
	BIBLIOGRAPHY	72

LIST OF TABLES

<u>Number</u>	<u>Title</u>	<u>Page</u>
1	General Sources of Various Metals	4
2	Average Concentrations of Various Metals.	5
3	General Health Effects of Various Metals.	6
4	Distribution of Metal in Humic Acid	13
5	Electrodialysis and Membrane Filtration of Sample A.	14
6	Sample Designation Scheme for Ultrafiltration of Lake Washington Water Samples.	20
7	Data for Metals Concentrations in Ultrafil- tration Process	42
8	Metals Concentrations	45
9	Percent of Metals Retained by Ultrafiltration .	47
10	Mass Balance Metals Concentrations.	48
11	Color in Ultrafiltration Filtrate Samples . . .	50

LIST OF FIGURES

<u>Number</u>	<u>Title</u>	<u>Page</u>
1	Mode of Operation of Millipore Ultrafiltration System for Filtration of Lake Washington Water Samples.	23
2	Concentration of Arsenic as a Function of Ultrafiltration Filter Size	51
3	Concentration of Cadmium as a Function of Ultrafiltration Filter Size	52
4	Concentration of Chromium as a Function of Ultrafiltration Filter Size	53
5	Concentration of Copper as a Function of Ultrafiltration Filter Size	54
6	Concentration of Iron as a Function of Ultrafiltration Filter Size	55
7	Concentration of Lead as a Function of Ultrafiltration Filter Size	56
8	Concentration of Nickel as a Function of Ultrafiltration Filter Size	57
9	Concentration of Zinc as a Function of Ultrafiltration Filter Size	58
10	Concentration of Magnesium as a Function of Ultrafiltration Filter Size	59
11	Arsenic - Percent Retained by Ultrafiltration .	60
12	Cadmium - Percent Retained by Ultrafiltration .	61
13	Chromium - Percent Retained by Ultrafiltration.	62
14	Copper - Percent Retained by Ultrafiltration. .	63

LIST OF FIGURES (Continued)

<u>Number</u>	<u>Title</u>	<u>Page</u>
15	Iron - Percent Retained by Ultrafiltration. . .	64
16	Lead - Percent Retained by Ultrafiltration. . .	65
17	Nickel - Percent Retained by Ultrafiltration. .	66
18	Zinc - Percent Retained by Ultrafiltration. . .	67
19	Magnesium - Percent Retained by Ultrafiltration	68
20	Color Levels in Ultrafiltration Filtrate Samples	69
21	Percent Color Removal by Ultrafiltration. . .	70

CHAPTER I

INTRODUCTION

General Discussion

Over the past fifteen years, growing concern over the quality of the water which we consume and use otherwise, has initiated the passage of Federal legislation for its protection. This legislation is designed to protect the waters for future use by setting maximum concentration limits on constituents that may be discharged to a water course. These maximum concentration limits were developed on past experience of the effects of certain constituents upon the health of man, animals, and aquatic life. These water quality criteria are therefore designed to protect not only significant and essential life in water and the direct users of water, but also the life that is dependent on aquatic life for its existence or which may consume edible portions of the aquatic life. These criteria cannot, however, be expected to protect all of the ecosystem organisms all the time. Economic and technical consideration prevent this.

In addition to the water quality criteria for the protection of our waters, there are also drinking water criteria for our protection. Quality standards for drinking water were first adopted by the Public Health Service in 1914, and revised in 1925, 1942, 1946, and 1962. Most recent of this drinking water regulation is

the US EPA 1975 National Interim Primary Drinking Water Regulations enacted in accordance with the provisions of the Safe Drinking Water Act (Public Law 92-523). Like the discharge regulations, these drinking water rules contain recommended maximum concentration levels (MCC) for certain constituents based on available data for the protection of human health.

Of major concern in both the discharge and the drinking water regulations are the concentrations of various heavy metals and other inorganics. Of the 103 known elements, 83 are metals. Metals are generally distinguished by their luster, malleability, conductivity, and ability to form positive ions. Sixty eight of these metals have a density five times greater than water and are classified as heavy metals. Heavy metals include all metals with atomic number greater than 23 except rubidium, strontium, yttrium, cesium, barium, and francium. (Zemansky, 1974). Man's activity over the past centuries has altered the distribution of heavy metals in the environment during their transfer from natural ores to various products and waste products. A fraction of these products is released to the environment often resulting in detrimental effects. Some of the heavy metals are known to be highly toxic to man and other mammals, while others are more toxic to fish and marine biota. Some metals are essential micronutrients for all living organisms and others are not known to have any essential role in the life cycle.

In spite of the relatively extensive studies made over the years, many key questions still remain unanswered due to the complex

relationships that govern the effects of each metal individually and in combination with others on various living organisms.

Human exposure to the toxic heavy metals in the aquatic environment may occur either directly through the consumption of water containing these materials or indirectly through ingestion of aquatic plants and animals grown in the water. It is well known that various living organisms in the aquatic environment are capable of concentrating some metals several orders of magnitude over the ambient level. The concentrated metal is passed from one organism to another until it reaches man at the top of the food chain.

Heavy metals in aquatic environments can result from natural occurrence and/or industrial pollution and may exist in at least four different forms: (1) true solutions as free or complexed ions, (2) solid precipitates, (3) adsorbed to other particles, or (4) incorporated into the biomass of living organisms. In drinking water, heavy metals can result from their occurrence in the source of raw water and/or from ions released through the distribution system by corrosion. Corrosion may occur as a result of the instability of the water. Corrosive waters are normally soft, however, hard water may produce calcium deposits in the system.

Tables 1, 2, and 3 summarize the sources, average concentrations, drinking water standards, and health effects of various contaminants in water.

TABLE 1

GENERAL SOURCES OF VARIOUS METALS

Contaminant	Common Valence Form	Most Likely Occurrence and Source of Contaminant
Arsenic	+3 (Arsenite) +5 (Arsenate)	groundwater-natural occurrence groundwater-natural occurrence surface water-natural occurrence or industrial pollutant
Cadmium	+2	surface water-industrial pollutant
Calcium	+2	natural occurrence to industrial waste
Chromium	+3 +6	groundwater-natural occurrence surface water-industrial pollutant
Copper	+2	surface water-industrial pollutant groundwater-natural occurrence
Iron	+3	natural occurrence
Lead	+2	surface water-industrial pollutant
Magnesium	+2	natural occurrence
Nickel	+2	surface water-industrial pollutant
Zinc	+2	surface water-industrial pollutant groundwater-natural occurrence

SOURCE: U.S. Environmental Protection Agency, Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations (Cincinnati, Ohio, 1977): p. 3.

All of the trace heavy metals present in a raw water source may not be removed in the water treatment plant and may therefore be introduced into the distribution system. Once inside the water distribution system, inorganic contaminants may be released into the water as a result of internal corrosion. These inorganic pollutants will eventually end up at the wastewater treatment plant where their fate during treatment is of particular interest to those interested in preserving our natural water resources. If the pollutants pass through the treatment plant, they will end up back in

TABLE 2

AVERAGE CONCENTRATIONS OF VARIOUS METALS

Metal	CONCENTRATION				
	Surface Water Mg/l	Water Treatment Plant Effluent Mg/l	Distribution System Mg/l	Mean Daily Intake, Mg*	Maximum Permissible Level, Mg/l
Arsenic	10.0	----	----	----	50.0
Cadmium	9.5	12.0	1.3	2.6	10.0
Chromium	9.7	7.5	2.3	4.6	50.0
Copper	15.0	4.3	134.5	269.0	[1000.0]
Iron	52.0	68.9	166.5	333.0	[300.0]
Lead	23.0	33.9	13.1	26.2	50.0
Nickel	19.0	34.2	4.8	9.6	----
Zinc	64.0	79.2	193.8	387.6	[5000.0]
# Samples analyzed	1577	380	969		

SOURCES: National Research Council, Drinking Water and Health (Washington, D.C.: Government Printing Office, 1977): pp. 210-211; G.F. Craun and L.J. McCabe, "Problems Associated with Metals in Drinking Water," Journal of the American Water Works Association 67 (November, 1975): p. 597; and U.S. Environmental Protection Agency, Quality Criteria for Water (Washington, D.C.: Government Printing Office, 1976).

* Assuming 2 liters/day/capita consumption

[] denotes secondary standard

TABLE 3

GENERAL HEALTH EFFECTS OF VARIOUS METALS

Contaminant	Health Effects
Arsenic	extremely toxic, cumulative poison, may be carcinogenic, can cause liver and heart ailments, death
Cadmium	toxic, gastrointestinal upsets, cramps, nausea, vomiting, diarrhea, cumulative poison, death
Calcium	necessary element, excessive amounts can lead to kidney stones, reported that high calcium is associated with low cardiovascular disease, insufficient calcium in diet can cause rickets
Chromium	large dose leads to corrosive effects in the intestinal tract and to nephritis, causes nausea, can cause death
Copper	essential for nutrition, large doses can cause gastroenteritis, can cause discoloration of skin and hair, no evidence of copper poisoning from drinking water
Iron	essential for nutrition
Lead	cumulative poison, causes constipation, loss of appetite, anemia, abdominal pain and tenderness, pain and gradual paralysis of muscles, can cause death
Magnesium	essential mineral element, relatively non-toxic, has a laxative effect
Nickel	very low toxicity to humans
Zinc	essential for nutrition, very high concentrations can cause nausea and fainting

SOURCE: California, State Water Quality Control Board, Water Quality Criteria, by J.E. McKee and H.W. Wolf, Publication No. 3-A (Sacramento, California, 1963).

our water courses. On the other hand, concern over concentrations of heavy metals in wastewater sludges has been expressed by scientists and researchers. These contaminants affect the methods of handling and disposing of sludge and its usefulness as a resource.

One of the available water/wastewater treatment methods is membrane filtration, more specifically, ultrafiltration. However, to be effectively utilized, the proper size of filter must be used in regards to the constituent that is desired to be removed. It is therefore desirable to know the size distribution of the constituent of interest.

Color in water is another quality descriptor in use today. The main concern over color is probably aesthetic, but, color also indicates the presence of other constituents. Color in water is due primarily to the presence of natural organic matter. This, in turn, is comprised largely of humic and fulvic acids. Humic acid is that compound which is soluble in a strong base but insoluble in a strong acid; fulvic acid is soluble in both acid and base. The most common method for color removal is coagulation/flocculation with a metallic salt, usually aluminum, iron, or magnesium. Humic acids have molecular weights ranging from several hundred to a few thousand. They can aggregate naturally into colloidal particles with much higher apparent molecular weights. They are composed primarily of aromatic compounds with carboxyl, phenolic and quinoid groups. Fulvic acids are similar in structure to humic acids but have lower molecular weights. Because of their carboxylic

and phenolic groups, humic substances have high cation exchange capacities and can concentrate or bind metal ions. Because of their carboxylic and phenolic groups, humic substances have high cation exchange capacities and can concentrate or bind metal ions. Because of their organic character, they can also accumulate hydrophobic organic compounds, including several pesticides.

Scope and Objectives

The broad objective of this research report is to study the molecular size distributions of heavy metals in raw water samples collected from the City of Melbourne, Florida water treatment plant. Source of the raw water is Lake Washington. In addition, one raw water sample was treated with $MgSO_4$ for coagulation/flocculation purposes and subsequent analysis for molecular size distributions of heavy metals.

Samples were collected from the Melbourne water treatment plant on two separate occasions. Each sample was then divided into two analysis runs giving a total of four analysis runs on the raw water. The Mg^{+2} treated water provided the fifth run.

All five samples were processed through a Millipore ultrafiltration cell using six different sizes of filters. Heavy metals concentrations of both retentate and filtrate samples were then obtained using a plasma spectrometer Spectraspan III. Elements measured were Arsenic, Cadmium, Chromium, Copper, Calcium, Iron, Lead, Magnesium, Nickel and Zinc.

Color of the samples was also determined to study the color removal capabilities of the ultrafiltration process.

Correlations between the occurrence of color and heavy metals was also studied.

CHAPTER II

LITERATURE REVIEW

Sources of Heavy Metals

Western civilization is now dependent on the large-scale use of a wide range of metals and most of these are naturally present only at trace levels in the biosphere and in biological materials. Most trace-element pollution problems involve metals, although problems can also arise quite frequently with two non-metals; arsenic and boron, which are often called metalloids because they exhibit properties characteristic of metals.

Most metals occur naturally as ores. We extract these metals in the form of ores from localized mineral deposits in the first instance; they are then manufactured into fashionable metal objects and when they are no longer in a serviceable condition, they are discarded. All metals contamination of the environment is associated with this overall process and with man's failure to develop an efficient internal cycle of metal resources within our society (Purves, 1977).

In the processing of these metal ores into fashionable objects, metals are released to the environment as pollutants in the form of liquid, particulate, and gaseous discharges. Metal contaminated liquid discharges usually cause direct pollution of our

watercourses. Particulates emitted to the atmosphere settle out or are washed out by precipitation and end up in the soil or in our waterways. Naturally occurring metals in our soils are also washed into our waterways by runoff. Trace-element contamination of the soil is general in urban areas of every size, but in the vicinity of industrial concentrations, the levels of contamination are exceptionally high.

Complexation of Heavy Metals by Other Materials

Studies by Matson (1968), Chau (1973), and Schindler (1972), indicate that the humic compounds can complex metal ions and keep them in solution. The organic compounds can solubilize metals by two possible mechanisms: they can form metal-ligand complexes with sorption characteristics different from those of the free metal ion or they could solubilize the iron and manganese oxides thus releasing the soluble trace elements (Theis and Singer, 1974).

Benes, et. al., (1976) has shown calcium in a water sample to be associated with humus materials. It was also shown that chromium, iron, and zinc were strongly complexed by humic or organic materials. Studies by Theis, et. al. (1974) support the conclusion that iron is strongly complexed by organic matter, i.e., tannic and humic acids.

Stiff (1971) concluded that there appeared to be no general pattern of humic complexing of copper in polluted fresh water.

Studies by Guy and Chakrabarti (1976) concluded that metal complexation involves humic and fulvic acids. Ultrafiltration separations were used to determine the size distribution of Cu^{+2} , Fe^{+3} , Pb^{+2} , and Mn^{+2} in humic and tanic acid solutions as well as several samples of natural water. The solutions consisted of 20 $\mu\text{g}/\text{ml}$ of complexing agent and 50 ng/ml each of Cu^{+2} , Pb^{+2} , and Fe^{+3} , and 25 ng/ml of Mn^{+2} . Size separations were made using Amicon ultrafilters (filters UM2, PM10, PM30, XM50, and XM100) and an Amicon ultrafiltration assembly, model 201. The metal concentrations in the filtrate were determined using graphite-furnace atomic absorption spectroscopy. Results of the ultrafiltration are shown in Table 4. The results show two important points: at pH 2, all the metal is present as small species, and at natural water pH (pH > 6), the metal ions are bound in the species with sizes greater than 5.0 nm (nm, nano meters, 10^{-9} meters, is the average diameter of the molecules).

In fractionation studies, Gjessing and Lee (1974) found most organic color to be in the molecular weight range of 10,000 - 50,000.

Schindler, et. al. (1972) used molecular weight fractionation to examine the possibility of organic-inorganic complex formation. Iron, magnesium, and manganese were found to be associated with fractions greater than 500 molecular weight.

Bender, et. al. (1970) also found that higher molecular weight fractions of a water sample, which are less likely to pass a given

size membranes, bind metals more strongly.

TABLE 4
DISTRIBUTION OF METAL IN HUMIC ACID

Size (nm)	METAL IN THE FRACTION (%)							
	pH 2				pH 6			
	Pb	Cu	Fe	Mn	Pb	Cu	Fe	Mn
> 5.1	---	---	---	---	64	32	43	24
> 3.2	---	---	---	---	36	67	45	30
> 2.4	---	---	---	---	--	--	--	16
> 1.9	---	---	---	---	--	--	--	14
> 1.9	100	100	100	100	--	--	11	16

SOURCE: Guy, R.D. and C.L. Chakrabarti, "Studies of Metal-Organic Interactions in Model Systems Pertaining to Natural Waters," Canadian Journal of Chemistry 54 (1976): 169-174.

Black and Christman (1963) conducted studies of various physical and chemical properties of organic color in water. Results of their electrodialysis and membrane filtration study of a water sample are given in Table 5. These data indicated that most of the color in this water sample was colloidal in nature, that most of the particles were in the 3.5 - 10 μ diameter range. These same general results were obtained when the investigators tested all of the water samples used in their study. It was also found that pH effects both particle size and number of particles in the solution.

TABLE 5

ELECTRODIALYSIS AND MEMBRANE FILTRATION
OF SAMPLE A

Material	Pore Size (μ)	Maximum Color Retained (%)
Membrane Filter*	10	13.0
Cellophane Membrane	4.8	87.5
Collodion Membrane	3.5	91.0

* A Millipore filter; a product of Millipore Filter Corporation, Bedford, Massachusetts.

SOURCE: Black, A.P. and R.F. Christman, "Characteristics of Colored Surface Waters," Journal of the American Water Works Association 55 (June 1963): 753.

Health Effects

When a potentially toxic element is absorbed by a living organism at abnormally high concentrations, it may cause structural damage or enter cells and inhibit enzyme activities to such an extent that normal cell functioning is impaired (Purves, 1977).

The general health effects of various metals were presented in Table 3, page 6.

Warren, et. al., have published a number of papers suggesting the possibility of causal relationships between a number of human disorders including cancer and multiple sclerosis and geochemically enhanced levels of a number of potentially-toxic trace elements in different areas. The finger of suspicion has been mainly

directed at lead as a possible cause of both cancer and multiple sclerosis, although a number of other elements, such as arsenic, chromium, copper, molybdenum and zinc have been suggested as being of epidemiological significance. Davies (Purves, 1977) has also reported that cancer and other diseases appear unusually prevalent in two historical metal-mining areas of Great Britain, namely, Cardiganshire and the Tamar Valley in the western part of England. Anderson, Davies, and James (Purves, 1977) have reported an association between a high incidence of dental caries and the soil lead content in 12-year old children resident in the Tamar Valley.

The most extensive literature on the connection between trace elements in water and human health relates to the relationship between water hardness and cardiovascular disease. In 1959, Sauer and Enterline examined the geographic distribution of cardiovascular heart diseases and observed considerable differences in rates in some instances. Schroeder (1960) examined the geographical variation in cardiovascular mortality and several parameters used to describe the chemical and physical characteristics of potable water in the United States. He found highly significant negative correlations between mortality from cardiovascular heart disease and magnesium, calcium, bicarbonate, sulfate, fluoride, dissolved solids, specific conductance, and pH. The most significant correlations were between hardness and cardiovascular heart disease. He concluded that some factor present in hard water, or missing from or entering soft water appeared to affect death rates from

degenerative cardiovascular diseases.

Morris, et. al. (1961) reported a highly significant correlation between water hardness and mortality from cardiovascular heart disease in 83 county boroughs in England and Wales.

Schroeder (1960) has suggested that trace metals in water may be an important factor in cardiovascular mortality.

Schroeder and Kraemer (1974) found highly significant inverse correlations between 15 constituents of water (12 were metals) and cardiovascular mortality. They also examined the corrosiveness of waters as measured by the Langlier Index and demonstrated a direct correlation with atherosclerotic heart disease at high levels of significance. Neri, et. al. (1971) also examined the relationship between water hardness and sudden death and suggested the possible significance of trace metals.

In view of the widely accepted relationship between environment and cancer, it is not surprising that the demonstration of suspected carcinogens in drinking water should receive considerable attention. Recently, Page, et. al. (1975) demonstrated statistically significant relationships between drinking water from the Mississippi River and all cancer and cancers of the urinary organs and the gastrointestinal tract.

Copper is frequently found in surface waters and in some ground waters in low concentrations (less than 1 mg/l) and is considered an essential and beneficial element in human metabolism. It can also be introduced into a drinking water by the solution of

copper from brass and copper pipe and by the use of copper sulfate as an algicide in reservoirs. Copper is of physiological importance as a supplement to iron for hemoglobin regeneration and is an essential constituent of tissue cells, but the body requirements must be met by the food intake since the amount of copper usually available in the drinking water is inadequate. Chronic copper poisoning is said to cause gastrointestinal catarrh and to be related to hemochromatosis, but the amount of copper required for poisoning is far in excess of the concentrations possible in drinking water. Copper in drinking water has practically no health significance.

Zinc ions are rarely present in natural waters in considerable concentrations, but zinc does enter water supplies by solution of the metal from zinc galvanizing on pipes and tanks. Zinc is a normal constituent of the human body. Its presence in drinking water in concentrations up to about 40 ppm appears to have no health significance, but it does impart an astringent taste to water and it will precipitate as $Zn(OH)_2$ or $ZnCO_3$ in alkaline waters to produce a milky turbidity (Camp, 1963).

Iron and manganese are both essential to the human body but their intake through drinking water is an insignificant part of the body requirement.

Small concentrations of lead continuously present in drinking water are known to cause lead poisoning or plumbism which may result in serious illness or death. Lead taken into the body in

quantities in excess of certain low limits is a cumulative poison. Poisoning may result from one, or all, of three common sources: food, air, and water. Only traces of lead may be found in natural waters and, then, only in waters from heavily mineralized watersheds or in waters contaminated with industrial wastes.

Arsenic is sometimes present in natural waters due to their contact with arsenic-bearing minerals such as arsenical pyrites. Arsenic is also a component of smelter wastes and other industrial wastes. Arsenic poisoning is known to have resulted from a water containing about 0.2 ppm of arsenic (Camp, 1963). It is probable that concentrations of about 0.15 ppm of arsenic in drinking water can be tolerated without injurious effect, according to Stoof and Haase (1937), provided there is no other major source of arsenic intake.

Cadmium has a high toxic potential when taken by mouth. It accumulates in the soft tissues at all concentration levels down to 0.1 ppm in drinking water, resulting in anemia, poor metabolism, possible adverse arterial changes in the liver of man and, at higher concentrations, death.

The salts of hexavalent chromium in industrial use (chromates and dichromates) are skin irritants which can produce ulcers. Chromium is known to be a carcinogenic agent for man, when inhaled. According to Fairhall (1957), trivalent chromium salts show none of the toxicity of hexavalent chromium and their presence in drinking water supplies should not cause concern.

CHAPTER III

EXPERIMENT

Sample Collection and Preparation

Samples were collected from the Melbourne water treatment plant on two separate occasions. Each sample was then divided into two analysis runs giving a total of four analysis runs on the raw water. Raw water was also taken from the second sample and treated with Mg^{+2} for a fifth analysis run. As a check, distilled water was processed through three of the filters. Table 6 presents the sample designation scheme.

Before being divided into the five analysis runs, all samples were filtered through a 0.45μ filter paper (from the Millipore Filter Corporation) to remove any large particles that might have clogged the ultrafiltration unit.

Jar tests were performed on one analysis run to determine the optimum magnesium sulfate dosage and pH for maximum color removal. The optimum dosage and pH were determined to be 360 mg/l and 11.5, respectively. An adequate volume of the sample to conduct the ultrafiltration portion of the experiment was then prepared using these determined values.

Ultrafiltration

Ultrafiltration of the samples was accomplished using a

TABLE 6

SAMPLE DESIGNATION SCHEME FOR ULTRAFILTRATION
OF LAKE WASHINGTON WATER SAMPLES

Sample Number	Sample Identification- Filter Size (nmwl)****	Volume Processed (ml)	Volume Produced (ml)
I-II	Raw Sample Used for Runs I&II	N/A	N/A
I- 1	10 ³ **** F*	2000	41
I- 2	P**		1959
I- 3	10 ⁴ **** F	4000	580
I- 4	R		3420
I- 5	2.5x10 ⁴ **** F	6000	500
I- 6	R		5500
I- 7	10 ⁵ **** F	2000	1165
I- 8	R		835
I- 9	10 ⁶ **** F	2000	985
I-10	R		1015
II- 1	10 ³ F	2400	55
II- 2	R		2345
II- 3	10 ⁴ F	5500	700
II- 4	R		4800
II- 5	2.5x10 ⁴ F	8000	550
II- 6	R		7450
II- 7	10 ⁵ F	1400	855
II- 8	R		545
II- 9	10 ⁶ F	2000	690
II-10	R		1310
III-IV	Raw Sample Used for Runs III&IV	N/A	N/A
III- 1	10 ³ F	4000	81
III- 2	R		3919
III- 3	10 ⁴ F	2000	600
III- 4	R		1400
III- 5	2.5x10 ⁴ F	3000	550
III- 6	R		2450
III- 7	10 ⁵ F	1500	920
III- 8	R		580
III- 9	10 ⁶ F	2000	1230
III-10	R		770
IV- 1	10 ³ F	4000	141
IV- 2	R		3859
IV- 3	10 ⁴ F	2000	525
IV- 4	R		1475

TABLE 6
(cont.)

Sample Number	Sample Identification- Filter Size (nmwl)****		Volume Processed (ml)	Volume Produced (ml)
IV- 5	2.5x10 ⁴	F	2000	375
IV- 6		R		1625
IV- 7	10 ⁵	F	1500	990
IV- 8		R		510
IV- 9	10 ⁶	F	2000	1120
IV-10		R		880
V	Mg ⁺² treated			
V- 1	10 ³	F	1500	150
V- 2		R		1350
V- 3	10 ⁴	F	1500	330
V- 4		R		1170
V- 5	2.5x10 ⁴	F	1500	620
V- 6		R		880
V- 7	10 ⁵	F	1500	990
V- 8		R		510
V- 9	10 ⁶	F	1500	1030
V-10		R		470
VI- 1	10 ³	F	----	----
VI- 2		R		----
VI- 3	10 ⁴	F	2000	955
VI- 4		R		1045
VI- 5	2.5x10 ⁴	F	2000	585
VI- 6		R		1415
VI- 7	10 ⁵	F	----	----
VI- 8		R		----
VI- 9	10 ⁶	F	2000	1315
VI-10		R		685

* Filtrate

** Retentate

*** nmwl: nominal molecular weight limit (see explanation in paper)

**** 10³, 10⁴, 2.5 x 10⁴, 10⁵, and 10⁶ are the sizes of the filters in nmwl.

Millipore Pellicon Cassette System and Pellicon Ultrafiltration Membranes. Figure 1 shows the arrangement of the Millipore equipment. In simplest terms, the cell can be regarded as a black box which separates the feed stream, or sample, into two product streams: the retentate which is a concentrated solution of those macromolecules that were held back by the filter, and the filtrate, which contains those smaller molecules that have passed through the filter. Looking at Figure 1, sample feeds into the upper right port and the macromolecules emerge concentrated (as retentate) at the lower left. Filtrate flows out of the cell from either the upper left port or the lower right port (as shown). The second filtrate port is not used and is therefore plugged.

A look "inside the black box" reveals that the separation is performed by membrane packets which consist of two Pellicon membranes bonded together, with a support screen between them. This sandwich is designed so that the sample flows over the outside of the packet. Large molecules remain outside, while smaller molecules which can pass through the membrane end up inside the packet. Because of the edges of the packet are treated with a sealant, no fluid can flow from outside to inside (or visa versa) except by passing through the membrane. In order to take advantage of this separation, the cell is designed to transport fluid from the outside of the packet to one exit port, while fluid from the inside of the packet flows to another port. The two streams do not mix.

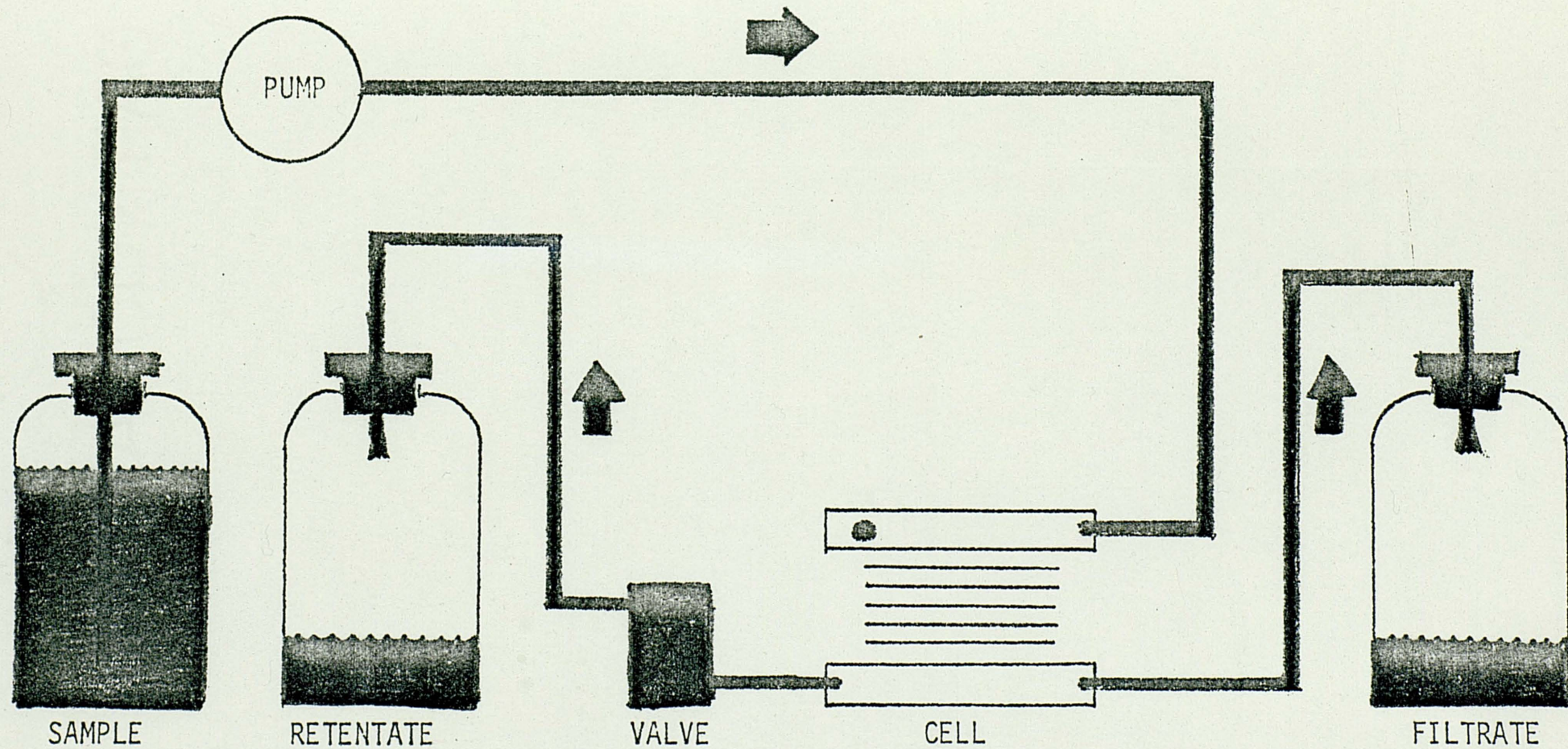


FIGURE 1

MODE OF OPERATION OF MILLIPORE ULTRAFILTRATION SYSTEM
FOR FILTRATION OF LAKE WASHINGTON WATER SAMPLES

The Nominal Molecular Weight Limit (nmwl) is a guide to separation performance. Globular molecules or particles of molecular weight equal to or greater than the nmwl are retained upstream of the membrane nearly quantitatively. Molecules of molecular weight less than or equal to 10% of the nmwl are passed through nearly quantitatively. Molecules with molecular weights between these two values are partially retained, the degree of retention increasing with molecular weight. The apparent wide range in sizes of partially retained molecules is largely due to the third order relationship between molecular dimension and molecular weight. Thus, the ten-fold difference in molecular weight required for nearly quantitative separation represents a two-fold difference in molecular diameter.

After being filtered through the 0.45 μ filter, each of the five samples were processed through five different sizes of ultrafiltration membranes. The five different sizes used were 10^3 , 10^4 , 2.5×10^4 , 10^5 , and 10^6 nmwl. The ultrafiltration process was not a successive filtration process, i.e., raw sample was filtered each time. Between filtration of samples, filters were rinsed with dilute acetic acid and distilled water. Before filtration, filters were also rinsed with the sample to be filtered. Volumes of sample filtered and retentate produced were recorded so that mass balance calculations could be made. Volumes of raw sample, retentate, and filtrate were then prepared for heavy metals and color determinations.

Heavy Metals Analysis

The most widely used method to analyze water samples for heavy metals content involves atomic absorption techniques.

In atomic absorption analysis, the sample is atomized by a flame. The chemical bonds between the molecules are broken, enabling individual atoms to freely float in the sample area and absorb radiation characteristic of it in that state. The wavelength bands that any particular element can absorb are very narrow and specific. The measurement of an element is determined by the amount a given wavelength of light is absorbed from a light beam directed through the flame into a monochromator and to a detector-meter recorder system. The amount of light absorbed is directly proportional to the concentration of the metal ion in the atomized sample. Atomic absorption is used by the cities of Chicago (Willey, et. al., 1972) and New York (Egan and Peterson, 1972) for metal analysis of their water supplies and both cities have reported excellent results.

A more recent technique which is still in the development stage involves the use of plasma spectrophotometry to measure heavy metals in water samples. During the course of this study, the plasma spectrophotometer, Spectraspan III by SMI, was used.

The flame temperature in this instrument reaches 6000-7000⁰K. The abundance of accessible energy from the plasma eliminates much of the chemical interferences which often plague flame atomic absorption/emission instruments. The high temperature enables

direct flame analysis of such non-metals as boron and phosphorus along with refractory type metals. A greater linear range is often achieved by measuring elemental concentrations using ionized spectra lines available with this high excitation energy.

The Spectraspan III is operated on argon gas. Benefits of using argon gas are reduced sample oxidation, the gas is non-toxic and non-explosive, and reduced operating costs.

The instrument accepts only liquid samples which are fed into a nebulizer by a pump. This results in even sample uptake, which is approximately 2.0 ml/minute. The liquid is converted to an aerosol by the nebulizer at an efficiency of about 20%. All samples were analyzed for the following heavy metals: Arsenic, Cadmium, Calcium, Chromium, Copper, Iron, Lead, Magnesium, Nickel, and Zinc.

Samples were prepared for heavy metals analysis according to Standard Methods for the Examination of Water and Wastewater, 14th Edition, 1976).

Color Analysis

Color analysis was performed on raw samples and on ultrafiltration filtrate samples using the following procedure. The initial pH was determined and adjusted to approximately 7.6 using a Corning Model 12 pH meter for pH readings and sodium hydroxide and sulfuric acid for pH adjustment. The absorbance of the meter was set at 465 nanometers (nm). The color of the samples was then

determined using their absorbance and a standard curve. The standard curve was prepared by plotting the absorbance of a standard 500 Platinum Cobalt Color Units solution. Actual values reported for color were determined using the linear regression analysis function of a TI SR-51A calculator.

CHAPTER IV

RESULTS AND DISCUSSION

Results

Results of the heavy metals determinations are presented in Tables 7, 8, 9, and 10 and in Figures 2-19. Table 7 gives the concentrations, in parts per million (ppm), of the various metals in the raw samples and the ultrafiltration filtrate and retentate samples. Table 8 gives the metals concentrations with respect to filter size of the raw samples. Table 9 gives the percent retained of the various metals for the different filter sizes based on the initial and filtrate metals concentrations. Table 10 gives a comparison of the mass balance of the metals concentrations in the filtrate and retentate samples with the initial concentrations in the raw samples. Figures 2-10 are graphs of the concentrations of the various metals molecules smaller than the filter size versus the ultrafiltration size in nmwl. Figures 11-19 are graphs of the percent retained versus the filter size.

Results of the color determinations are presented in Table 11 and Figures 20 and 21. Table 11 gives the absorbance, color (PCU), and percent color removed for each of the filtrate samples. Figure 20 plots filtrate color (PCU) versus filter size (nmwl) while Figure 21 plots percent color removal versus filter size.

Note that in all of the Figures, 2-21, the following symbols are used:

- o: Sample I
- Δ: Sample II
- : Sample III
- ▼: Sample IV
- : Sample V

Discussion

In reviewing the operation of the ultrafiltration unit, it can be seen that two different, strict interpretations of the results can be formulated. The first assumes that the metals concentrations in the filtrate samples are the concentrations of the molecules smaller than the filter size and that this concentration of "smaller" molecules is uniform throughout the entire sample, i.e., raw, filtrate, and retentate. This would, therefore, mean that the filtrate concentration would always be less than or equal to the initial concentration or that there is no concentrating of the smaller molecules in the filtrate. The second interpretation assumes that in the ultrafiltration process, all of the metals molecules are given the chance to pass through the filter membrane and all that physically can, do. Thus, the "smaller" molecules are concentrated in the filtrate and the larger molecules are concentrated in the retentate. To obtain an accurate assessment of the metals concentration, this concentrating effect must be accounted

for. In actuality, a combination of these two interpretations occurs as was mentioned in the discussion of the system. For the purpose of this study, the second interpretation was taken to occur and all calculations were performed accordingly.

Table 7 gives the concentrations of the various metals in the raw, filtrate, and retentate samples. They include no calculations for the correction of the concentrating effects of the ultrafiltration process.

Table 8 gives the concentrations of the various metals smaller in size than the respective ultrafiltration filter sizes for each of the five samples. These values were obtained by taking the filtrate concentrations in Table 7 and correcting them for the concentrating effect using the following formula:

$$\text{concentration less than filter size} = \frac{(\text{filtrate conc.})(\text{filtrate volume})}{\text{initial sample volume}}$$

The percent retained values in Table 9 were obtained by using the following formula:

$$\frac{(\text{initial conc.}) - (\text{conc. less than filter size})}{(\text{initial conc.})} = \% \text{ retained}$$

Negative values indicate that the concentration less than the filter size was greater than the initial concentration and therefore some contamination or error exists.

Table 10 mass balance values were calculated as follows:

$$\text{mass balance value} = \frac{(\text{filtrate conc.})(\text{filtrate vol}) + (\text{retentate conc.})(\text{retentate vol})}{\text{initial sample volume}}$$

In some cases, these calculated mass balance concentrations were higher than the initial concentrations of the various metals. Because all of the metals concentrations decreased with respect to filter size or molecular weight, based on initial and filtrate concentrations, it can be concluded that the cause of the higher mass balance concentrations is contamination of the retentate samples. This is logical due to the operational characteristics of the ultrafiltration unit and the continued reuse of the filters. If filters were inadequately rinsed and were dirty, molecules retained in earlier filtrations could easily have been washed out into the retentate sample.

The graphs of Figures 2-10 show concentrations of the various metals molecules smaller than the respective filter sizes for each of the five samples. The graphs are constructed such that filter size (based on nmwl) decreases from left to right. A horizontal line between two filter sizes indicates no change in the metals concentration and that the molecular size of the metals molecules is less than the smaller of the two filter sizes. A downward sloping line from left to right between two filter sizes indicates a decrease in metals concentration from one filter size to the next and that there are metal molecules greater in size than the smaller of the two filter sizes. An upward sloping line from left to right between two filter sizes indicates an increase in metals concentrations from one filter size to the next. Theoretically, this condition should not exist as it indicates a greater concen-

tration of molecules in one size range than in a size range greater than and including the first size range.

Figures 11-19 are graphs of the percent retained of the various metals for the different filter sizes. These graphs are also constructed with filter size decreasing from left to right. A horizontal line between two filter sizes indicates no additional retention and that the metal molecules are smaller in size (nmwl) than the smaller of the two filters. A downward sloping line between two filters indicates a decrease in percent retained and an increase in metals concentration, and the presence of metal molecules greater in size than the smaller of the two filter sizes.

Each of the metals and the color results will be discussed separately.

Arsenic

As can be seen in the Tables and in Figures 2 and 11, all of the arsenic data and plots have the same general shape and indicate a definite decrease in arsenic concentrations with respect to molecular weight distribution or filter size. The greatest increase in percent retained or reduction in concentration occurs upon filtration through the 2.5×10^4 nmwl filter indicating that the majority of the arsenic molecules are complexed with other matter forming a compound with size greater than 2.5×10^4 nmwl. Practically all of the arsenic molecules were retained by the 10^3 nmwl filter.

The magnesium treated sample showed increased levels of arsenic with respect to the untreated samples. Decrease in concentration with decrease in filter size did agree with the untreated samples.

Calculated mass balance concentrations for arsenic were consistently higher than the initial concentrations. As stated earlier, this was probably due to contamination of the retentate samples.

Cadmium

The plotted data for cadmium concentrations and percent cadmium retained are given in Figures 3 and 12. Although the initial concentrations of cadmium were low (approximately 0.003 ppm), removal through the different filter sizes was observed. Cadmium concentrations in the magnesium treated sample were higher than in the untreated samples but exhibited corresponding concentration reduction with respect to filter size. The untreated samples exhibited retention at the 10^6 nmwl and the 2.5×10^4 nmwl filter sizes. The magnesium treated sample exhibited the greatest retention at the 2.5×10^4 nmwl filter size. Filtrations at nmwls smaller than 2.5×10^4 showed no greater retention or reduction in concentration.

Calculated mass balance concentrations for cadmium in the untreated samples were all less than or equal to the initial concentrations indicating no gross cadmium contamination from else-

where and a slight absorption of cadmium onto the filter.

Chromium

Figures 4 and 13 present graphs of the data for chromium. All five of the sample concentration graphs (Figure 4) agree in shape and indicate a gradual and fairly uniform decrease in chromium concentration with respect to filter size. The graph of percent retained (Figure 13) shows greater than 50% retained through the 10^6 nmwl filter and 81-94% retained through the 2.5×10^4 nmwl filter. Subsequent filtration through the 10^3 nmwl filter increased the retention to only 88-96% of the initial chromium concentration in all five samples.

Chromium concentrations were much higher in the magnesium treated sample than in the untreated samples.

Copper

Copper concentrations and percent copper retained data are graphed in Figures 5 and 14. Graphs for samples I, II, and III agree with each other, except for sample III at the 10^6 nmwl filter, and indicate a gradual reduction in concentration with respect to filter size. The graphs indicate the greatest copper concentration reduction and percent copper retained (71.5-94.9%) for samples I, II, and III at the 2.5×10^4 nmwl filter size. Further filtration with smaller size filters produces only 87.9-99.7% retained for all five samples.

The magnesium treated sample had higher copper concentrations than the untreated samples but indicated basically the same results, i.e., greatest percent retention at the 2.5×10^4 nmwl filter.

Iron

As can be seen in Figure 6, the data for iron for samples I-IV is fairly consistent and shows that concentrations are greatly reduced through the 10^6 nmwl filter. Samples I and II showed greater than 50% reduction through the 10^6 nmwl filter. Figure 15 shows 49.7-73.1% retention of iron by the 10^6 nmwl filter. Both figures also show equal results at the 2.5×10^4 nmwl filter with little change upon further filtration with smaller filters.

The magnesium treated sample had a higher iron concentration than the untreated samples and showed a uniform reduction in concentrations with respect to decreasing filter size. Filtration through the smallest filter produced only an 81.2% retained value.

Calculated mass balance concentrations for samples I-IV were all less than the initial concentrations indicating some loss of iron molecules possibly through absorption onto the filter.

Lead

Lead concentrations gradually and uniformly decreased with respect to filter size as can be seen in Figure 7. Percent retained varied from 24.1-72.1% at the 10^6 nmwl filter size to 95.4-98.3% at the 10^3 nmwl filter size as shown in Figure 16. However, at

the 2.5×10^4 nmwl filter size, the percent retained ranged from 82.3 to 95.9% for the four untreated samples.

Lead concentrations in the magnesium treated sample were much higher than in the untreated samples but were also decreasing with respect to decreasing filter size. Percent retained ranged from 24.1% at the 10^6 nmwl filter to 95.4% at the 10^3 nmwl filter.

In most cases, the calculated mass balance concentration were slightly less than the initial concentrations indicating possible adsorption onto the filter.

Nickel

Nickel concentrations in all four untreated samples were initially low, 0.002-0.016 ppm, and were therefore difficult to evaluate. Results of filtration (Figures 8 and 17) show most of the nickel (above 93%) retained by the 10^6 nmwl filter indicating location of the nickel molecules in the size range greater than 10^6 nmwl.

The magnesium treated samples showed higher nickel concentrations than the untreated samples but the data indicated a uniform reduction in concentrations with respect to filter size.

Zinc

As shown in Figures 9 and 18, the data for zinc generally agrees as graphs of concentration and percent retained for all five samples have basically the same shape. Concentrations of zinc molecules in the untreated samples that pass through the 10^6 and 10^5

nmwl filters are approximately the same as the initial concentration in these samples. Less than 40% retention is obtained by these two filters indicating that the majority of the zinc molecules in the untreated samples are in the size range less than 10^5 nmwl. The concentration of zinc molecules passing the 2.5×10^4 nmwl filter is greatly reduced as shown in Figure 9. Figure 18 shows 71.9-95.6% retained by the 2.5×10^4 nmwl filter for the four untreated samples indicating that the majority of the zinc molecules in the four untreated samples are located in the size range greater than 2.5×10^4 nmwl. Overall, it can be seen that in the untreated samples, the zinc molecules are located in the size range greater than 2.5×10^4 nmwl and less than 10^5 nmwl.

Zinc concentrations in the magnesium treated sample were higher than in the untreated samples and showed a uniform decrease with respect to decreasing filter size.

Magnesium

Values for concentrations of magnesium were not obtained for the four untreated samples because they were greater than the range selected on the plasma spectrophotometer (standardized at 10 ppm). To be obtainable, the concentrations would have had to have been approximately 12.0 ppm or less. With this in mind, magnesium concentrations obtained for the 10^3 nmwl filtrate samples, I-1, II-1, and III-1, indicate considerable retention of magnesium by the 10^3 nmwl filter. The major portion of the magnesium molecules in the

four untreated samples is therefore located in the size range greater than 10^3 nmwl.

Magnesium concentrations in the magnesium treated sample were obtained and the data are graphed in Figures 10 and 19. Filtration through the 10^6 nmwl filter resulted in a significant decrease in magnesium concentration as shown in Figure 10. Figure 19 shows a 45% retention by this filter. Results of filtration through the 10^5 nmwl filter were not significantly different. The 2.5×10^4 nmwl filter, however, reduced the concentration again and had a 77% retention as shown in Figure 19. Retention by the remaining filters, 10^4 and 10^3 nmwl, was 87.5 and 96.1% respectively.

Calcium

Values for calcium concentrations were not obtained because they were greater than the range selected on the plasma spectrophotometer. To be obtainable, the concentrations would have had to have been approximately 12.0 ppm or less.

Magnesium Treated Sample

As can be seen in Figures 2-19, the concentrations of metal molecules smaller than the respective filter sizes are greater in the magnesium treated sample than in the untreated samples, except for magnesium which was greatly reduced. Also, in most cases, the percent retained by the filters was lower. Therefore, a higher percentage of the various metals was passing through the filters. Consequently, the magnesium treatment for maximum color removal

also resulted in the breaking down of the large molecular complexes holding the metal molecules into smaller molecular complexes more capable of passing through the filters. The metal molecules were more evenly distributed through the molecular sizes.

Distilled Water Sample

The distilled water sample was analyzed to provide a check on the filtration, digestion, and analysis process and on the contamination of and by the filters. Levels of metals in the distilled water were very low initially and in most cases were lower after filtration, digestion, and analysis. Results of the distilled water analysis would indicate no problems with the filtration, digestion, analysis process and no gross contamination of the filters.

Color

The effects of ultrafiltration on color can readily be seen in Figures 20 and 21. In Figure 20, the graphs of color units (PCU) vs. filter size (nmwl) for the four untreated samples are in agreement with each other and indicate considerable color removal. Filtration through the 10^6 nmwl filter resulted in color removal efficiencies of 13.6 to 32.6% with an average of 18.9%. Filtration through the 10^5 nmwl filter resulted in no additional color removal. Filtration through the 2.5×10^4 nmwl filter resulted in color removal efficiencies ranging from 68.2% to 85.4% with an average of 77.1%. Further filtration through the remaining two filters results in average color removal efficiencies of 69.9%

and 95.9% for the 10^4 nmwl and 10^3 nmwl filters, respectively. The majority of the color causing material in the four untreated samples is located in the fraction greater than 2.5×10^4 nmwl.

Correlations Between Color and Metals

In most cases of the four untreated samples, percent retention of metals at the 10^6 nmwl filter was above 30-40% and in some instances was as high as 60-75%, i.e., arsenic, cadmium, iron, copper, and nickel. For each metal, there was usually no significant increase in percent retained by the 10^5 nmwl filter as opposed to the 10^6 nmwl filter. At the 2.5×10^4 nmwl filter, however, there was, in all cases, a great decrease in metals concentration and an increase in percent retained. Further filtration at the 10^4 and 10^3 nmwl levels produced no significant decrease in metals concentrations or increase in percent retained in any case. These results correspond to the color analysis and tend to indicate a fairly strong correlation between the color and the metals concentrations in the untreated samples.

In the case of nickel, however, filtrations through the 10^6 nmwl filter retained approximately 90% or greater (samples I and II) and thus lessens the possibility of a correlation between color and nickel.

In the magnesium treated sample, the concentrations of the various metals passing the respectively smaller filter sizes were greater than with the untreated samples indicating that in the

absence of color causing materials, the metal molecules were bound in smaller molecular complexes. Thus, when the color causing materials, greater than 2.5×10^4 nmwl, were removed, more of the metals molecules passed the smaller filters, i.e., 2.5×10^4 , 10^4 , and 10^3 nmwl. This also indicates a fairly strong correlation between the molecular size distribution of metals and the color present in the samples.

In all cases, filtration through the 10^3 nmwl filter significantly reduced the metals concentrations.

TABLE 7

DATA FOR METALS CONCENTRATIONS IN ULTRAFILTRATION PROCESS

Sample	Metals Concentration (ppm)									
	Zn	Cd	As	Ni	Cu	Mg	Fe	Pb	Ca	Cr
I-II	.017	.003	.038	.016	.031		.340	.068	-	.003
I- 1	.032	.001	-*	.016	.058	3.635	.762	.058	-	.007
I- 2	.028	.003	.050	.003	.016	-	.306	.053	-	.006
I- 3	.015	.001	.050	.002	.015	-	.160	.048	-	.003
I- 4	.029	.002	.055	.003	.017	-	.308	.053	-	.003
I- 5	.009	.001	.021	.005	.019	-	.168	.044	-	.002
I- 6	.013	.001	.068	.009	.020	-	.337	.053	-	.003
I- 7	.036	.000	.054	.002	.023	-	.280	.052	-	.003
I- 8	.026	.001	.051	.002	.015	-	.355	.052	-	.003
I- 9	.032	.002	.051	.002	.024	-	.271	.053	-	.003
I-10	.036	.001	.090	.003	.013	-	.318	.053	-	.004
II- 1	.046	.005	.078	.005	.030	3.818	.738	.074	-	.015
II- 2	.028	.002	.092	.003	.018	-	.329	.055	-	.005
II- 3	.016	.002	.051	.002	.020	-	.170	.047	-	.003
II- 4	.025	.001	.041	.003	.014	-	.331	.053	-	.003
II- 5	.020	.000	.045	.002	.024	-	.124	.041	-	.002
II- 6	.038	.000	.036	.002	.016	-	.310	.051	-	.003
II- 7	.022	.001	.051	.002	.018	-	.256	.050	-	.002
II- 8	.031	.001	.048	.004	.019	-	.353	.050	-	.004
II- 9	.030	.002	.048	.003	.028	-	.265	.055	-	.004
II-10	.039	.002	.045	.003	.017	-	.351	.057	-	.004

TABLE 7 (Continued)

Sample	Metals Concentration (ppm)									
	Zn	Cd	As	Ni	Cu	Mg	Fe	Pb	Ca	Cr
III-IV	.010		.039	.002	.018		.308	.052	-	.006
III- 1	.041	.001	.104	.010	.003	4.186	.785	.054	-	.017
III- 2	.018	-	.115	.003	.019	-	.279	.050	-	.005
III- 3	.012	.001	-	.003	.020	-	.175	.046	-	.005
III- 4	.016	.000	.038	.005	.024	-	.305	.054	-	.005
III- 5	.013	.001	.022	.003	.028	-	.157	.046	-	.006
III- 6	.014	.000	.048	.004	.030	-	.273	.053	-	.005
III- 7	.010	.001	.066	.005	.020	-	.195	.052	-	.006
III- 8	.012	-	.062	.004	.016	-	.325	.054	-	.003
III- 9	.018	.001	.067	.004	.156	-	.252	.058	-	.005
III-10	.015	-	.072	.003	.055	-	.292	.055	-	.005
IV- 1	.020	.001	-	.003	.027	-	.435	.048	-	.006
IV- 2	.019	.001	.063	.004	.016	-	.298	.058	-	.006
IV- 3	.008	.001	.024	.003	.033	-	.171	.049	-	.005
IV- 4	.016	.001	.067	.004	.029	-	.317	.058	-	.005
IV- 5	.015	.001	.059	.005	.256	-	.185	.049	-	.005
IV- 6	.015	.000	.080	.004	.091	-	.283	.058	-	.004
IV- 7	.015	.002	.133	.005	.017	-	.227	.059	-	.005
IV- 8	.013	.002	.085	.006	.018	-	.339	.059	-	.006
IV- 9	.016	.001	.060	.004	.188	-	.219	.055	-	.014
IV-10	.016	.001	.064	.004	.047	-	.276	.059	-	.006

TABLE 7 (Continued)

Sample	Metals Concentration (ppm)									
	Zn	Cd	As	Ni	Cu	Mg	Fe	Pb	Ca	Cr
V	.005	.003	.194	.029	.038	2.479	.205	.435	-	.071
V- 1	.016	.004	.083	.037	.046	.963	.385	.200	-	.060
V- 2	.019	.005	.135	.062	.069	1.210	.273	.249	-	.099
V- 3	.026	.008	.218	.093	.092	1.405	.281	.412	-	.151
V- 4	.030	.010	.226	.113	.078	1.058	.260	.349	-	.173
V- 5	.041	.013	.207	.143	.065	1.397	.388	.443	-	.218
V- 6	.044	.015	.300	.166	.103	1.585	.318	.482	-	.253
V- 7	.055	.018	.276	.187	.243	2.094	.344	.467	-	.279
V- 8	.060	.020	.305	.215	.200	2.401	.376	.526	-	.321
V- 9	.066	.021	.279	.233	.153	1.976	.388	.481	-	.342
V-10	.074	.023	.354	.259	.167	2.247	.385	.521	-	.379
VI	.006	.000	.013	.002	.024	.009	.142	.003	.079	.002
**VI- 1										
**VI- 2										
VI- 3	.006	.000	.026	.001	.012	.008	.126	.004	.124	.001
VI- 4	.005	-	-	.001	.018	.006	.106	.004	.134	.002
VI- 5	.018	-	.016	.002	.157	.020	.110	.003	.087	.001
VI- 6	.021	.000	-	.002	.209	.014	.075	.003	.069	.002
**VI- 7										
**VI- 8										
VI- 9	.025	.000	.010	.001	.209	.016	.117	.005	.095	.002
VI-10	.024	.000	-	.002	.232	.031	.158	.006	.241	.008

* Data not obtained

** Filter not used for this sample

TABLE 8

METALS CONCENTRATIONS

Sample	Filter Size (nmwl)	As	Cd	Cr	Cu	Fe	Pb	Ni	Zn	Mg	Ca
Raw I & II	NA	.038	.003	.003	.031	.340	.068	.016	.017	-*	-
I	10 ³	-	.000	.000	.001	.016	.001	.000	.002	.075	-
	10 ⁴	.007	.000	.000	.002	.023	.007	.000	.002	-	-
	2.5 x 10 ⁴	.002	.000	.000	.002	.014	.004	.000	.001	-	-
	10 ⁵	.031	.000	.002	.013	.163	.030	.001	.021	-	-
	10 ⁶	.025	.001	.001	.012	.133	.026	.001	.016	-	-
II	10 ³	.002	.000	.000	.001	.017	.002	.000	.001	.087	-
	10 ⁴	.006	.000	.000	.003	.022	.006	.000	.002	-	-
	2.5 x 10 ⁴	.003	.000	.000	.002	.009	.003	.000	.001	-	-
	10 ⁵	.031	.001	.001	.011	.156	.031	.001	.013	-	-
	10 ⁶	.017	.001	.001	.010	.091	.019	.001	.010	-	-
Raw III & IV	NA	.039	-	.006	.018	.308	.052	.002	.010	-	-
III	10 ³	.002	.000	.000	.000	.016	.001	.000	.001	.085	-
	10 ⁴	-	.000	.002	.006	.053	.014	.001	.004	-	-
	2.5 x 10 ⁴	.004	.000	.001	.005	.029	.008	.001	.002	-	-
	10 ⁵	.040	.001	.004	.012	.120	.032	.003	.006	-	-
	10 ⁶	.041	.001	.003	.096	.155	.036	.002	.011	-	-
IV	10 ³	-	.000	.000	.001	.015	.002	.000	.001	-	-
	10 ⁴	.006	.000	.001	.009	.045	.013	.001	.002	-	-
	2.5 x 10 ⁴	.011	.000	.001	.048	.035	.009	.001	.003	-	-
	10 ⁵	.088	.00	.003	.011	.150	.039	.003	.010	-	-
	10 ⁶	.034	.001	.008	.105	.123	.031	.002	.009	-	-

TABLE 8 (Continued)

Sample	Filter Size (nmwl)	As	Cd	Cr	Cu	Fe	Pb	Ni	Zn	Mg	Ca
Raw V	NA	.194	.003	.071	.038	.205	.435	.028	.005	2.479	-
V	10 ³	.008	.000	.006	.005	.039	.020	.004	.002	.096	-
	10 ⁴	.048	.002	.033	.020	.062	.091	.020	.006	.309	-
	2.5 x 10 ⁴	.086	.005	.090	.027	.160	.183	.059	.017	.577	-
	10 ⁵	.182	.012	.184	.160	.227	.308	.123	.036	1.382	-
	10 ⁶	.192	.014	.235	.105	.266	.330	.160	.045	1.357	-
Raw VI	NA	.013	.000	.002	.024	.142	.003	.002	.006	.009	.079
	**10 ³										
	10 ⁴	.612	.000	.000	.006	.060	.002	.000	.003	.004	.059
	2.5 x 10 ⁴	.005	-	.000	.046	.032	.001	.001	.005	.006	.025
	**10 ⁵										
	10 ⁶	.007	.000	.001	.137	.077	.003	.001	.016	.011	.062

* Data not obtained

** Filter not used for this sample

TABLE 9

PERCENT OF METALS RETAINED BY ULTRAFILTRATION

Sample	Filter Size (nmwl)	% Retained									
		Zn	Cd	As	Ni	Cu	Mg	Fe	Pb	Ca	Cr
I- 1	10 ³	90.1	99.3	--*	98.0	96.2	--	95.4	98.3	--	95.2
I- 3	10 ⁴	98.2	95.2	80.9	98.2	93.0	--	93.2	89.8	--	85.5
I- 5	2.5 x 10 ⁴	95.6	97.2	95.4	97.4	94.9	--	95.9	94.6	--	94.4
I- 7	10 ⁵	- 23.4	100.0	17.2	92.7	56.8	--	52.0	55.5	--	41.8
I- 9	10 ⁶	7.3	67.2	33.9	93.8	61.9	--	60.7	61.6	--	50.8
II- 1	10 ³	93.8	96.2	95.3	99.3	97.8	--	95.0	97.5	--	88.5
II- 3	10 ⁴	88.0	91.5	82.9	98.4	91.8	--	93.6	91.2	--	87.3
II- 5	2.5 x 10 ⁴	91.0	100.0	91.9	99.1	94.7	--	97.5	95.9	--	95.4
II- 7	10 ⁵	21.0	79.6	18.0	92.4	64.5	--	54.1	55.1	--	59.3
II- 9	10 ⁶	39.1	77.0	56.4	93.5	68.8	--	73.1	72.1	--	54.0
III- 1	10 ³	91.7	--	94.6	89.9	99.7	--	94.8	97.9	--	94.3
III- 3	10 ⁴	64.0	--	--	55.0	66.7	--	83.0	73.5	--	75.0
III- 5	2.5 x 10 ⁴	76.2	--	89.7	72.5	71.5	--	90.7	83.8	--	81.7
III- 7	10 ⁵	38.7	--	3.8	53.3	31.9	--	61.2	38.7	--	38.7
III- 9	10 ⁶	- 10.7	--	5.7	23.0	-433.0	--	49.7	31.4	--	48.8
IV- 1	10 ³	93.0	--	--	94.7	94.7	--	95.0	96.7	--	96.5
IV- 3	10 ⁴	79.7	--	83.8	60.6	51.9	--	85.4	75.3	--	78.1
IV- 5	2.5 x 10 ⁴	71.9	--	71.6	53.1	-166.7	--	88.7	82.3	--	84.4
IV- 7	10 ⁵	1.0	--	-125.1	65.0	37.7	--	51.4	25.1	--	45.0
IV- 9	10 ⁶	10.4	--	13.8	12.0	-484.9	--	60.2	40.8	--	-30.7
V- 1	10 ³	68.0	86.7	95.7	86.8	87.9	96.1	81.2	95.4	--	91.5
V- 3	10 ⁴	- 14.4	41.3	75.3	26.9	46.7	87.5	69.8	79.2	--	53.2
V- 5	2.5 x 10 ⁴	-238.9	- 79.1	55.9	-111.1	29.3	76.7	21.8	57.9	--	- 26.9
V- 7	10 ⁵	-626.0	- 29.6	6.1	-340.8	-322.1	44.3	-10.8	29.1	--	-159.4
V- 9	10 ⁶	-806.4	-380.7	1.2	-471.4	-176.5	45.3	-30.0	24.1	--	-230.8

* Data not obtained

TABLE 10

MASS BALANCE METALS CONCENTRATIONS

Sample	Filter Size (nmwl)	Mass Balance Metals Concentrations									
		As	Cd	Cr	Cu	Fe	Pb	Ni	Zn	Mg	Ca
Raw I & II	NA	.038	.003	.003	.031	.340	.068	.016	.017	-*	-
I	10 ³	-	.003	.006	.017	.315	.053	.003	.029	-	-
	10 ⁴	.054	.002	.003	.017	.287	.052	.003	.027	-	-
	2.5 x 10 ⁴	.064	.001	.003	.020	.323	.052	.009	.013	-	-
	10 ⁵	.053	.000	.003	.020	.311	.052	.002	.032	-	-
II	10 ⁶	.071	.001	.004	.018	.295	.053	.003	.034	-	-
	10 ³	.092	.002	.005	.018	.338	.055	.003	.034	-	-
	10 ⁴	.042	.001	.003	.015	.311	.052	.003	.024	-	-
	2.5 x 10 ⁴	.037	.000	.003	.017	.297	.050	.002	.037	-	-
Raw III & IV	10 ⁵	.050	.001	.003	.018	.294	.050	.003	.026	-	-
	10 ⁶	.046	.002	.004	.021	.321	.056	.003	.036	-	-
	NA	.039	(-)	.006	.018	.308	.052	.002	.010	-	-
	10 ³	.115	(-)	.005	.019	.289	.050	.003	.018	-	-
III	10 ⁴	(-)	.000	.005	.023	.266	.052	.004	.015	-	-
	2.5 x 10 ⁴	.043	.000	.005	.030	.252	.052	.004	.014	-	-
	10 ⁵	.064	(-)	.005	.018	.245	.053	.005	.011	-	-
	10 ⁶	.069	(-)	.005	.117	.267	.057	.004	.017	-	-
IV	10 ³	(-)	.001	.006	.016	.303	.058	.004	.019	-	-
	10 ⁴	.056	.001	.005	.030	.279	.048	.004	.014	-	-
	2.5 x 10 ⁴	.076	.000	.004	.122	.265	.056	.004	.015	-	-
	10 ⁵	.117	.002	.005	.017	.265	.059	.005	.014	-	-
IV	10 ⁶	.062	.001	.010	.126	.244	.057	.004	.016	-	-

TABLE 10 (Continued)

Sample	Filter Size (nmwl)	Mass Balance Metals Concentrations									
		As	Cd	Cr	Cu	Fe	Pb	Ni	Zn	Mg	Ca
Raw V	NA	.194	.003	.071	.038	.205	.435	.028	.005	2.479	-
V	10 ³	.130	.005	.095	.067	.284	.244	.060	.019	1.185	-
	10 ⁴	.224	.010	.168	.081	.265	.363	.109	.029	1.134	-
	2.5 x 10 ⁴	.262	.014	.239	.087	.347	.466	.156	.043	1.507	-
	10 ⁵	.286	.019	.293	.228	.355	.487	.197	.057	2.198	-
	10 ⁶	.303	.022	.354	.157	.387	.494	.241	.069	2.061	-
Raw VI	NA	.013	.000	.002	.024	.142	.003	.002	.006	.009	.079
VI	**10 ³	-	-	.002	.015	.116	.004	.001	.005	.007	.129
	10 ⁴	-	-	.002	.194	.085	.003	.002	.020	.016	.074
	2.5 x 10 ⁴	-	-	.002	.194	.085	.003	.002	.020	.016	.074
	**10 ⁵	-	-	.002	.194	.085	.003	.002	.020	.016	.074
	10 ⁶	-	.000	.004	.217	.131	.005	.001	.025	.021	.145

* Data not obtained

** Filter not used for this sample

TABLE 11

COLOR IN ULTRAFILTRATION FILTRATE SAMPLES

Sample	Filter Size (nmwl)	Absorbance	Color (PCU)	Percent Color Removal From Raw
Raw Water for Samples I & II	NA	.227	177.3	NA
I - 1	10^3	*	*	*
I - 3	10^4	.069	53.9	69.6
I - 5	2.5×10^4	.048	37.5	78.8
I - 7	10^5	.196	153.1	13.6
I - 9	10^6	.196	153.1	13.6
II - 1	10^3	*	*	*
II - 3	10^4	.053	41.4	76.6
II - 5	2.5×10^4	.033	25.8	85.4
II - 7	10^5	.157	122.7	30.8
II - 9	10^6	.153	119.5	32.6
Raw Water for Samples III & IV	NA	.170	132.8	NA
III - 1	10^3	.008	6.3	95.3
III - 3	10^4	.061	47.7	64.1
III - 5	2.5×10^4	.041	32.0	75.9
III - 7	10^5	.150	117.2	11.7
III - 9	10^6	.149	116.4	12.3
IV - 1	10^3	.006	4.7	96.5
IV - 3	10^4	.052	40.6	69.4
IV - 5	2.5×10^4	.054	42.2	68.2
IV - 7	10^5	.148	115.6	13.0
IV - 9	10^6	.141	110.2	17.0
500 PCU Standard	NA	.640	500.0	NA

* Data not obtained due to lack of sufficient sample volume

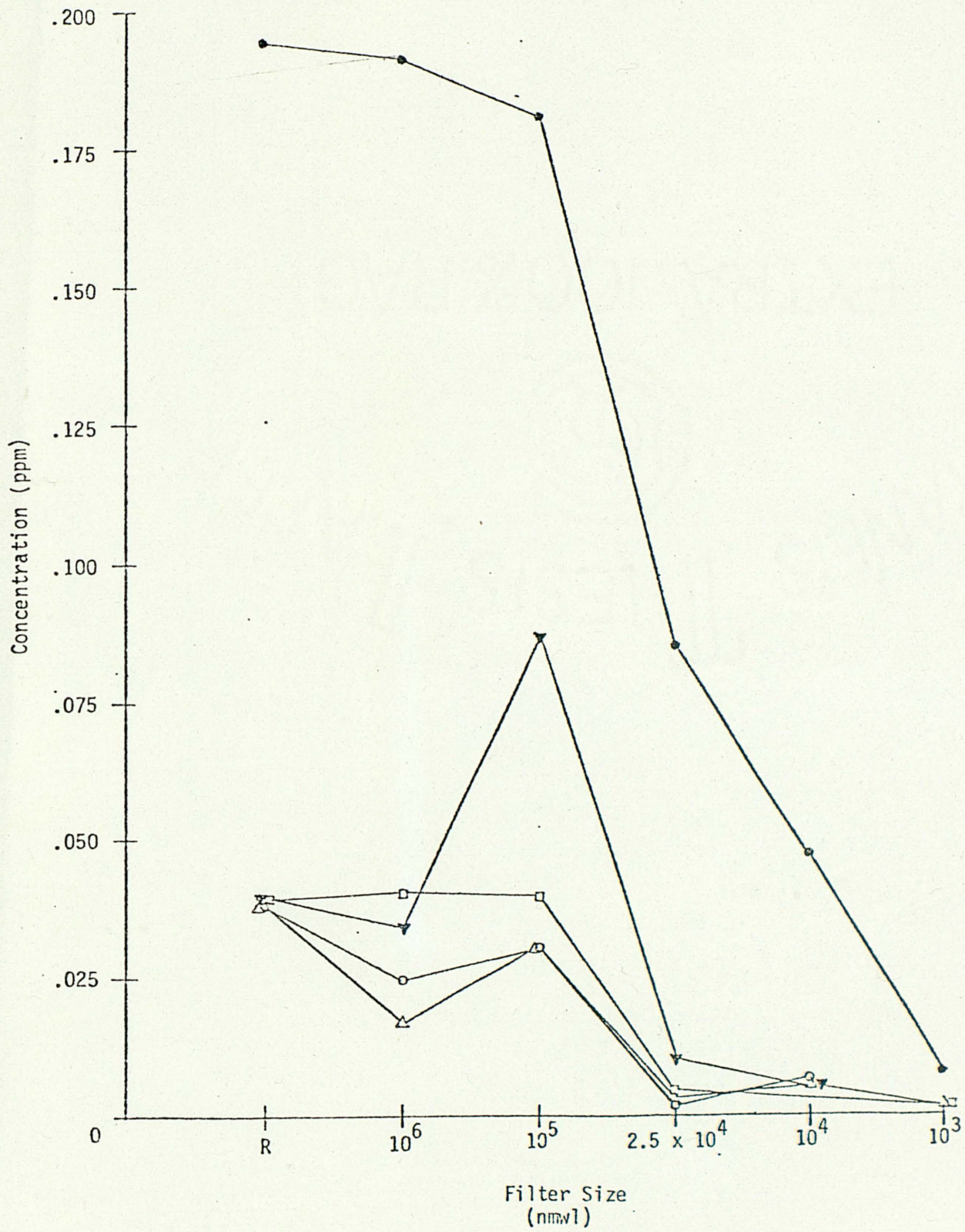


FIGURE 2

CONCENTRATION OF ARSENIC AS A FUNCTION
OF ULTRAFILTRATION FILTER SIZE

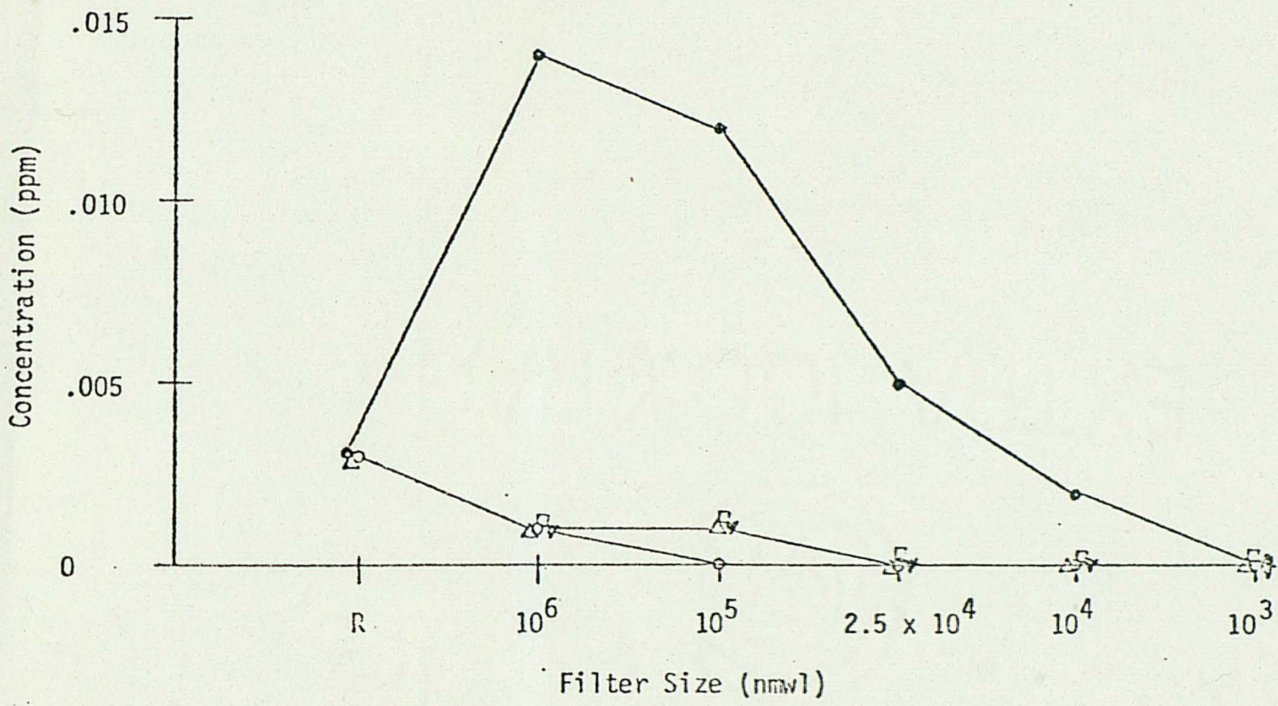


FIGURE 3

CONCENTRATION OF CADMIUM AS A FUNCTION
OF ULTRAFILTRATION FILTER SIZE

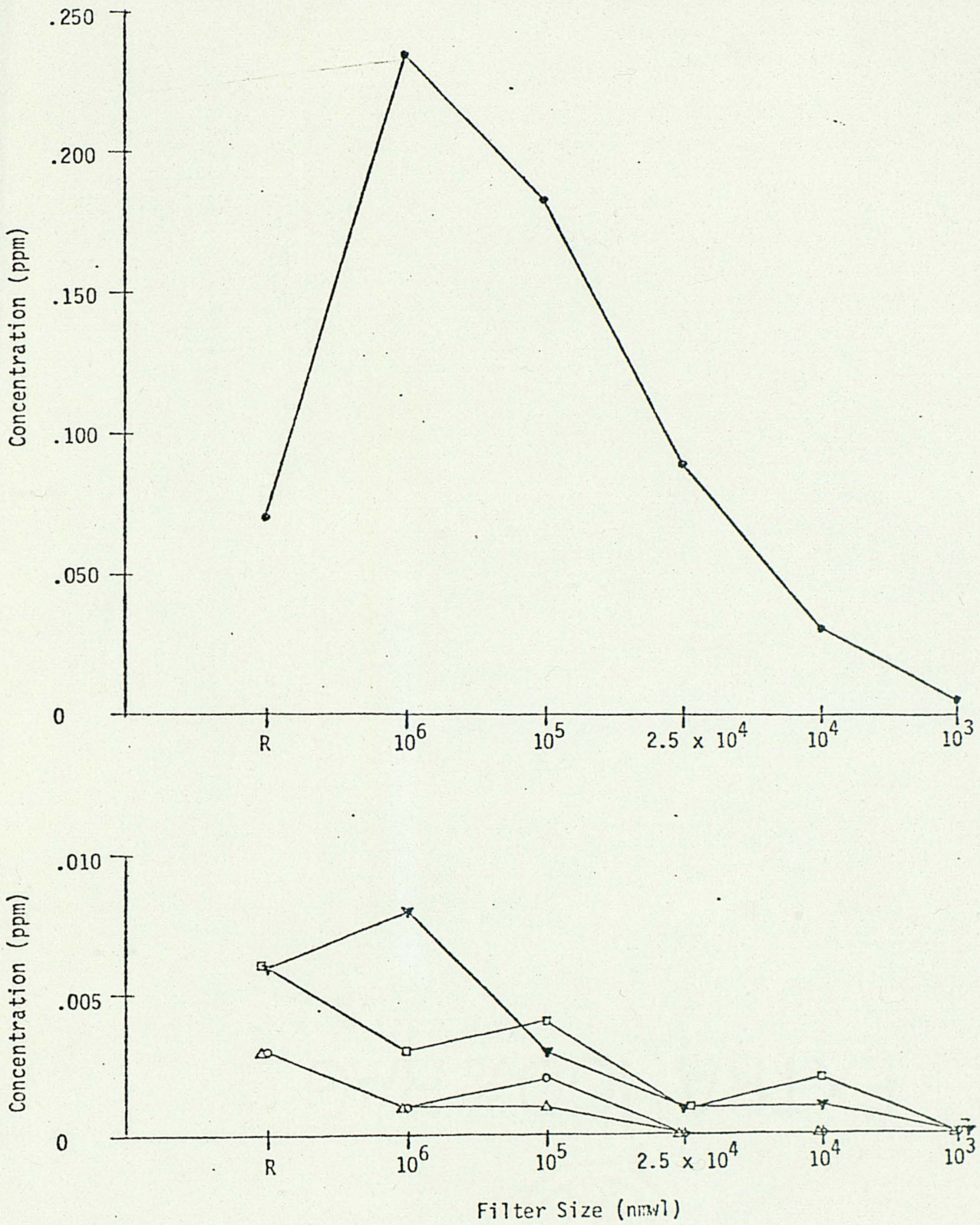


FIGURE 4

CONCENTRATION OF CHROMIUM AS A FUNCTION
OF ULTRAFILTRATION FILTER SIZE

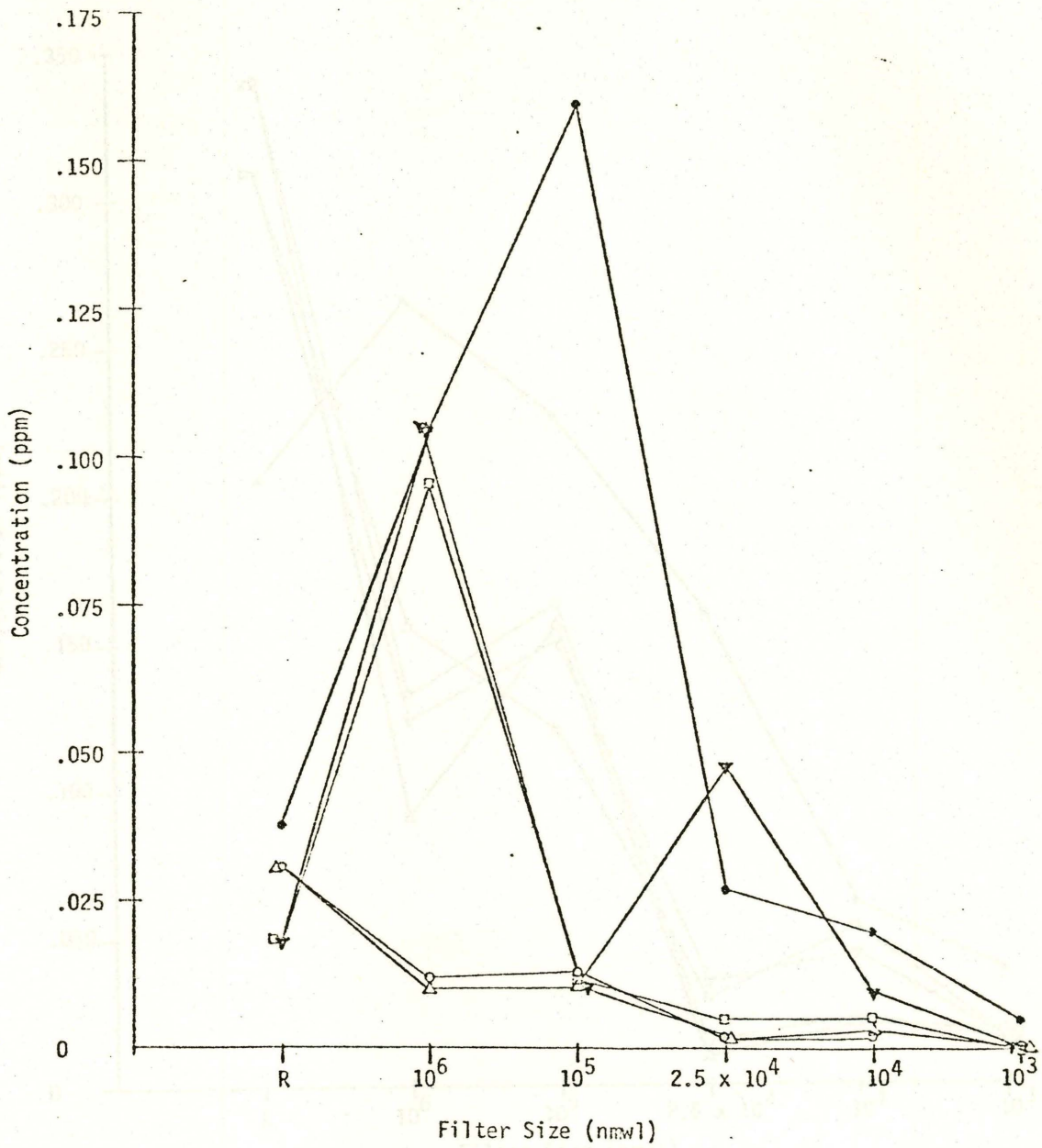


FIGURE 5

CONCENTRATION OF COPPER AS A FUNCTION
OF ULTRAFILTRATION FILTER SIZE

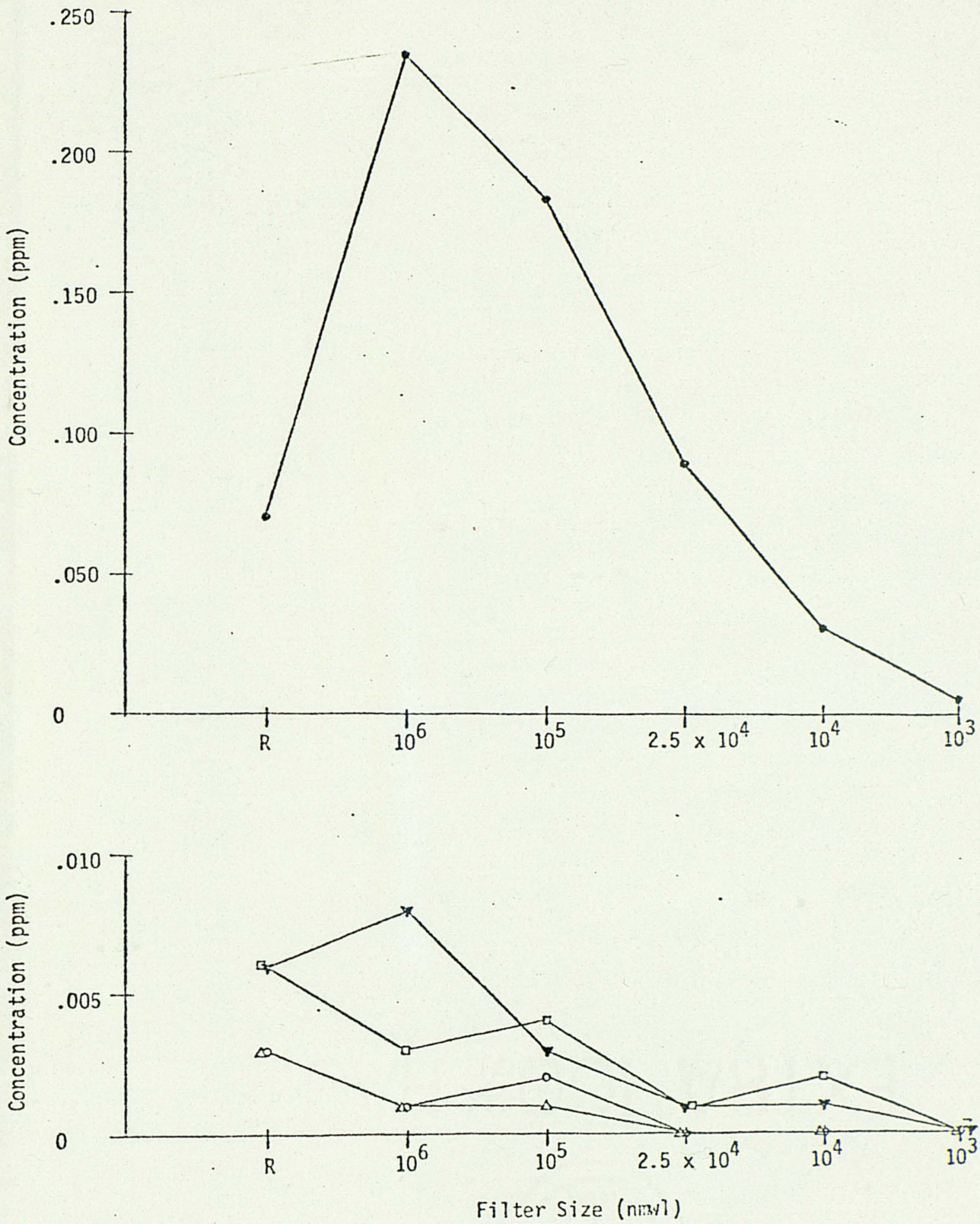


FIGURE 4

CONCENTRATION OF CHROMIUM AS A FUNCTION
OF ULTRAFILTRATION FILTER SIZE

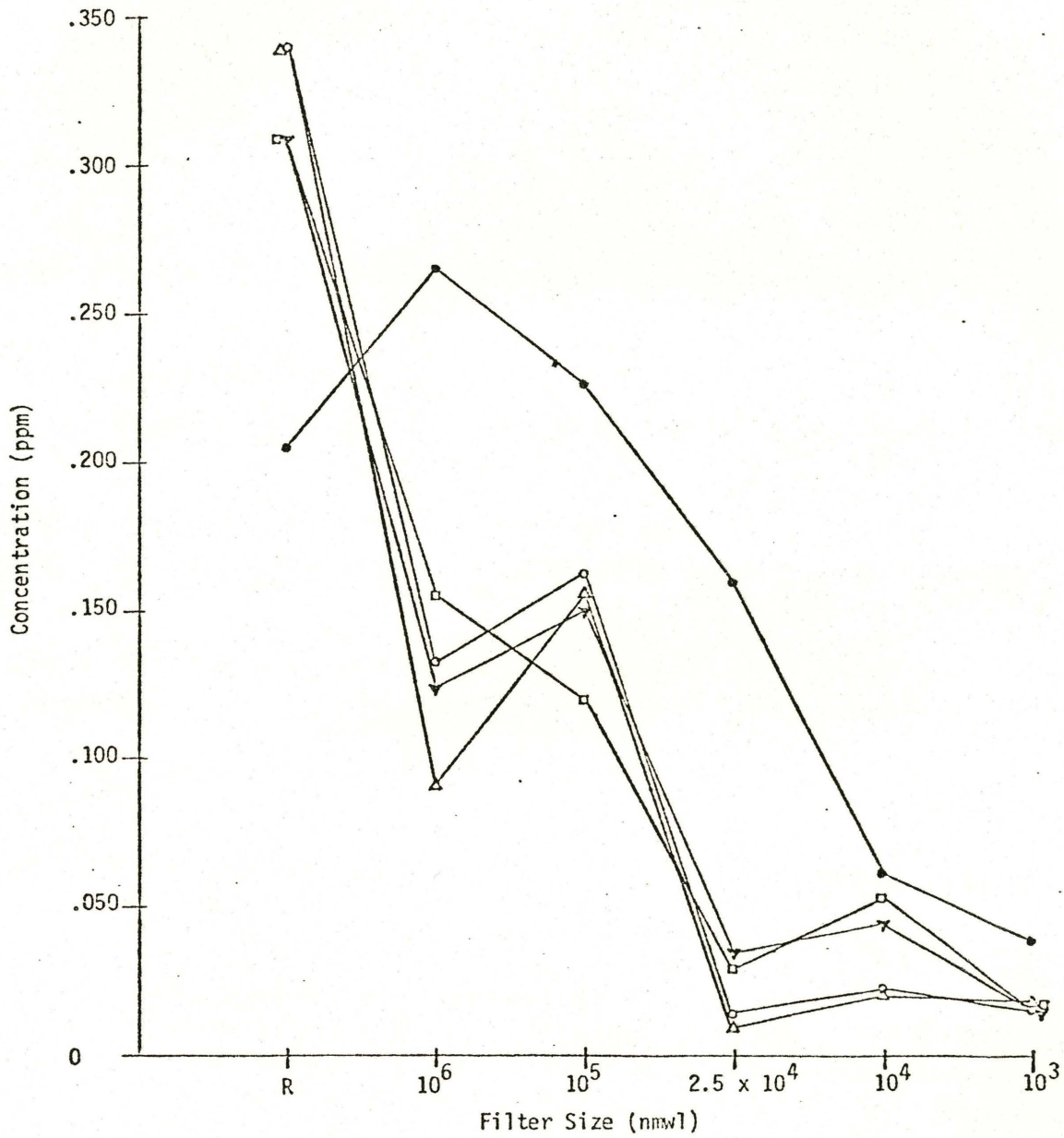


FIGURE 6

CONCENTRATION OF IRON AS A FUNCTION
OF ULTRAFILTRATION FILTER SIZE

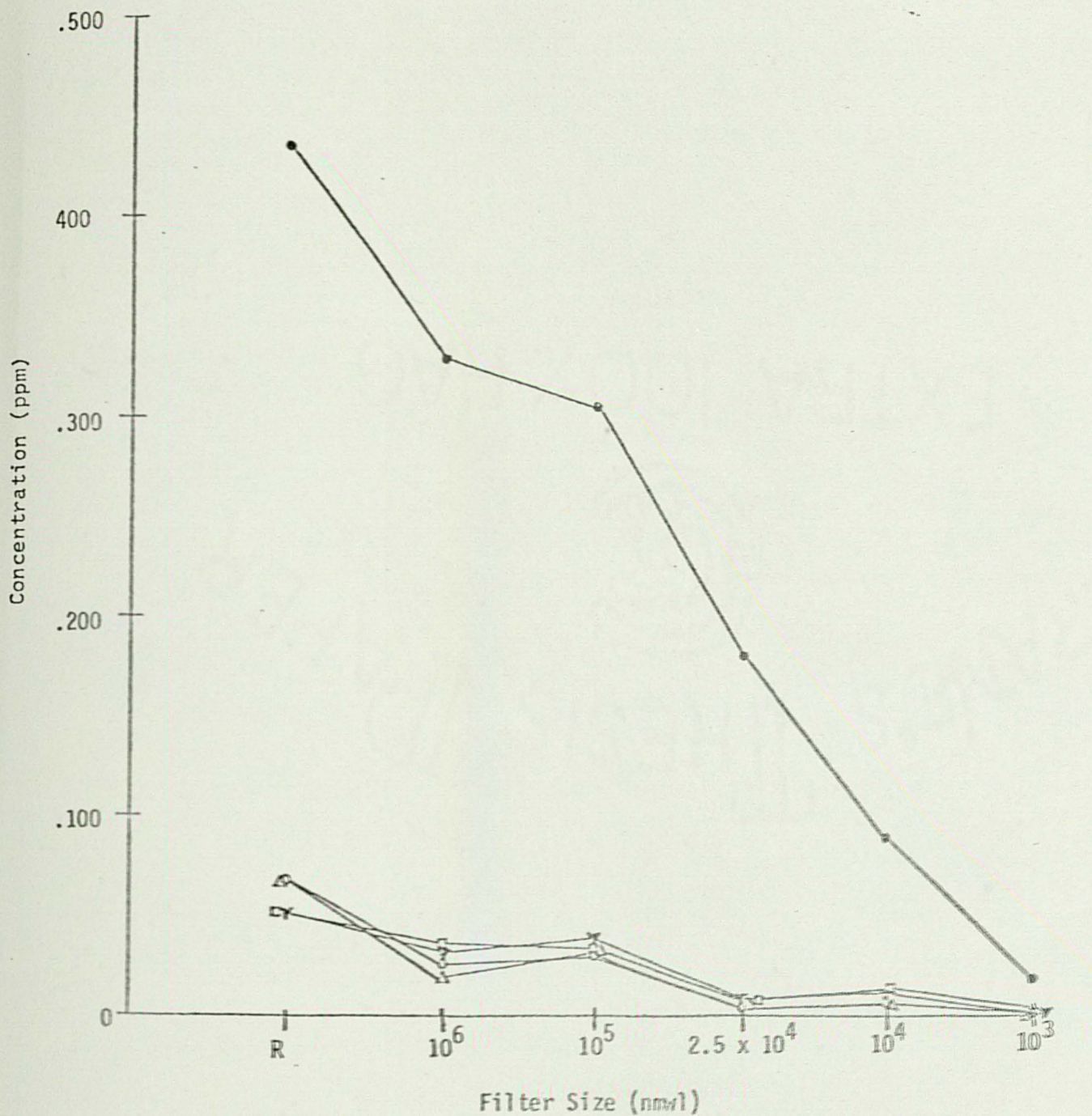


FIGURE 7

CONCENTRATION OF LEAD AS A FUNCTION
OF ULTRAFILTRATION FILTER SIZE

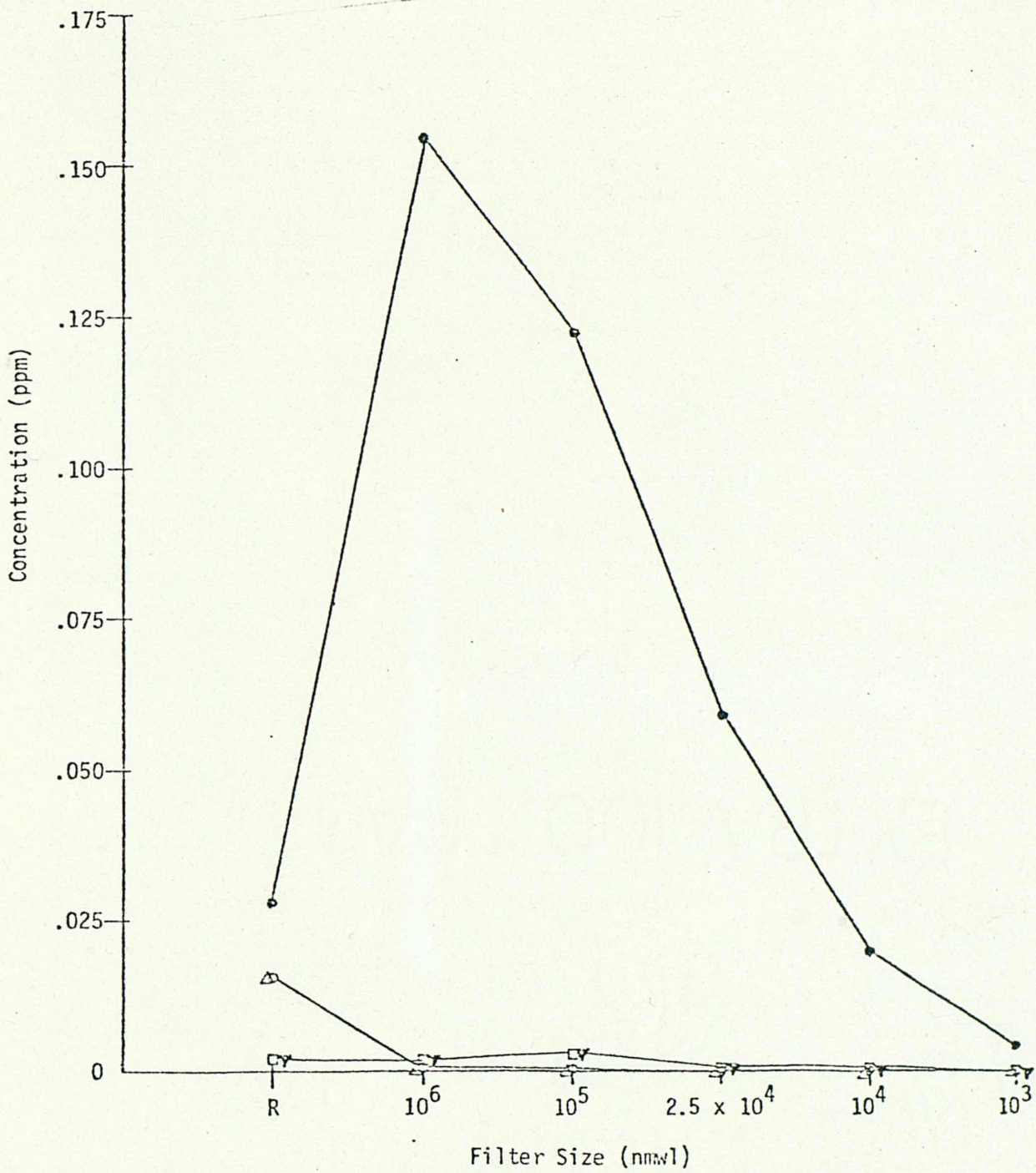


FIGURE 8

CONCENTRATION OF NICKEL AS A FUNCTION
OF ULTRAFILTRATION FILTER SIZE

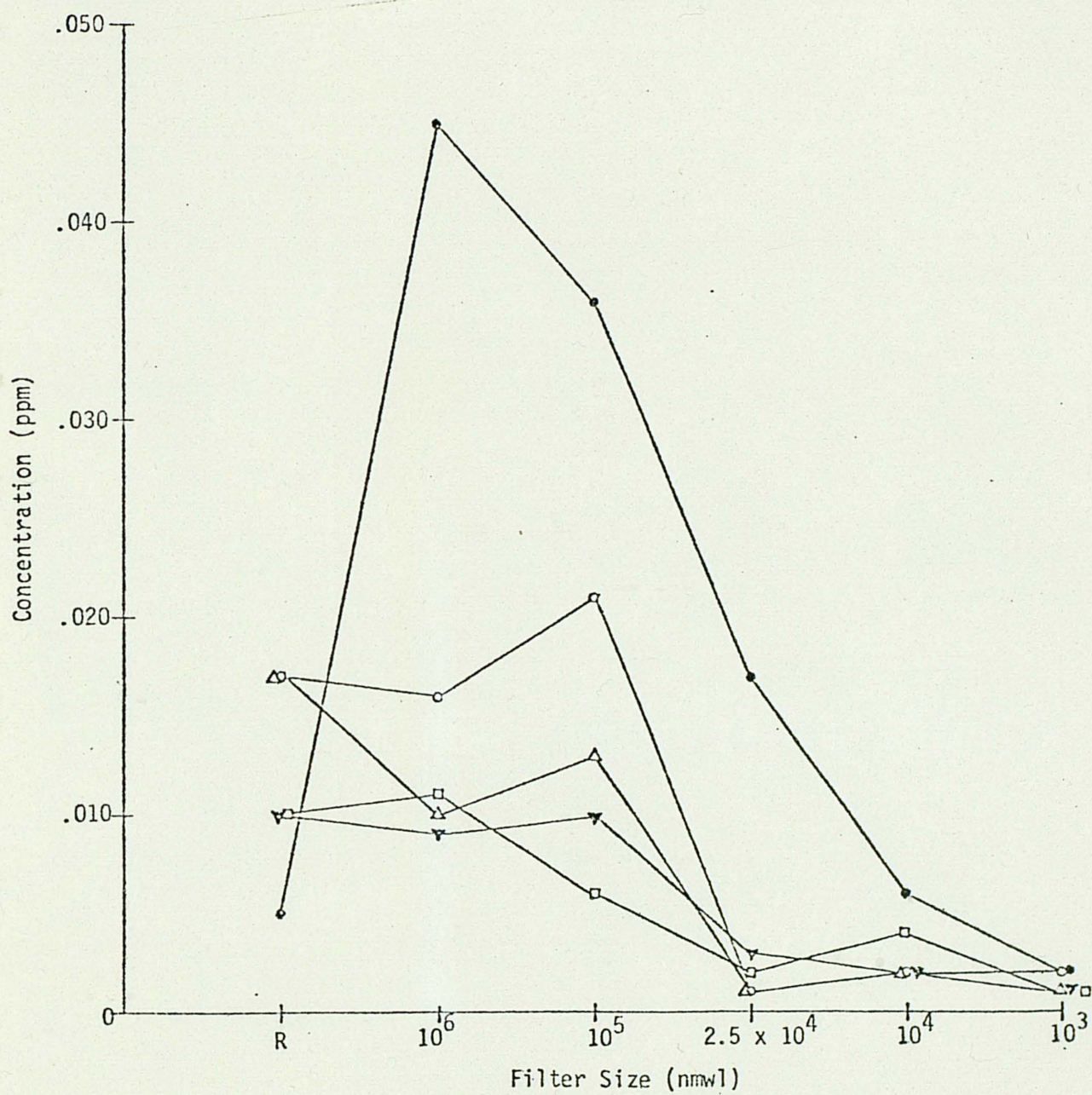


FIGURE 9

CONCENTRATION OF ZINC AS A FUNCTION
OF ULTRAFILTRATION FILTER SIZE

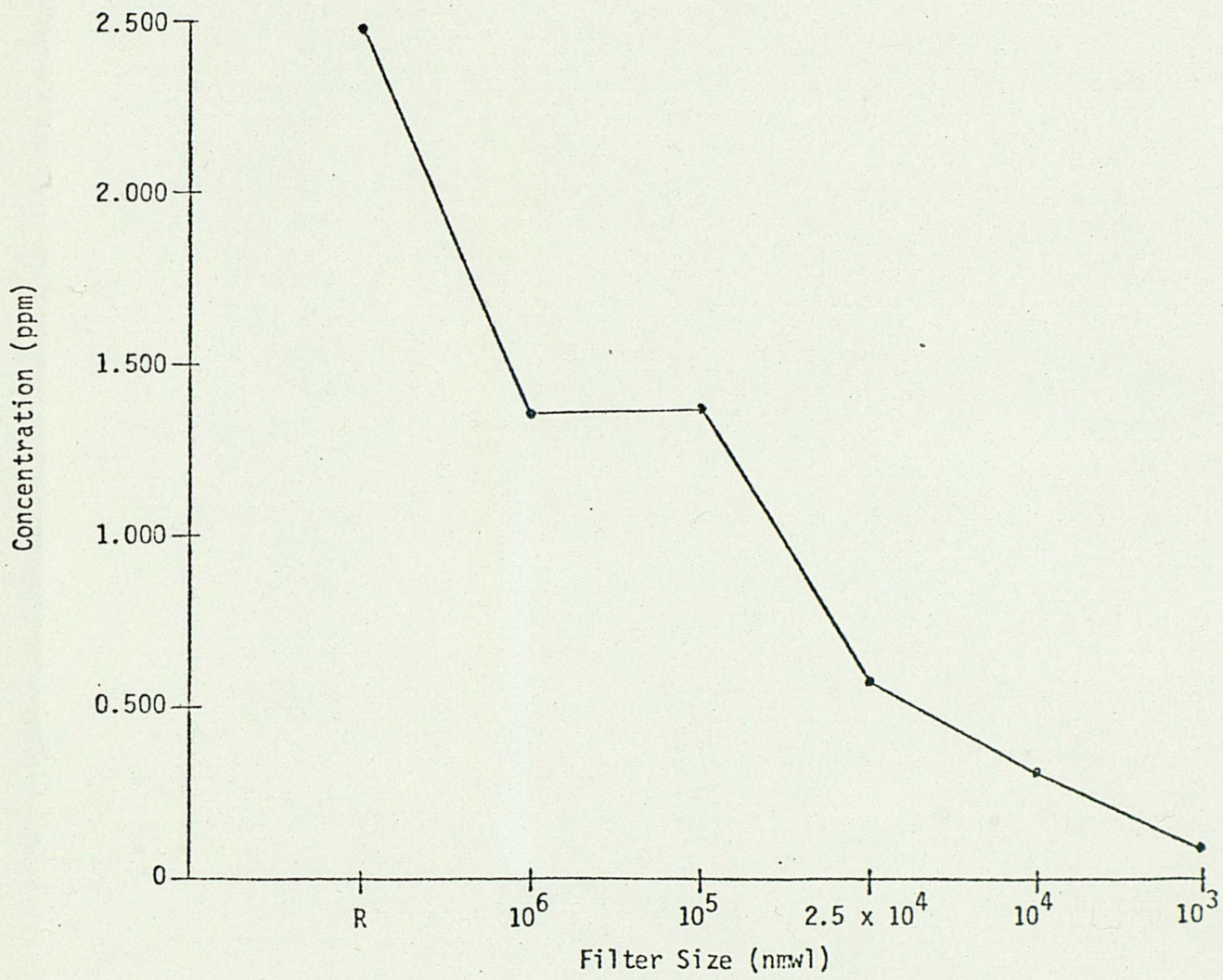


FIGURE 10

CONCENTRATION OF MAGNESIUM AS A FUNCTION
OF ULTRAFILTRATION FILTER SIZE

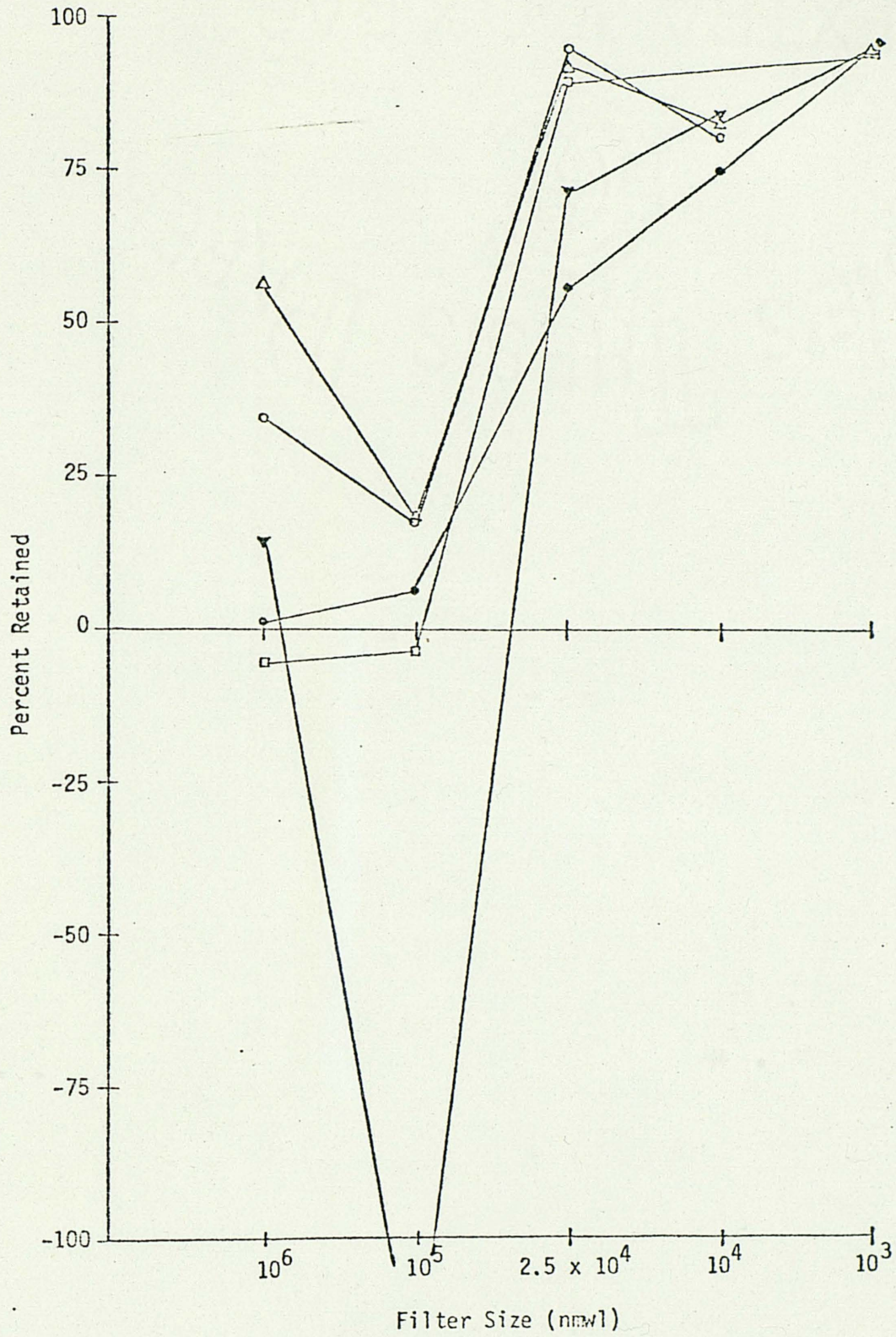


FIGURE 11

ARSENIC - PERCENT RETAINED BY ULTRAFILTRATION

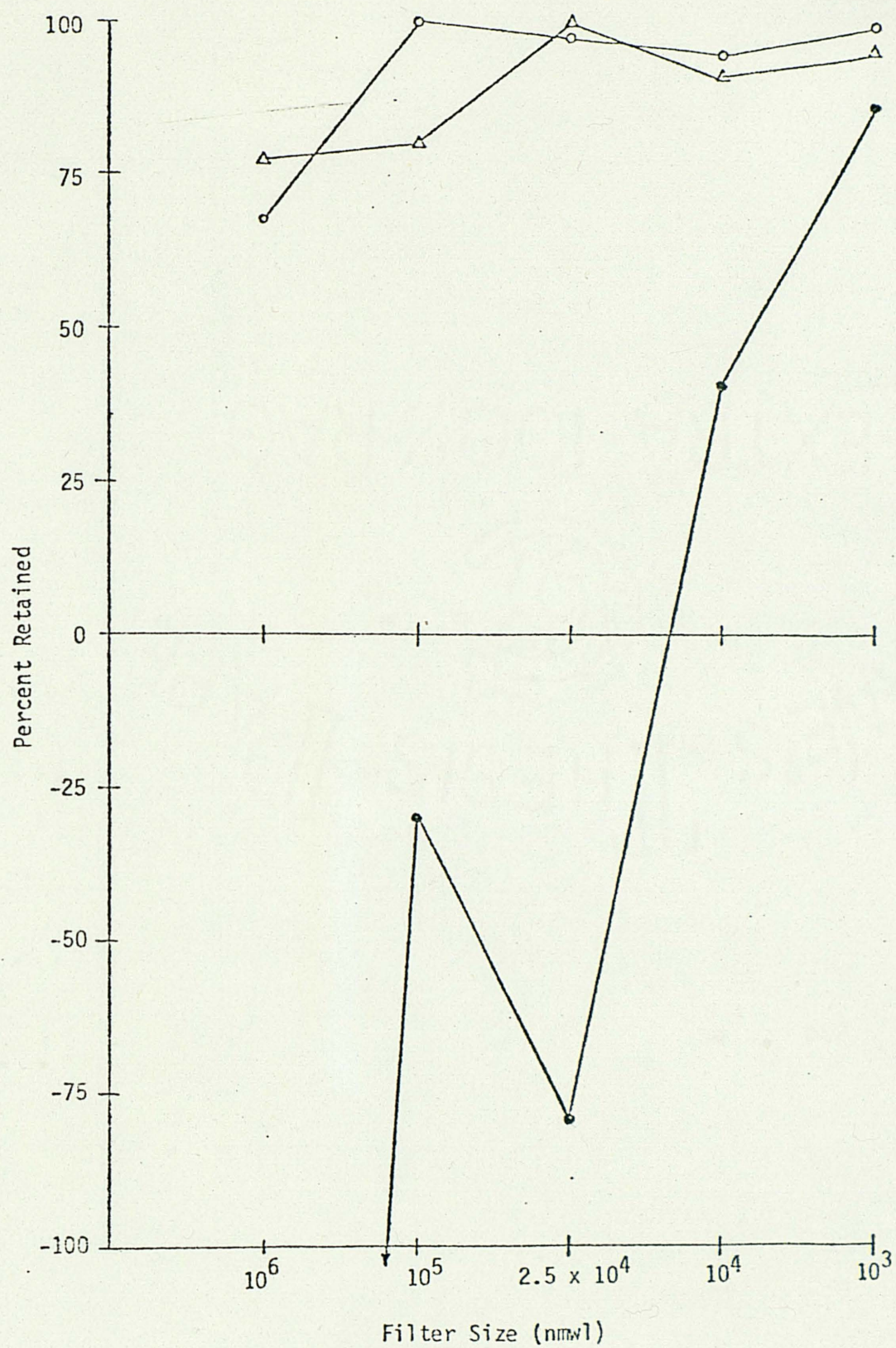


FIGURE 12

CADMIUM - PERCENT RETAINED BY ULTRAFILTRATION

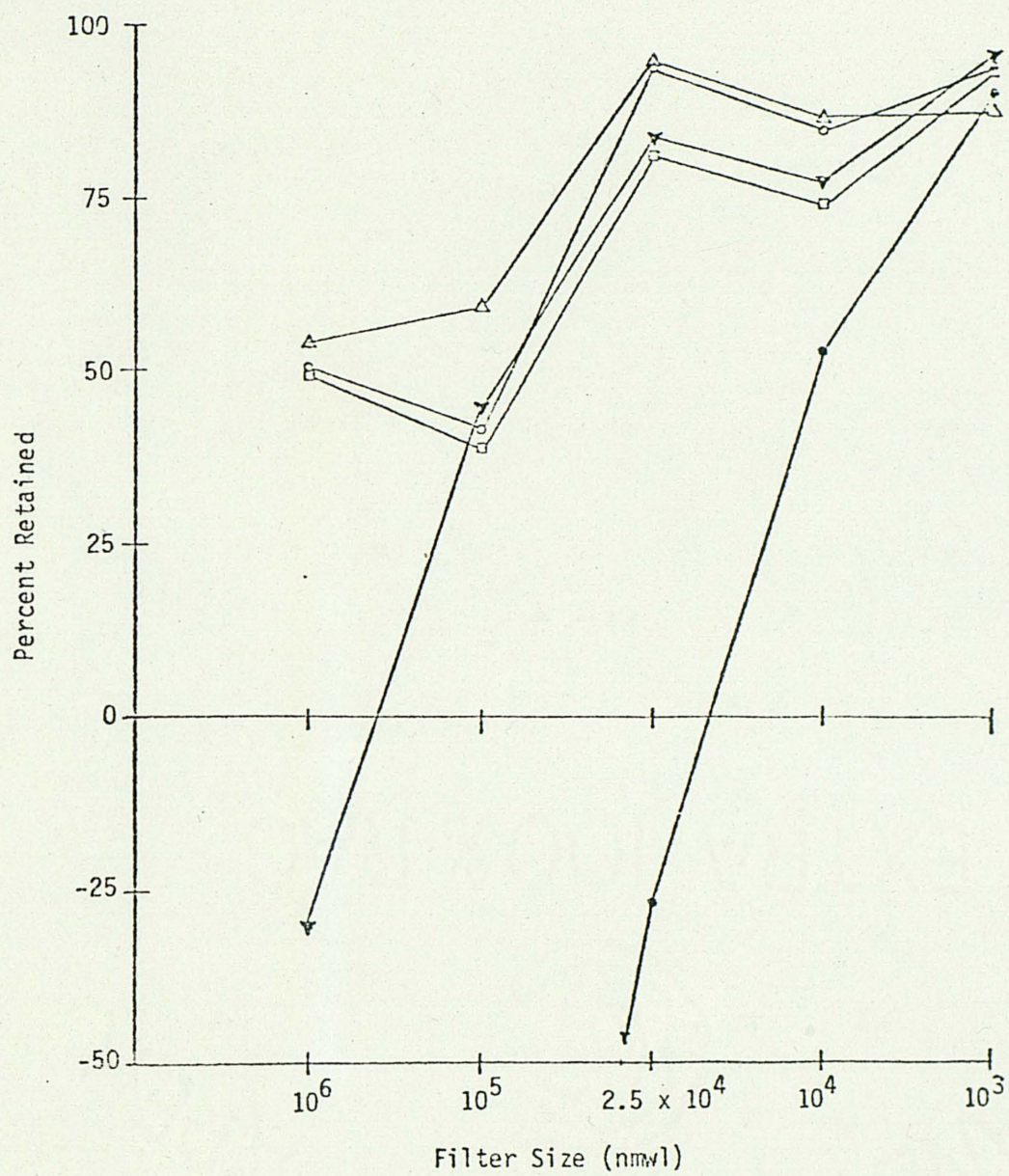


FIGURE 13

CHROMIUM - PERCENT RETAINED BY ULTRAFILTRATION

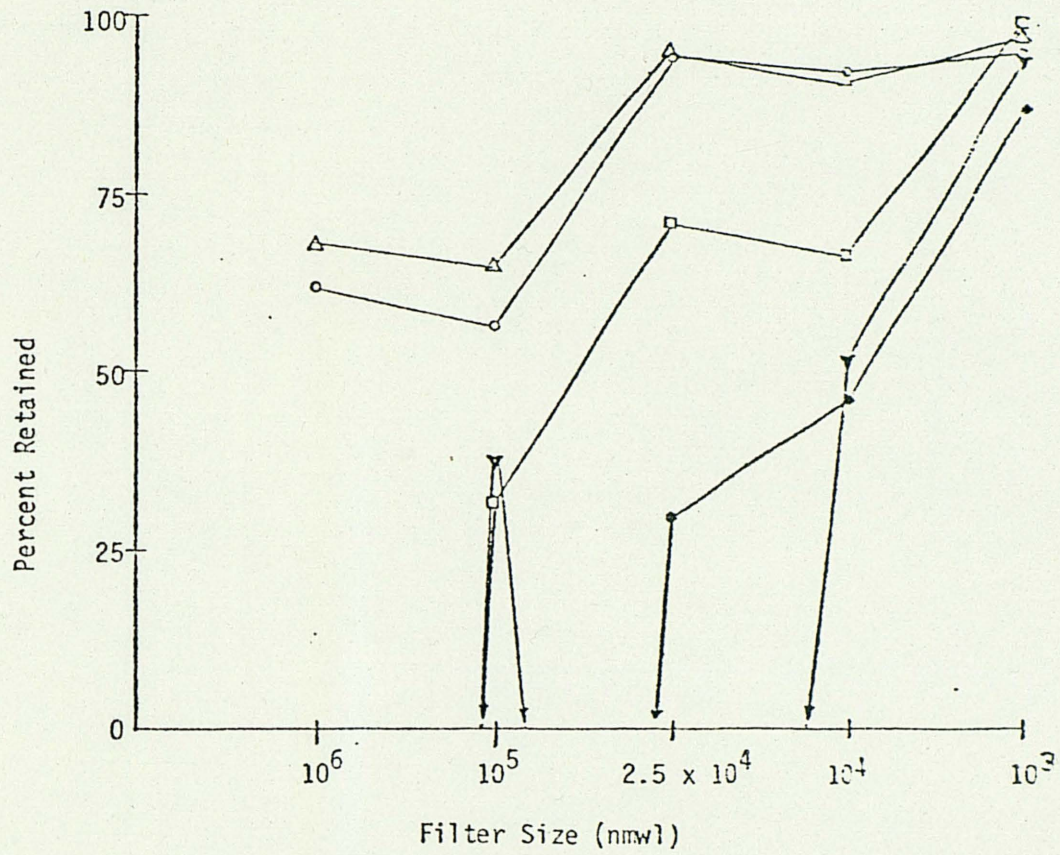


FIGURE 14

COPPER - PERCENT RETAINED BY ULTRAFILTRATION

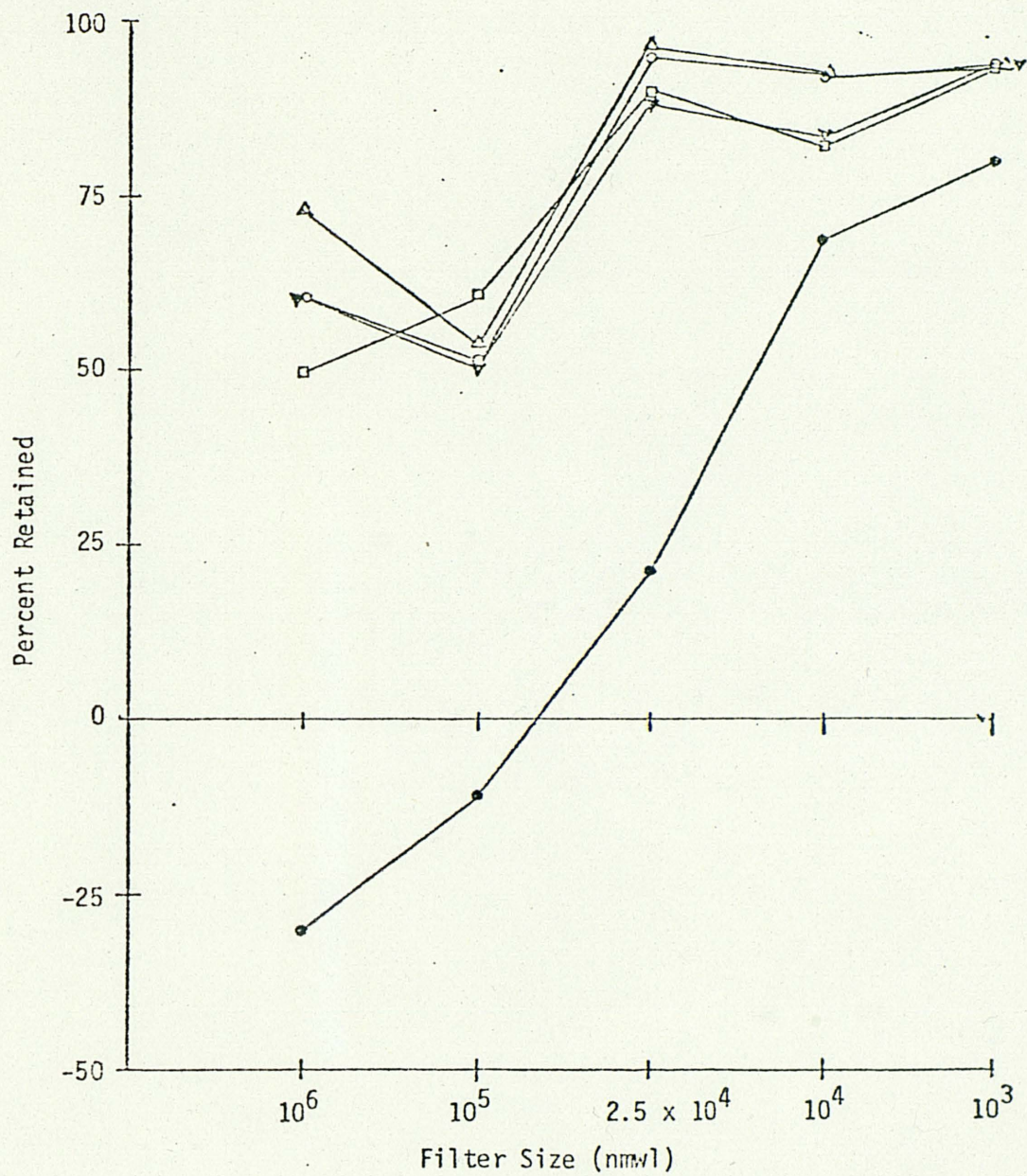


FIGURE 15

IRON - PERCENT RETAINED BY ULTRAFILTRATION

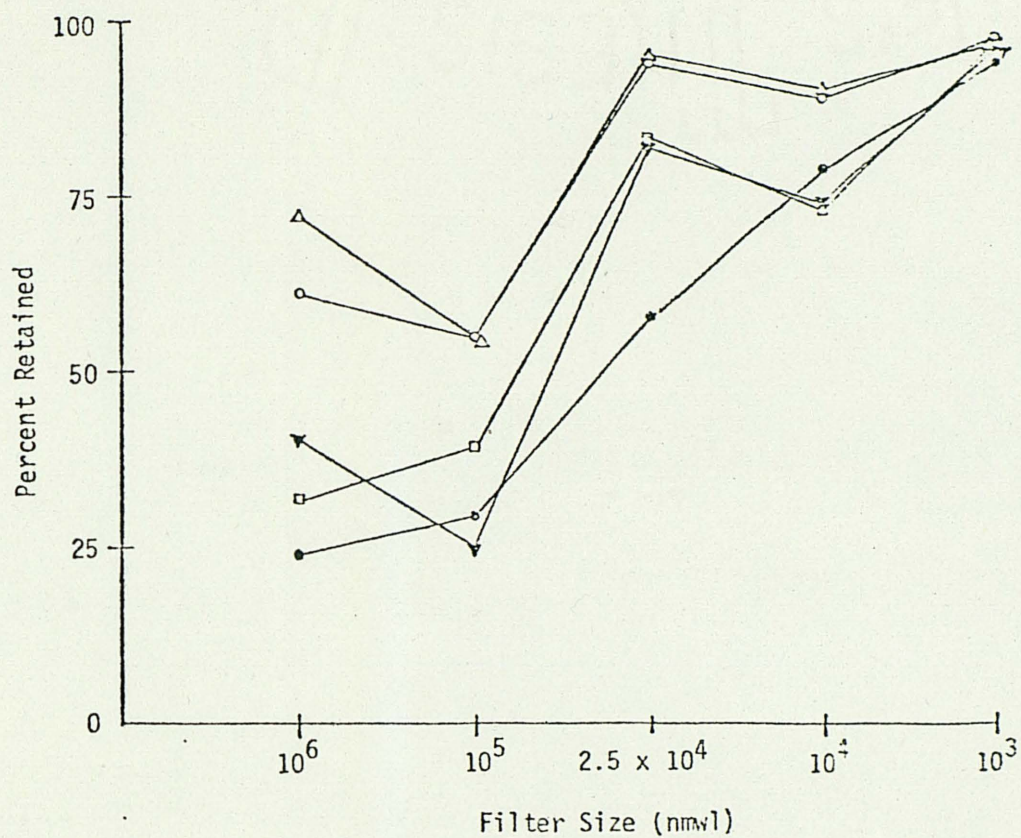


FIGURE 16

LEAD - PERCENT RETAINED BY ULTRAFILTRATION

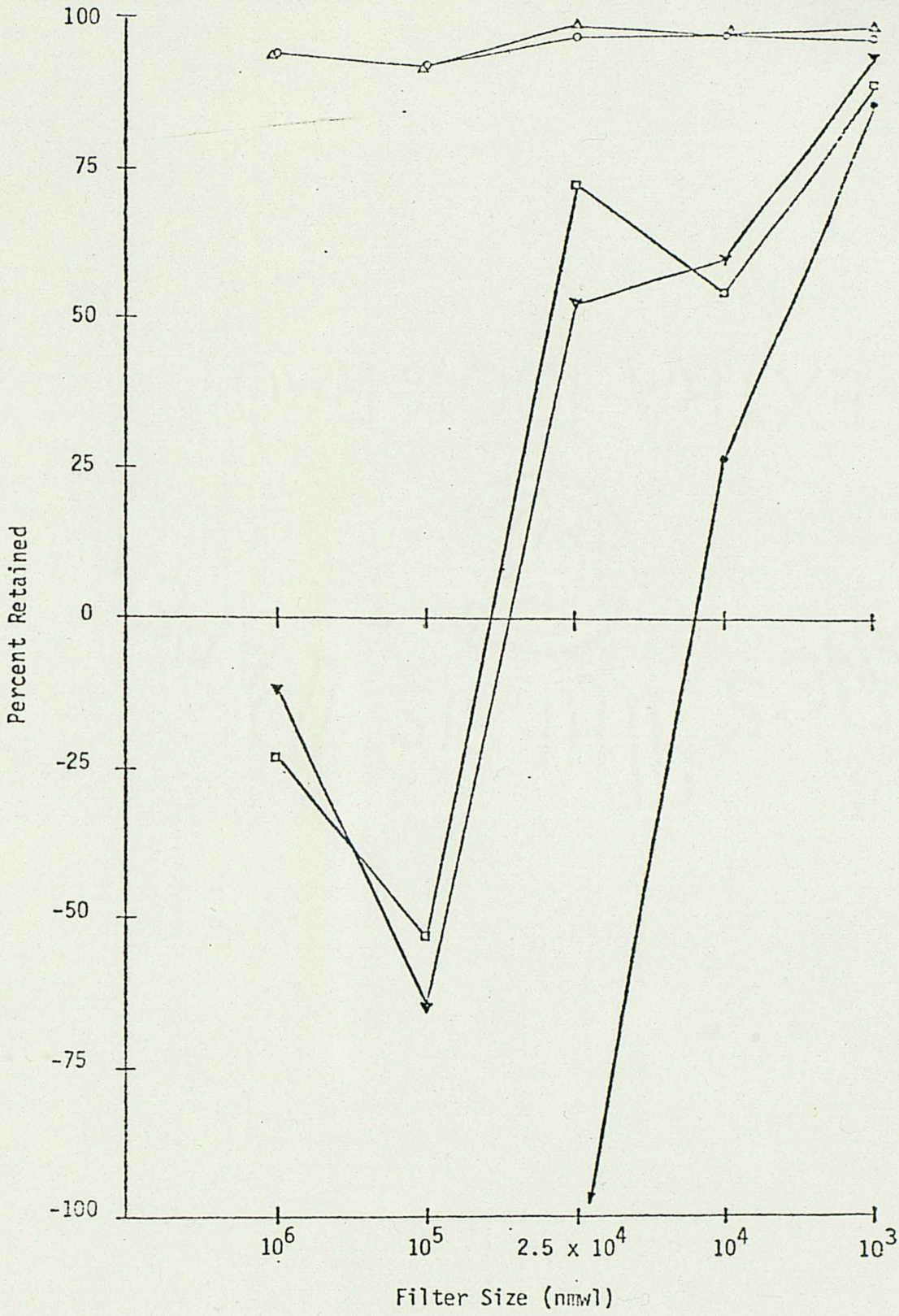


FIGURE 17

NICKEL - PERCENT RETAINED BY ULTRAFILTRATION

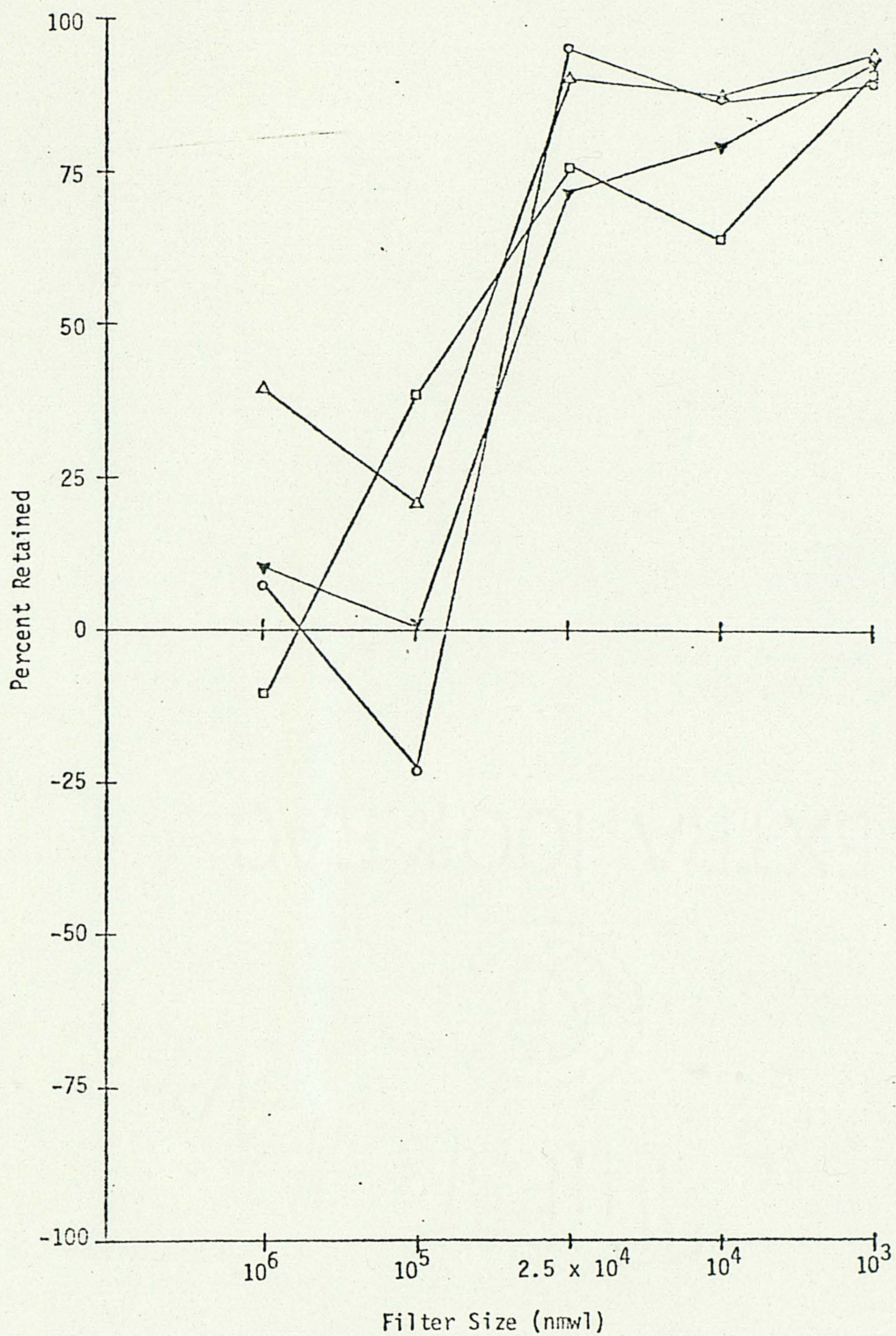


FIGURE 18

ZINC - PERCENT RETAINED BY ULTRAFILTRATION

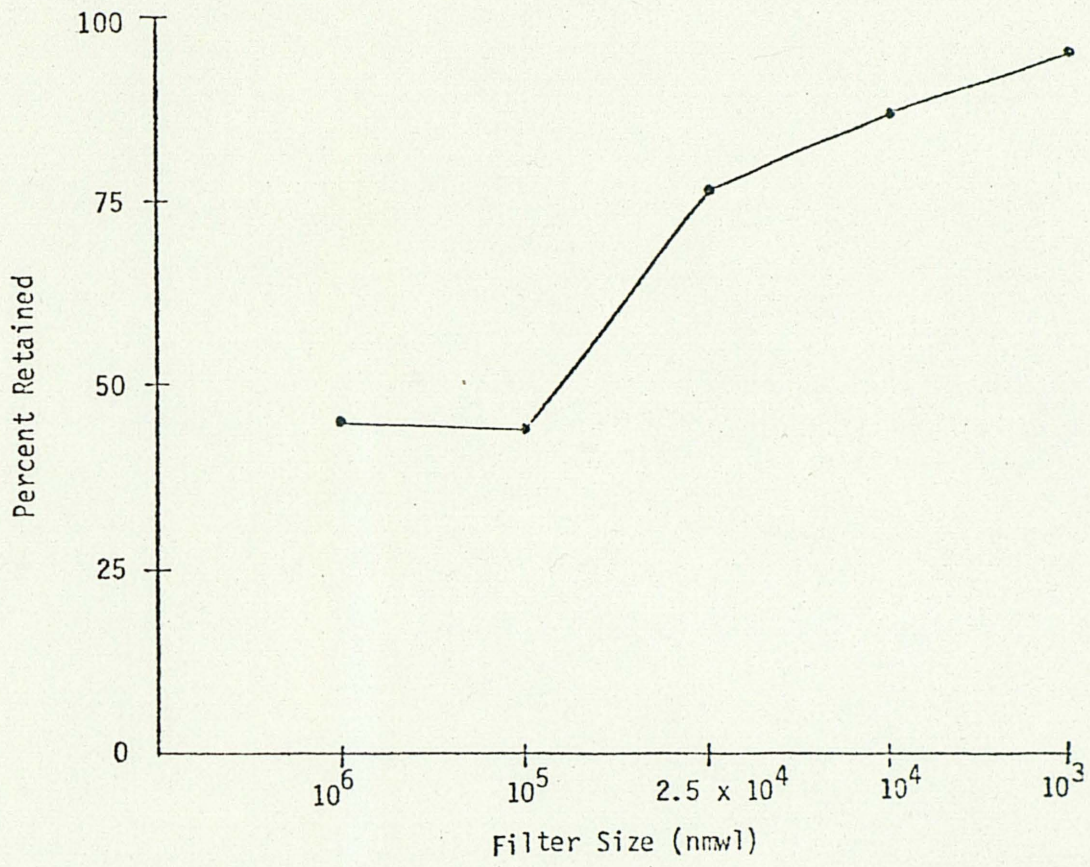


FIGURE 19

MAGNESIUM - PERCENT RETAINED BY ULTRAFILTRATION

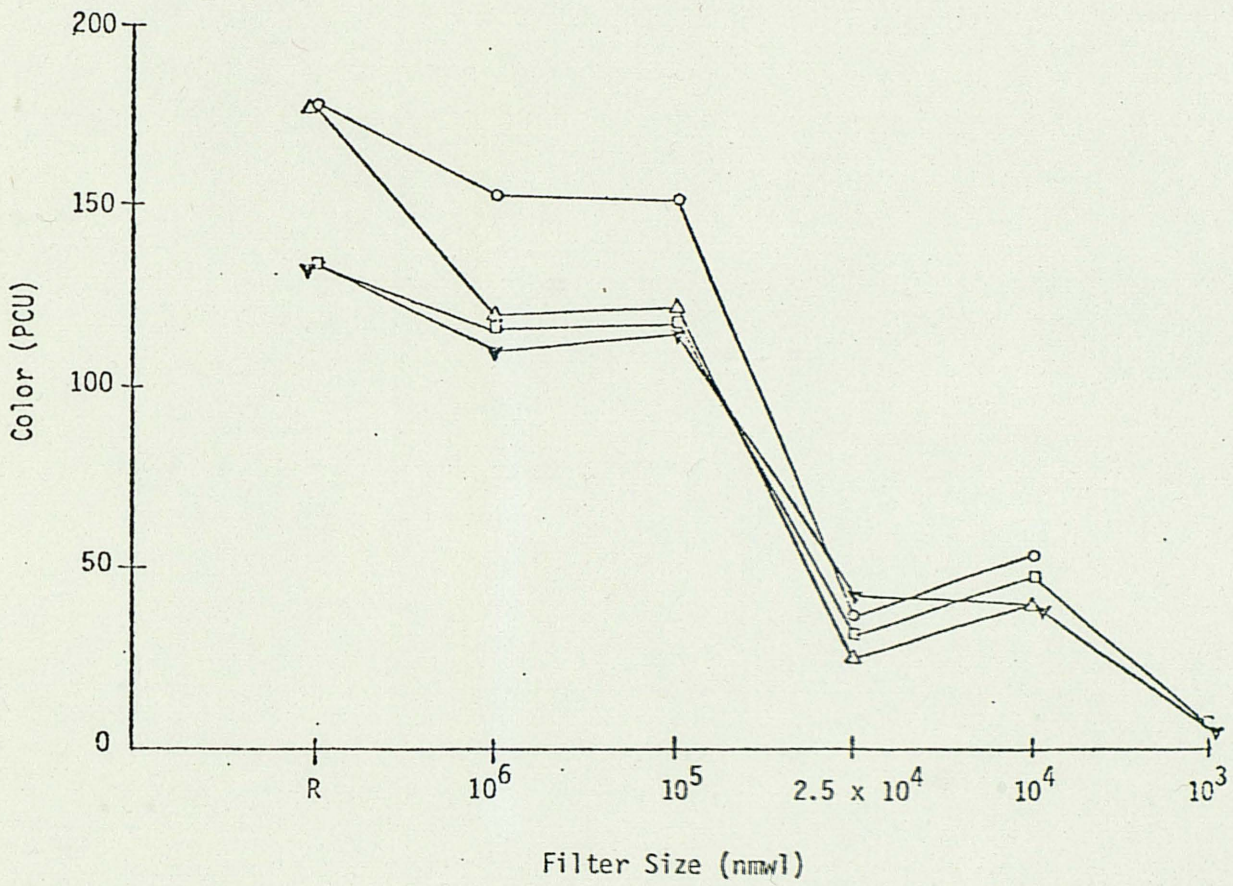


FIGURE 20

COLOR LEVELS IN ULTRAFILTRATION
FILTRATE SAMPLES

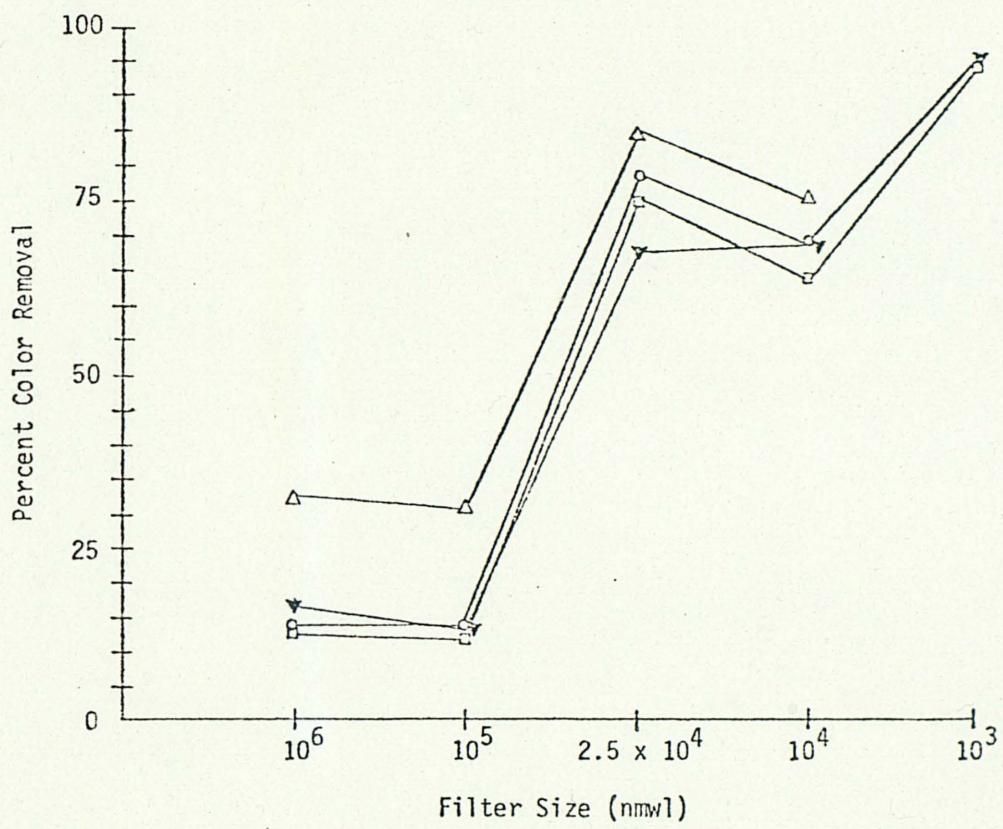


FIGURE 21

PERCENT COLOR REMOVAL BY ULTRAFILTRATION

CHAPTER V

CONCLUSIONS

Ultrafiltration of untreated Lake Washington water samples indicate definite molecular size distributions of color causing materials and heavy metals. Color causing materials in Lake Washington are located in the molecular weight fractions greater than 2.5×10^4 nmwl. In most cases, greater than 80% of the arsenic, cadmium, copper, chromium, iron, lead, nickel, and zinc concentrations are located in the molecular weight fraction greater than 2.5×10^4 nmwl indicating a fairly strong correlation between color and these metals in the Lake Washington water samples. This is in agreement with the sited literature.

When the Lake Washington water samples were treated with magnesium for maximum color removal, the metals concentrations passing the filters increased thus indicating that the metals were less restricted and were bound in smaller molecular weight complexes. Thus, we can conclude that the color causing materials were complexing the metals molecules.

BIBLIOGRAPHY

- Argaman, Y., and Weddle, C.L. "Fate of Heavy Metals in Physical-Chemical Treatment Processes," in Water-1973, AIChE Symposium Series 70, No. 136 (1974).
- Bender, M.E.; Matson, W.R.; and Jordan, R.A. "On the Significance of Metal Complexing Agents in Secondary Sewage Effluent." Environmental Science and Technology 4 (June 1970): 52-59.
- Benes, P.; Gjessing, E.T.; and Steinnes, E. "Interactions Between Humus and Trace Elements in Fresh Water." Water Resources 8 (1974): 947.
- Black, A.P., and Christman, R.F. "Characteristics of Colored Surface Waters." Journal of the American Water Works Association 55 (June, 1963): 753.
- California. State Water Quality Control Board. Water Quality Criteria. By McKee, J.E. and Wolf, H.W. Publication No. 3-A. Sacramento, California, 1963.
- Chau, Y.K. Journal of Chromatology Science 2 (1973): 579.
- Christman, R.F., and Mineau, R.A. "Organics in Lakes." Organic Compounds in Aquatic Environments. New York: Marcel Dekker, 1971.
- Cordes, E.H., and Schaeffer, R. Chemistry. New York: Harper & Row, 1973.
- Craun, G.F., and McCabe, L.J. "Problems Associated with Metals in Drinking Water." Journal of the American Water Works Association 67 (November 1975): 593-599.
- Egan, J.T., and Peterson, G.E. "Trace Metal Analysis Using Atomic Absorption Spectrophotometry." Journal of the American Water Works Association 65 (October 1972): 669-673.
- Fair, G.M.; Geyer, J.C.; and Okum, D.A. Elements of Water Supply and Wastewater Disposal. New York: John Wiley and Sons, 1971.
- Fairhall, L.T. Industrial Toxicology. Baltimore, Maryland: Williams & Wilkins, 1957.

- Faust, S.J., and Hunter, J.V. Organic Compounds in Aquatic Environments. New York: Marcell Dekker, 1971.
- Flinn, J., ed. Membrane Science and Technology, New York: Plenum Press, 1970.
- Gjessing, E.T., and Lee, G.F. "Fractionation of Organic Matter in a Mesomictic Lake." Water Resources 8 (1974): 239.
- Greenberg, A., et. al. Standard Methods for the Examination of Water and Wastewater. Washington, D.C.: American Public Health Association, 1975.
- Guy, R.D., and Chakrabarti, C.L. "Studies of Metal-Organic Interactions in Model Systems Pertaining to Natural Waters." Canadian Journal of Chemistry 54 (1976): 169-174.
- Hammer, D.H., et. al. "Hair Trace Metal Levels and Environmental Exposure," American Journal of Epidemiology 93 (1973): 84.
- Matson, W.R. "Trace Metals, Equilibrium and Kinetics of Trace Metal Complexes in Natural Media." Ph.D. dissertation, Massachusetts Institute of Technology, 1968.
- Millipore Corporation. Millipore Ultrafiltration Membranes and Systems, Cat. No. PB819, Bedford, Massachusetts, 1977.
- Millipore Corporation. Pellicon Cassette System - Assembly, Operation and Maintenance, Cat. No. OM029, Bedford, Massachusetts, 1975.
- Minear, R.A. "Analytical Techniques for Measuring and Monitoring Trace Metals." Journal of the American Water Works Association 67 (January 1975): 9-14.
- Morris, J.N.; Crawford, M.A.; and Healy, J.A. "Hardness of Local Water Supplies and Mortality from Cardiovascular Disease." Lancet 4 (1961): 161.
- McCabe, L.J. "Problems of Trace Metals in Water Supplies - An Overview in Trace Metals in Water Supplies: Occurrence, Significance, and Control." University of Illinois Bulletin. Vol. 71, No. 108 (1974): 1.
- Namerow, N.L. Industrial Water Pollution Origins, Characteristics and Treatment. Reading, Massachusetts: Addison-Wesley, 1978.

- National Research Council. Drinking Water and Health. Washington, D.C.: Government Printing Office, 1977.
- Neri, L.C.; Hewitt, D.; and Mandel, J.S. "Risk of Sudden Death in Soft Water Areas." Journal of Epidemiology 94 (1971): 101.
- Page, T.; Harris, R.H.; and Epstein, S.S. "Drinking Water and Cancer Mortality in Louisiana." Science 193 (1975): 55.
- Punsar, S., et. al. "Coronary Heart Disease and Drinking Water." Journal of Chronic Disease 23 (1975): 259.
- Purves, David. Trace Element Contamination of the Environment. New York: Elsevier-North Holland Scientific, 1977.
- Sanks, R.L. Water Treatment Plant Design for the Practicing Engineer. Ann Arbor, Michigan: Ann Arbor Science, 1979.
- Sauer, H.I., and Enterline, P.E. "Are Geographic Variations in Death Rate for Cardiovascular Diseases Real?" Journal of Chronic Disease 10 (1959): 513.
- Sawyer, Clair N., and McCarty, Paul L. Chemistry for Environmental Engineering. Hightstown, New Jersey: McGraw-Hill, 1978.
- Schindler, J.E.; Alberts, J.J.; and Honick, K.R. "Preliminary Investigation of Organic-Inorganic Associations in a Stagnating System." Limnology and Oceanography 17 (1972): 952.
- Schroeder, H.A. "Relation Between Mortality from Cardiovascular Disease and Treated Water Supplies." Journal of the American Medical Association 172 (1960): 1902.
- Schroeder, H.A., and Kraemer, L.A. "Cardiovascular Mortality, Municipal Water and Corrosion." Archives of Environmental Health 28 (1974): 303.
- Shapiro, J. "Effects of Yellow Organic Acids on Iron and Other Metals in Water." Journal of the American Water Works Association 56 (1964): 1062-1082.
- Shapiro, J. "The Relation of Humic Color to Iron in Natural Waters." Int. Ver. Theor. Angew. Limno. Verh. 16 (1966): 477-484.
- Shapiro, J. "Yellow Acid-Cation Complexes in Lake Water." Science 127 (1958): 702-704.

- Singer, O.C. Trace Metals and Metal-Organic Interactions in Natural Waters. Ann Arbor, Michigan: Ann Arbor Science, 1973.
- Stavenger, P.L. "Putting Semipermeable Membranes to Work." Chemical Engineering Progress 67 (March 1971): 3.
- Stiff, M.J. "The Chemical States of Copper in Polluted Fresh Water." Water Resources 5 (1971): 585.
- Stoof, H., and Haase, L.W. Von Wasser 12 (1937): 111.
- Theis, T.L., and Singer, P.C. "Complexation of Iron (II) by Organic Matter and its Effects on Iron (II) Oxygenation." Environmental Science and Technology 8 (June 1974): 64-66.
- U.S. Environmental Protection Agency. Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations. Cincinnati, Ohio: Environmental Protection Agency, 1977.
- U.S. Environmental Protection Agency. Quality Criteria for Water. Washington, D.C.: Government Printing Office, 1976.
- Webber, W.J., Jr. Physicochemical Processes for Water Quality Control. New York: Wiley-Interscience, 1972.
- Willey, B.F., et. al. "Atomic Absorption Spectrophotometry Simplifies Heavy Metals Analysis." Journal of the American Water Works Association 64 (May 1972): 303-306.
- Wolman, A. "Notes and Comments." Journal of the American Water Works Association 68 (April 1976): 216-217.
- Zemansky, G.M. "Removal of Trace Metals During Conventional Water Treatment." Journal of the American Water Works Association 66 (October 1974): 606-609.