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Recovery of trace organic pollutants by solvent extraction and freeze concentration

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RECOVERY OF TRACE ORGANIC POLLUTANTS
BY SOLVENT EXTRACTION AND FREEZE CONCENTRATION

BY

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THESIS

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ABSTRACT

The objective of this investigation was to evaluate the use of batch type solvent extraction and freeze concentration in recovering trace organic pollutants from water.

The work was performed using a simplified water system containing known concentrations of phenol, and natural water systems collected from three sources (Meramec Spring, Gasconade River near Jerome, and Missouri River in Jefferson City) with different levels of pollution. The simplified water system was used to evaluate the effect of the number of extractions, solvent to sample ratio, extraction time, initial organic concentration, pH, and turbidity on solvent extraction; and the effect of volumetric concentration and flash freezing on freeze concentration. The natural water systems were employed to evaluate the practical application of the method, and emphasis was placed on the selection and sequence of solvents, pH adjustment, and effect of turbidity. Benzene and chloroform were the solvents used.

The proper selection of solvents and the solvent to sample ratio were the most important factors in the solvent extraction method; the number of sequential extractions and pH adjustment were also important variables. Serial extraction with chloroform and benzene yielded a larger recovery at natural pH than extraction with benzene and chloroform; and extraction with chloroform sequentially at pH 4 and 10 produced a greater recovery than extraction with benzene. The concentration of trace organics in spring and river water was subject to significant seasonal variation. The efficiency of phenol recovery by freeze concentration depended on the volumetric concentration ratio and almost complete recovery was obtained at ratios ranging from 6 to 9.

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I. INTRODUCTION

The presence of organic pollutants in water supplies is of major concern to the water works industry. These pollutants are present in trace amounts and may cause taste and odor, color, foaming, and toxicity problems; they are difficult to treat or remove by conventional water treatment processes, such as flocculation, filtration, and even chemical oxidation by chlorine or chlorine dioxide; and their presence results in an increased cost of water purification.

The allowable limit of organic pollutants in drinking water has been set by the U.S. Public Health Service at 0.2 mg/l (200 μg/l) of carbon chloroform extract (1). However, the American Water Works Association has recently adopted considerably more exacting goals for potable water of 0.04 mg/l (40 μg/l) for carbon chloroform extract and 0.1 mg/l (100 μg/l) for carbon alcohol extract (2). In most waters, trace organics are present in very small concentrations, in the microgram per liter range, below the lower limit of detection by the presently available analytical techniques. Although at these concentrations there is no evidence of acute physiological effects of the organics on human beings, the acute and long-term cumulative toxic effects of these pollutants on fish have been indicated (3), and consequently their chronic physiological effects on man need to be investigated. Because of the increased discharge of wastes, widespread application of pesticides, new chemicals that are constantly being developed, algal metabolic products, as well as the recycling and reuse of water which is necessary to meet future water demand, the concentration of trace organics can be expected to increase.

Therefore, these pollutants can present a serious threat to aquatic life and human beings, especially in view of the available evidence that their effects can be cumulative.

There is no doubt that the study of trace organics needs to be intensified. Recognizing this need, the Water Quality Division of the American Water Works Association has recently established a committee on "Organic Contaminants in Water Supplies" whose purpose is to review the problem of organic contaminants and make realistic recommendations to the water treatment industry (4). Essential to further investigation of organic micropollutants is the development of better recovery techniques to obtain sufficient quantities of these substances from natural waters. At present, the standard (1,2,5) and widely used method for recovering trace organics is the carbon adsorption method; however, solvent extraction (liquid-liquid extraction) and freeze concentration (freeze drying) have also been employed and may potentially possess several advantages over the carbon adsorption method. Of the latter two methods, solvent extraction has been proposed as a tentative method by the American Society for Testing and Materials (6). Table I summarizes the main advantages, limitations and disadvantages, and variables of the three methods, as reported in the literature.

The carbon adsorption method was developed at the Robert A. Taft Water Research Center in Cincinnati (15). This technique consists of passing a known volume of water through an activated carbon bed and desorbing the adsorbed materials by a chloroform extraction procedure. Many modifications (3,6,16,17,18) have been made to improve the efficiency of this method, including pH adjustment, turbidity removal, two or three carbon filters operating in series, and sequential

Table I

Comparison of the Carbon Adsorption, Solvent Extraction, and Freeze Concentration Methods for Recovering Trace Organics

Method	Advantages	Limitations & Disadvantages	Variables	Ref.
Carbon Adsorption	Large volumes of water can be passed through the filter and large quantities of organics can be obtained; solvent does not need to be immiscible in water.	Carbon may not adsorb all the organics; solvent may not recover all the materials adsorbed; adsorbed organics may oxidize on the carbon surface; carbon filters are often clogged by particulate matter; method is time consuming.	Time of contact; particle size of adsorbent and quantity of particulate matter in water; type of organics in water; pH; sample or carbon volume and flow rate; number of carbon filters in series; solubility of organics.	6 7 8 9 10
Solvent Extraction	No chemical or biochemical alteration of organics; higher recovery efficiency; time saving.	Solvent must be immiscible in water; emulsion formation when turbidity is high; separation of solvent from recovered organics is often difficult; batch type extraction is tedious and cumbersome; large volumes of sample need to be extracted to recover significant quantities of organics.	Solvent to sample ratio; number of sequential extractions; pH; type of solvent; relative proportion of solvents when a mixed system is used; turbidity.	11 12
Freeze Concentration	No biological, chemical or physical alteration of organics; equipment is inexpensive and procedure is uncomplicated.	Flash freezing; difficulty in maintaining temperature of coolant; turbidity and other inorganic solids remain in concentrate; large volumes of sample need to be freeze dried to recover significant quantities of organics.	Freezing time; temperature of coolant; immersed depth of flask; frozen volume to sample volume ratio.	13 14

extraction of the activated carbon with several solvents. The main limitations of this method are that the carbon may not adsorb all the organics present in the water and the solvent may not recover all the materials adsorbed. In addition, the adsorbed organics may tend to oxidize on the carbon surface.

Solvent extraction is performed by shaking or stirring the water with an organic solvent which is immiscible in it. The trace organics are dissolved in the solvent, the solvent is separated, and the organics are concentrated by distiling off the solvent (19,20). Extraction can be either of the batch (20) or the continuous flow type (21,22). To date, most studies employing solvent extraction have been concerned with pesticides; however, limited application in the organic contaminants area has shown that this method can produce more yields than the unmodified standard carbon adsorption method with chloroform elution of the carbon (11).

In freeze concentration (13,14), the water is frozen slowly in a rotating container to form relatively pure, clear ice crystals on the inner wall of the container, while the dissolved organics and other matter remain in the residual water portion. Gradually, the residual water becomes more concentrated with respect to the original solution, and the process is stopped prior to complete freezing. A mixture of ice and salt is usually employed as the coolant. The main advantage reported for this method is that no biological, chemical, or physical alteration of organics occurs during freeze concentration.

Compared to the carbon adsorption method, few studies have been undertaken to evaluate either the solvent extraction or the freeze concentration method. Solvent extraction has been employed in many fields, especially in studies of pesticides in water; its application in the recovery of trace organics other than pesticides needs to be researched further. Freeze concentration on the other hand, is a relatively new concept as far as the recovery of organic micropollutants is concerned. Several factors could affect the efficiency and performance of the two methods, including turbidity, dissolved solids, and concentration of trace organics, and these need to be investigated further.

The objective of this investigation was, therefore, to evaluate the use of batch type solvent extraction in recovering trace organic pollutants, with emphasis on the effects of the initial concentration of organics, turbidity, pH, type of solvent, number of sequential extractions, solvent to sample ratio, and the reuse of solvent. An additional objective was the preliminary evaluation of the freeze concentration technique, with emphasis on the effect of the volumetric concentration and flash freezing.

II. REVIEW OF LITERATURE

The purpose of this review of literature is to present investigations pertaining to the recovery of trace organics, including pesticides, from water with solvent extraction and freeze concentration.

A. SOLVENT EXTRACTION

The use of solvents to concentrate and recover trace organic contaminants from water is being employed more and more in micropollution analysis. The solvent must be immiscible with water; when it is added to water containing organic micropollutants and the mixture is thoroughly agitated, the micropollutants leave the water phase and enter the solvent phase. The two phases are allowed to separate and the solvent phase is recovered. A second or third extraction may be made, if necessary, using additional amounts of solvent. The solvent phase, which contains the organic substances, can be directly subjected to instrumental analysis or the solvent can be removed and the organics recovered. The most desirable solvents are those which are totally immiscible with water. Some of the most common solvents in use are chloroform, hexane, petroleum ether, benzene, and combinations of two or more of these (12). Solvent extraction may be performed on either batch or continuous flow basis.

1. Batch Extraction.

Investigators at Washington University (11,12) have found solvent extraction to be a practicable and efficient method for extracting organics from water. Organic micropollutants were recovered from Missouri River water using three sequential extractions with chloroform, and a ratio of total volume of solvent to sample of 1 to 10. A sample size of as little as 2 liters was found sufficient for extraction, and the yields obtained were greater than with the unmodified standard carbon adsorption method with chloroform elution of the carbon. They attributed the increased yields to the following factors: (a) more intimate contact between the solvent and the organic materials, (b) greater recovery by direct solution than was possible by elution of carbon, and (c) subjection of all the turbidity-causing particles to elution by the solvent. They reported that one of the major operational difficulties was the formation of an emulsion between the water and solvent. Turbidity in water increased the emulsion formation, but lowering the pH decreased it and increased the recovery efficiency. Three water samples were extracted after their pH had been adjusted to 2, 7 and 11, and the results were as follows (12):

	Organics Recovered, μg/l		
Sample	pH 2	pH 7	pH 11
1	900	570	420
2	900	770	450
3	850	570	600

According to these investigators (12), major considerations in solvent extraction are the ratio of solvent to water and the most suitable number of extractions of each sample. Two samples of Missouri River water were fortified with 0.4 mg/l of the pesticide lindane, and then extracted with benzene using benzene to water ratios of 1 to 10 and 1 to 20. The corresponding average recovery of lindane was 79 and 68 percent. A 1 to 10 ratio has been commonly used.

The problem of identifying and measuring pesticides in water has received considerable interest in the past several years. Pesticides are of special interest to municipal water plants which need a quick method for their determination. To be practicable, any procedure used for the detection and determination of pesticides in potable water supplies must be rapid, relatively inexpensive, and easy to perform (23). Teasley and Cox (23) have used solvent extraction to recover from water insecticides present at concentrations ranging from 50 to 100 ng/l (0.05 to 0.10 μg/l) and subjected the recovered material to determination by microcoulometric gas chromatography. One liter volumes of water samples containing various insecticides were sequentially extracted with 100, 50, 50, 50, and 50 ml of redistilled solvent (1 to 1 mixture of diethyl ether and petroleum ether, or chloroform) using 2 liter separatory funnels and shaking for at least one minute each time. The extracts were combined, dried by passing through a column of sodium sulfate, and evaporated to apparent dryness first on a water bath at 40°C and then with a slow stream of dry air. The residue was taken up in 50 or 100 μl benzene, and a 50 to 75 percent aliquot was injected into the gas chromatograph with a microsyringe. The following recoveries were reported.

Insecticide	Original Sample Concentration, ng/l	Recovery, %
DDT	100	85
Toxaphene	100	90
Aldrin	50	85
Dieldrin	50	90
BHC	50	90
Parathion	100	90
Diazinon	100	90

In order to develop a technique for the determination of trace organics in surface waters which could be conducted with sufficient rapidity to allow the study of taste and odor problems at particular locations, Caruso, et al. (20) have investigated solvent extraction and used this method in river and lake surveys. The organics in the water were extracted with diethyl ether and the procedure employed consisted of adjusting the pH of the sample to 4, extracting, adjusting the pH to 10, and extracting again, thus allowing the recovery of both acidic and basic compounds, as well as neutral. A 6 liter volume of sample was extracted using a 2 liter volume of ether in serial extractions; sodium chloride was added to the water prior to extraction in order to reduce the solubility of the organics. Following extraction, the solvent was reduced by vacuum evaporation to 1 ml, and 2 µl portions were injected into a gas chromatograph. The chromatograms furnished a "fingerprint" of the organic components of the water. According to Caruso and associates, this technique might be used as a survey tool to identify sources and to trace the assimilation of organics in surface water by natural processes.

Because taste and odor producing organic constituents often vary considerably over even short periods of time, volatile substances may evolve from the water, and biological degradation of the organics may occur, rapid separation of organic micropollutants from grab samples is desirable in determining the organoleptic quality of the water (24). Concentration of organics by solvent extraction followed by gas-liquid chromatographic analysis has been applied by Baker and Malo (24) in order to develop a correlation between instrumental chemical profiles and sensory quality characteristics.

The extraction procedures employed were based upon those developed by Caruso, <u>et al</u>. (20), and consisted of batch type sequential extraction with diethyl ether of the sample after its pH had been adjusted to 3, 7, and 10 in order to promote the recovery of acidic, neutral, and basic compounds. The ether layer was dried with anhydrous sodium sulfate and then vacuum distilled to one ml volume. One thousand fold concentration, or more, was obtained. Emulsion formation was a difficulty which could be overcome by increasing the volume of solvent used.

The generalized sampling scheme shown in Figure 1 was described by Baker and Malo; it utilized both solvent extraction and freeze concentration procedures to obtain the recovery of less volatile and highly volatile organics.

Kawahara, <u>et al</u>. (19,25) developed a semiautomatic device for the rapid, simultaneous, single extraction of twelve or more samples without removing the water from the sample bottle. This device was designed for recovering chlorinated hydrocarbon pesticides and other organic compounds from water. Extraction was accomplished by placing a magnetic impeller in a sample bottle and adding an appropriate volume of organic solvent with a density of less than one; the sample bottle was then capped and inverted on a magnetic stirrer. The rotating motion of the impeller when the stirrer was operating created a vertical vortex in the sample, producing intimate contact between the sample and solvent. After a 30 minute extraction period, air under pressure was employed to recover the solvent. The extract was concentrated to a volume of approximately 0.5 ml and then subjected to gas chromatographic analysis. Kawahara, <u>et al</u>. (19) reported the

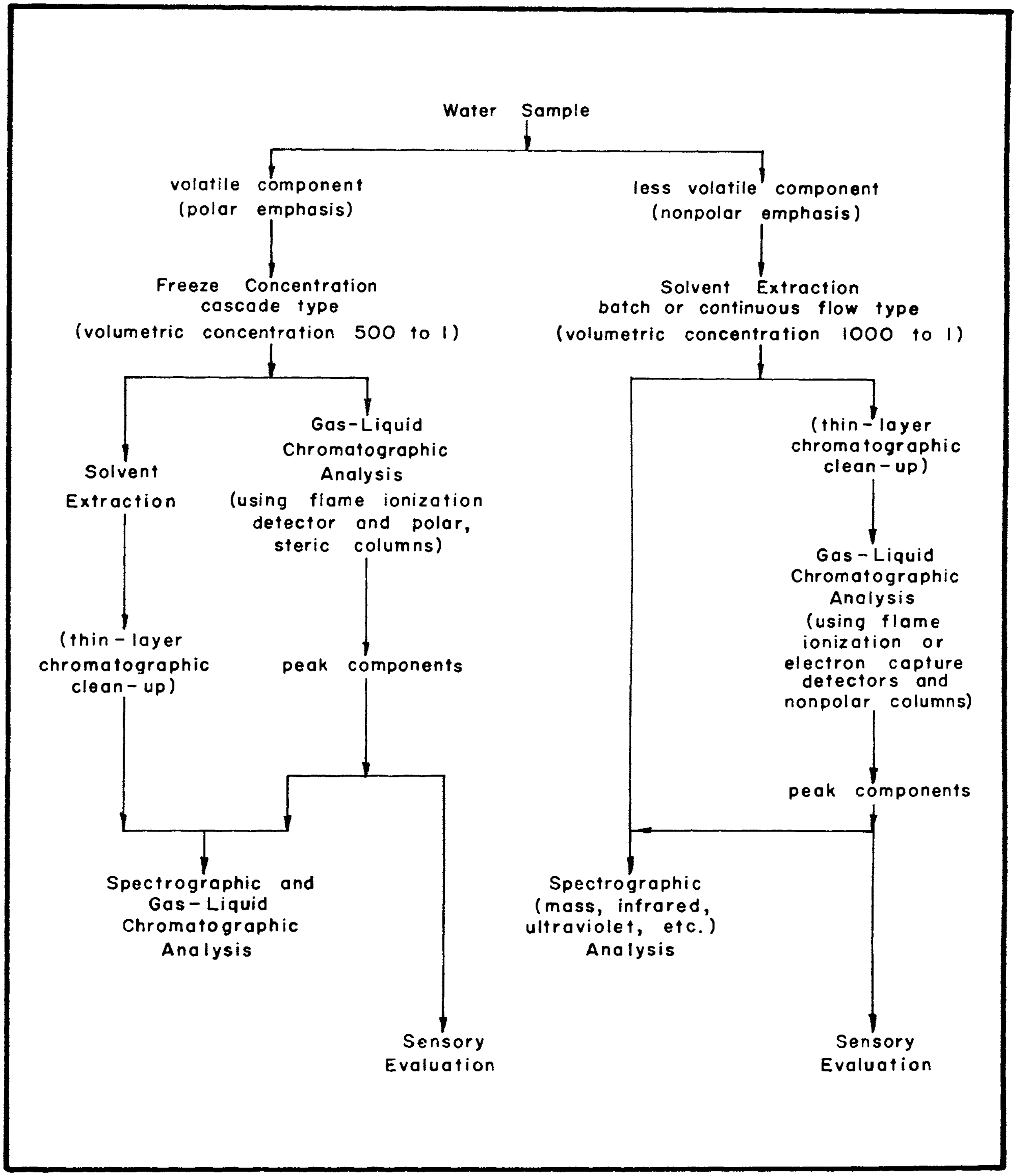

Figure 1. Microcontaminant Evaluation Scheme (after Baker and Malo (24))

following average pesticide recoveries using this method.

Sample	Solvent	Recovery
850 ml distilled water containing:	50 ml of:	
200 ng dieldrin + 400 ng endrin	purified hexane	61.1% dieldrin, 62.6% endrin
200 ng dieldrin + 400 ng endrin	hexane with 4% benzene	94.7% dieldrin, 77.8% endrin
500 ng aldrin	hexane with 4% benzene	63.6% aldrin

The application of solvent extraction in the study of sea water has been reported by Khailov (26). A 2.5 liter sea water sample was first filtered through a thick porous glass filter, and then shaken sequentially with 270, 50, and 50 ml of redistilled saturated phenol solution. The combined extract was centrifuged to remove the water, mixed with an equal volume of diethyl ether and 40 ml of 0.14M ammonium carbonate solution, shaken, and centrifuged again. After the aqueous layer had been separated, the remaining portion was extracted again with ammonium carbonate. The aqueous extracts were extracted twice with diethyl ether to remove phenol and evaporated at 50°C to dryness. The residue was dissolved in 5 µl of water and analyzed on a spectrophotometer in the range of 210 to 400 mµ at 5 mµ intervals. The volatile matter was measured partly at 220 to 240 mµ and mostly at 305 to 400 mµ. According to Khailov, the metabolites of sea plants and animals could be followed successfully using this method.

2. Continuous Flow Extraction.

Batch type extraction, especially when a large number of samples is involved, is time consuming, tedious, and cumbersome (19). The equipment required for batch extraction is quite simple on a small scale, however, it is not readily portable for large scale operations and the method is not very applicable when the concentration of the organic contaminants is small (27). The continuous flow type solvent extraction of trace organics from water is, therefore, a significant improvement.

Hoak (8) has reported that an 18 stage Scheibel countercurrent extraction column appeared to be most suitable for the recovery of phenol from water, and that methyl isobutyl ketone (MIK) was the best extractant for phenol. Other solvents tested included chloroform, carbon tetrachloride, benzene, petroleum ether, pentane, isopropyl ether, and heptane. Two systems were studied; one consisted of phenol in tap water and the other of phenol in Ohio River water. The latter system introduced a complication because of emulsification with the MIK solvent at the agitator speed of 344 rpm, however, it was found that emulsion formation could be avoided by reducing the agitator speed to 150 rpm. In general, the higher the agitator speed the greater was the difficulty of separating the solution and solvent. The recovery efficiency was found to depend upon the ratio of solvent to solution and the agitator speed. Phenol concentration was determined using the 4-amino antipyrine method. Major findings of this study were as follows:

Water System	Initial phenol content µg/l	Agitator speed rpm	Solution feed ml/min.	MIK solvent feed ml/min.	Solution to solvent ratio	Phenol recovery efficiency %
Tap	96.5	344	2,000	107.2	18.7	94
Ohio River	65.0	150	2,000	74.6	26.8	53

A field countercurrent extractor for recovering organic microcontaminants from water was developed by Bunch and Ettinger (27). This extractor made possible multiple stage extraction with a minimum amount of solvent, and consisted of a Podbielniak model 6000 SP centrifugal contactor with the necessary pumps, flow meters, pressure gauges, and other accessory equipment. The unit was designed to operate with both heavier and lighter than water solvents and to be capable of extracting water containing finely divided silt at a combined solvent and water flow of 5 gpm. Maximum operating flexibility was incorporated into the unit to permit changing the ratio of water to solvent from 10 to 1 to 100 to 1. In addition, provision was made for introducing either acid or caustic into the water system before it entered the extractor. A 55 gallon drum served both as a water feed tank and a clarifier for removing silt. The results of three runs using Little Miami and Ohio River water and a sample to solvent ratio of 10 to 1 are summarized below:

		Organic Matter Removed		
Sampling Site	Solvent	mg/l	COD/l	COD/mg
Little Miami River	Freon T F	0.2	0.3	1.5
Little Miami River	Chloroform	0.6	0.9	1.5
Ohio River	Chloroform	0.9	1.6	1.8

Sanderson and Ceresia (21) developed a gravity fed system which they reported to be simple, inexpensive, fairly rapid, and efficient for the continuous extraction of chlorinated aromatic pesticides in the microgram per liter range. This system consisted of an 18 liter constant head water reservoir connected to two 500 ml extractors in series. Each extractor was equipped with a Friedrich's condenser and was connected to a common solvent evaporator. Evaporated solvent was condensed in the condensers and fed into the extractors. Magnetic stirring was employed to provide intimate contact between the water and solvent. Sanderson and Ceresia employed this system to recover several pesticides from aqueous solutions using petroleum ether as the solvent, and found that the efficiency of extraction depended upon the flow rate of the aqueous solution and of the solvent, and the amount of agitation.

Werner and Waldichuk (22) in their study of pollution in coastal sea waters designed and built a continuous flow solvent extractor, based on the principle of contact by countercurrent flow of the sea water and solvent with continuous recovery of the solvent which, consequently, could be used over and over again. The efficiency of the equipment was evaluated using a water-benzoic acid-hexane system and was found that the extractor facilitated the laboratory extraction of small quantities of material from large volumes of solution and that it was possible to control the recovery efficiency within wide limits by changing the ratio of flow rates of the solvent and the solution under extraction.

Continuous flow solvent extraction has also recently been employed for the recovery of phenolic materials from waste water (28) and the removal of salt from saline water (29,30,31).

B. FREEZE CONCENTRATION

The principle involved in freeze drying is well known, however, freeze concentration of trace organics in water is a relatively new technique which is particularly valuable for the recovery of volatile or reactive compounds which could be chemically altered or selectively separated by thermal or solvent concentration. Attention to the usefulness of the freezing out technique for the concentration of dilute solutions in the laboratory was called by Shapiro (32) in 1961 who described a procedure for the treatment of sample volumes of one liter or less. This procedure consisted of pouring the sample into either a glass or plastic bottle leaving enough room for the expansion which accompanies freezing, attaching the bottle to a mechanical shaker, such as the Burrell Wrist Action shaker, and placing the bottle in a freezing chamber at -30°C. After several hours of gentle shaking, most of the solution was frozen except for a core containing the concentrated solutes which could be separated. Shapiro reported that recoveries in excess of 99 percent could be obtained after a 20 fold volumetric concentration.

Kobayashi and Lee (33) studied the effectiveness of progressive freeze concentration of dilute aqueous solutions containing Rhodamine B or sodium chloride using the procedure developed by Shapiro (32). Rhodamine B was determined spectrophotometrically at a wavelength of 554 mμ, and initial concentrations of 10 to 55 μg/l were employed. Several runs were made and resulted in recoveries of 82.3 to 94.2 percent at an average volumetric concentration of 7 fold. Better recoveries of 97.7 to 102.7 percent were obtained with sodium chloride at an average 9 fold concentration and initial chloride levels at 1.2 to 5.0 mg/l; chloride was determined potentiometrically.

Baker (13) investigated the merits of freeze concentration combined with gas chromatographic analysis for the study of trace organics in water. The equipment used for freeze concentration consisted of a Rinco vacuum evaporator equipped with a one liter round bottom flask which was immersed in an ice-salt mixture maintaining a temperature of -12°C. A ternary mixture of 2 mg/l phenol, 5 mg/l m-cresol, and 5 mg/l 2,4-dichlorophenol in either distilled water or water of known ionic concentration was used as the organic material in these studies, and 200 ml volumes were reduced to different residual volumes giving volumetric concentrations of up to 57 fold. Volumetric concentrations up to 10 fold were found to be efficient, while concentrations between 20 and 57 fold gave variable results. Efficiencies of 63, 72, and 40 percent and of 81, 90, and 97 percent were obtained for phenol, m-cresol, and 2,4-dichlorophenol with volumetric concentrations of 57 and 3.17 fold, respectively. According to Baker, concentration efficiency depended on a number of factors, including the rate of cooling, mixing, and the composition of the initial sample.

In a later paper, Baker (14) discussed the effect of mixing and other parameters on the freeze concentration process in the absence of inorganic salts. He employed essentially the same equipment used in his previous study (13), except that a variable speed Swissco evaporator was also employed and vacuum was not used. The recovery of several organic substances, including phenol and various substituted phenols, propionic through caproic volatile fatty acids, and acetophenone, was investigated. Flash freezing of the aqueous solution was found to be a frequent problem, but could be eliminated by precooling the sample and precooling and seeding the flask in which concentration was to be made. On the basis of his studies, Baker concluded that the recovery efficiency: (a) was not affected by the initial sample volume, (b) did not vary as a function of mixing over a range from 0 to 260 rpm, (c) was the same for all the organic substances studied when concentrated to comparable volumetric ratios, and (d) was not affected by the presence of other organic substances. Baker also suggested that the recovery of low concentrations of organics (μg/l or less) could be obtained by a cascade arrangement of single-stage freezers.

Baker and Malo (24) have reported that the recovery efficiency was appreciably affected by the presence of dissolved inorganic salts which impaired the separation of the organics at the ice-liquid interface. The mixing rate was, therefore, an important factor and efficiency improved with increased turbulence. Suspended matter was not a problem unless the concentration was very high; however, the sample could be clarified by centrifugation at 2,000 rpm, and acidification to approximately a pH value of 3 was also helpful.

The freeze concentration technique has also been employed for the treatment of the sludge from a water treatment plant (34) and the production of fresh water by desalination of sea water (35,36).

III. MODE OF STUDY

The purpose of this investigation was to evaluate the use of batch type solvent extraction in recovering trace organic pollutants, with emphasis on the effects of the initial concentration of organics, turbidity, pH, type of solvent, number of sequential extractions, solvent to sample ratio, and the reuse of solvent. An additional objective was the preliminary evaluation of the freeze concentration technique, with emphasis on the effect of the volumetric concentration and flash freezing. Solvent extraction studies were made using a simplified system containing known concentrations of phenol and natural water systems collected from three sources with different levels of pollution, while only the simplified water system was used in the freeze concentration studies. The water systems, sources of natural water, materials, equipment, and procedures employed in the investigation are described in this section.

A. WATER SYSTEMS

Three water systems were selected for use in this investigation, a simplified water system, a natural water system, and a modified natural water system.

1. Simplified Water System.

This system was prepared by dissolving a known concentration of phenol in deionized water. Phenol was selected as the organic material in this system because phenolic substances are the end products of natural, domestic, and industrial activities and are present in almost all waters (37); phenol is also the chemical used by many investigators. The simplified water system was employed to determine the effect on solvent extraction of several variables, including the use of fresh and reused solvent, the number of sequential extractions, the volumetric ratio of solvent to sample, pH, extraction time, initial concentration of organics, and turbidity; and to guide the conduct of the studies with natural water systems. This system was also used in a preliminary study of the freeze concentration method to evaluate the effect of the frozen volume to original volume ratio on the recovery efficiency.

2. Natural Water System.

This system consisted of spring and river water samples obtained from three different sources over a period of several months. The natural water system was used to investigate the effect of pH, sequence of chloroform and benzene extraction, and turbidity on the recovery of organic micropollutants naturally present in the water by solvent extraction.

3. Modified Natural Water System.

Because it was believed that turbidity played an important role in solvent extraction by increasing emulsion formation and decreasing recovery efficiency, the modified natural water system was employed to further evaluate the effect of this variable. This system was prepared by mixing at appropriate proportions Missouri River water with turbidity-free water obtained by passing the river water through glass wool.

B. SAMPLING LOCATIONS FOR SPRING AND RIVER WATER

Spring and river water samples were obtained at Meramec Spring, Gasconade River near Jerome, and Missouri River in Jefferson City. The location of the three sampling sites is shown in Figure 2.

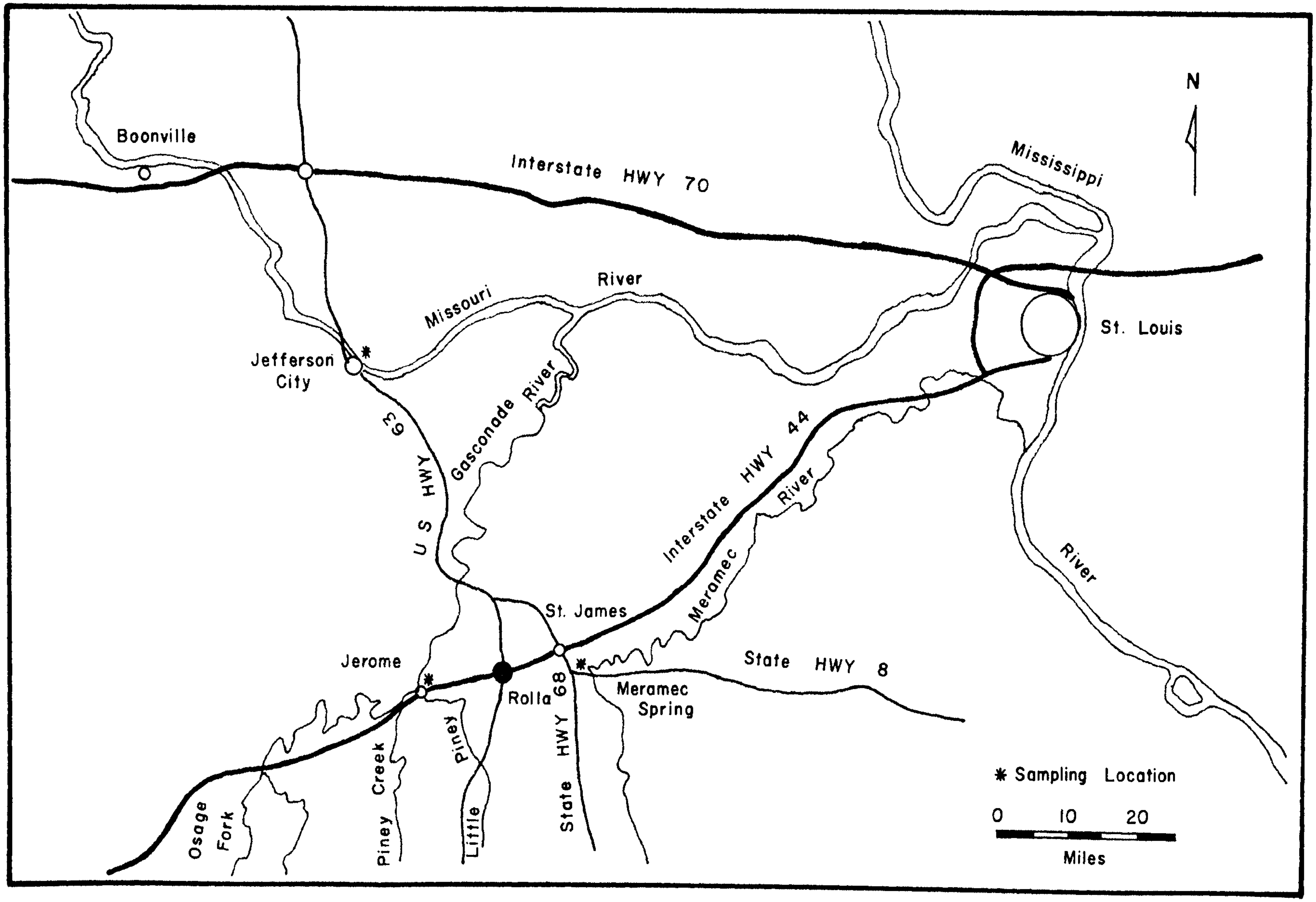

Figure 2. Sampling Locations for Spring and River Water

Meramec Spring is located 9 miles east of St. James, Missouri, on Route 8. It has been reported (38) that the spring receives water from an area which lies to its south, west and southwest, and that its underground supply routes connect with surface feeder routes. Meramec Spring had also served as the sampling site for previous studies in the trace organics area which employed the carbon adsorption method (3,38).

The Gasconade River is relatively unpolluted with domestic and industrial wastes. Samples were collected under the highway bridge near Jerome, Missouri, 17 miles west of Rolla.

Missouri River water samples were obtained at the low lift pump station of the Capital City Water Company, Jefferson City, Missouri, and were collected from an extension rubber hose connected to an outlet on the discharge pipe. Before sampling, the system was flushed in order to remove the dead water so that fresh water could be obtained. The Missouri River is obviously a polluted river since it receives waste discharges from several large and smaller communities upstream from sampling area.

C. MATERIALS

1. Deionized Water.

Deionized water was produced by passing tap water through a Bantam Demineralizer (model BD-1*) equipped with a red cap, mixed bed cartridge (catalog No. 0808*).

2. Solvents.

Chloroform, ethyl alcohol, benzene, and acetone are the organic solvents which are usually employed in eluting trace organics adsorbed

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*A product of the Barnstead Still and Sterilizer Co., Boston, Massachusetts.

on activated carbon in the carbon adsorption method (38). The characteristics of these chemicals as well as others which could be utilized in solvent extraction are given below (12,39).

Solvent	Formula	Solubility in Water ml/l	Boiling Point °C
Chloroform	$CHCl_3$	6.67	61.2
Ethyl Alcohol	CH_3CH_2OH	Miscible	78.4
Acetone	CH_3COCH_3	Miscible	56.2
Benzene	C_6H_6	0.93	80.1
Hexane	$CH_3(CH_2)_4CH_3$	0.21	68.7
Perchloroethylene	CCl_2CCl_2	Insoluble	121.2

Because immiscibility in water was a necessary consideration in solvent extraction, and to enable comparison with carbon adsorption data, chloroform and benzene were selected for use in this study. Analytical reagent (ACS) grade solvents, which were further purified by distillation in the laboratory prior to use, were employed. Solvents which had already been used in solvent extraction were redistilled and then reused. Both the initial distillation and subsequent redistillations of the solvents were accomplished using the all-glass distillation apparatus shown in Figure 4 (p.26).

3. Chemicals.

Analytical reagent (ACS) grade phenol was used in preparing the simplified water system. Technical (USP) grade sodium chloride was employed with the natural water systems in order to reduce the solubility of organics in water, and rock salt was used in the freeze concentration studies to lower and maintain the temperature of the coolant.

4. Clay.

Grundit clay was employed to provide turbidity in the simplified water system. This material was finely ground in a mortar before being used.

D. EXPERIMENTAL AND ANALYTICAL EQUIPMENT

1. Solvent Extraction Apparatus.

When the simplified water system was studied, solvent extraction was performed using appropriate size (250 to 1,000 ml) separatory funnels equipped with a Teflon stopcock. When the natural water systems were investigated, solvent extraction was performed using two 3.5 gallon Pyrex bottles. The preliminary separation of the solvent was accomplished by means of a number of glass siphons, and the solvent was then transferred for final separation into a 1,000 ml separatory funnel in order to remove any remaining traces of water. When the modified natural water system was employed, a micro Soxhlet extractor (Pyrex 3360*) equipped with a Glas-Col heating mantle** was used to elute the glass wool and recover any organics that might have been sorbed on the turbidity-causing particles retained in the wool. The Soxhlet extractor and the solvent extraction apparatus used with the natural and simplified water systems are shown in Figure 3 (left to right).

2. Distillation Apparatus.

The distillation system shown in Figure 4 was used to recover excess solvents and concentrate the trace organics in the residual solvent. Each unit consisted of a Glas-Col heating mantle** equipped

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*A product of the Corning Glass Works, Corning, New York.
**A product of the Glas-Col Apparatus Co., Terre Haute, Indiana.

Figure 3. Solvent Extraction Apparatus and Micro Soxhlet Extractor

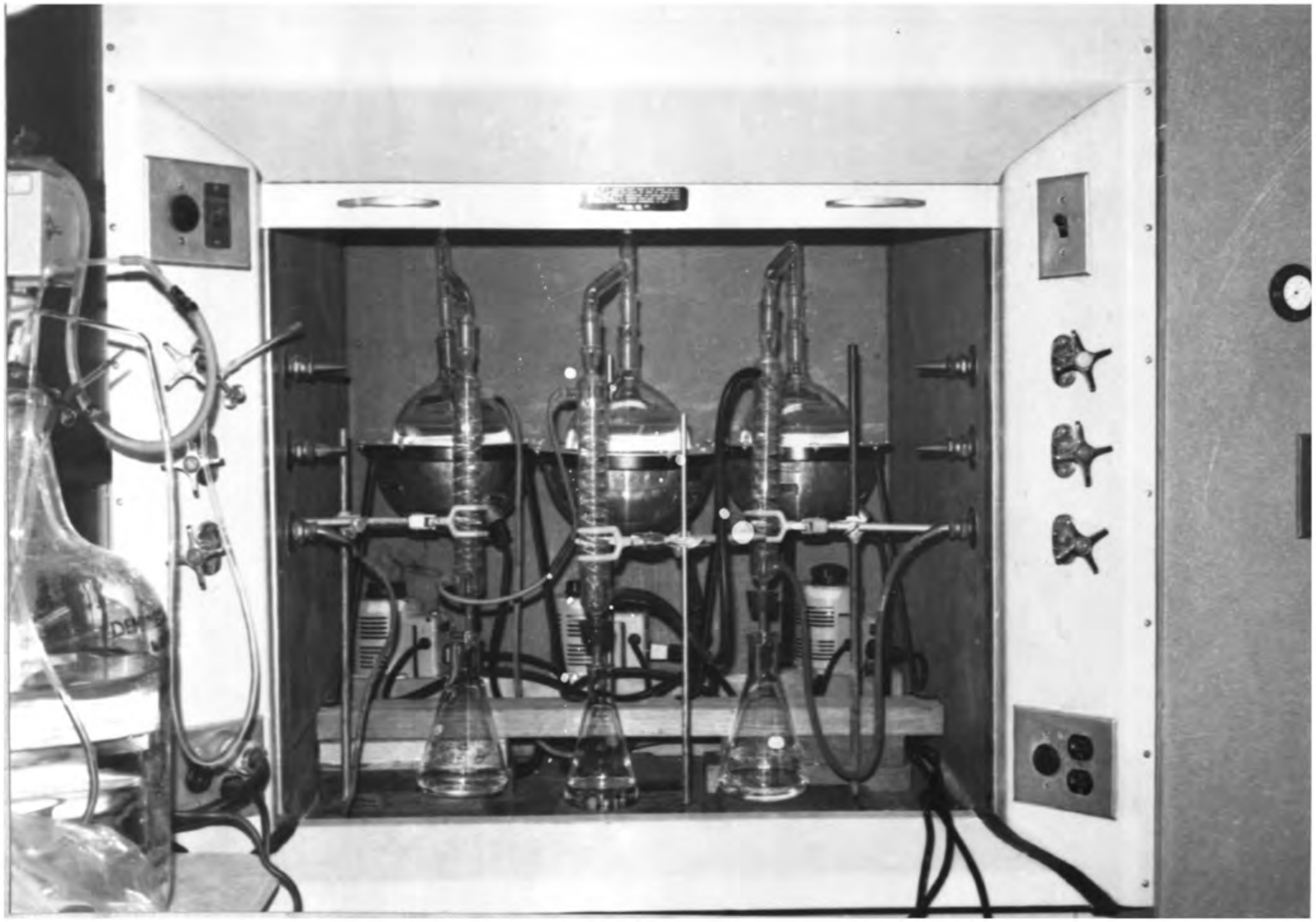

Figure 4. Distillation Apparatus

with a variable transformer,* a 3,000 ml Pyrex boiling flask, a connecting tube (Pyrex 9060**), a Graham condenser (Pyrex 2540**), and a receiving Erlenmeyer flask. The temperature of the heating mantle was controlled by the transformer and could be measured by connecting its thermocouple to an indicating pyrometer.[#]

3. Steam Bath.

The steam bath was used after distillation to drive-off the residual solvent. It was an electrically heated unit equipped with a constant water level device (Precision 66738[##]).

4. Freeze Concentration Apparatus.

The equipment used in the freeze concentration studies is shown in Figure 5. It consisted of two Rinco rotating evaporators (model VE-1000-B[+]) connected to a vacuum system and housed in a coolant container. The coolant employed was a mixture of ice cubes and rock salt adjusted to maintain the temperature at -7 to -9°C.

5. Gas Chromatograph.

A Varian Aerograph (model 1520-1B[++]) dual column, dual hydrogen flame gas-liquid chromatograph was employed for the quantitative analysis of phenol in the simplified water system studies. It was equipped with a Leeds & Northrup recorder.[+++] High purity compressed nitrogen was used as the carrier gas.

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*Powerstat, a product of the Superior Electric Co., Bristol, Connecticut.

**A product of the Corning Glass Works, Corning, New York.

[#] Model 32-J, a product of the Fisher Scientific Co., Pittsburgh, Pennsylvania.

[##] A product of the Precision Scientific Co., Chicago, Illinois.

[+] A product of the Rinco Instrument Co., Inc., Greenville, Illinois.

[++] A product of Varian Aerograph, Walnut Creek, California.

[+++] Speedomax W, a product of the Leeds & Northrup Co., Philadelphia, Pennsylvania.

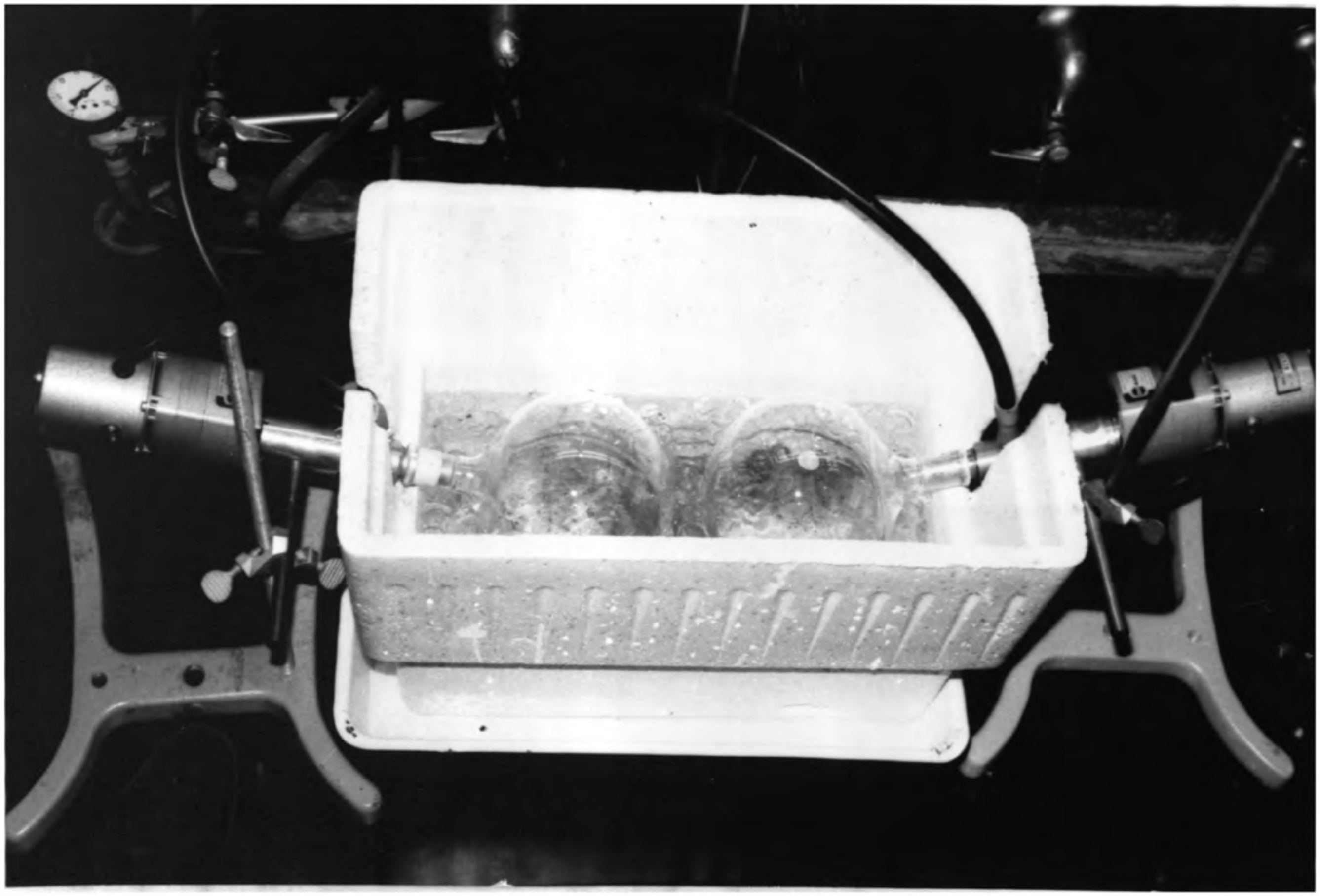

Figure 5. Freeze Concentration Apparatus

6. Infrared Spectrophotometer.

A Beckman IR10 infrared spectrophotometer* was used to detect any changes in the character of the organic micropollutants that might have occurred during the long drying procedure at higher temperature which was necessary for the complete removal of benzene, and to assure that the benzene extracts **were** not altered during this process. The potassium bromide pellet technique was employed to analyze the trace organics in solid form.

E. ANALYTICAL DETERMINATIONS

1. Phenol Determination.

Phenol was determined by gas chromatographic analysis using the following operating conditions:

Column**: 5 foot long, 1/8 inch diameter stainless steel packed with 10% FFAP on 60/80 chromosorb W.
Temperature: Injector 245°C, column 200°C isothermal maintained for 6 minutes, hydrogen flame ionization detector 225°C.
Flow rate: Nitrogen carrier gas 30 ml/min., hydrogen 30 ml/min., air 300 ml/min.#
Attenuation: As required.
Recorder chart speed: 30 inches/hour.
Operation: Single column.

A 1 to 3 μl sample was injected into the injector port where it was vaporized, mixed with the carrier gas, and passed into the column. As the phenol was eluted from the column, it was carried into the detector where it was combusted in the hydrogen flame. This resulted in the release of negative ions causing a change in the electron potential between two electrodes located above the flame and this

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*A product of Beckman Instruments, Inc., Fullerton, California.
**A product of Varian Aerograph, Walnut Creek, California.
#This gave a 1:1:10 relative flow ratio of hydrogen/nitrogen/air which is recommended for proper operation of the flame ionization detector (40).

change was shown by the recorder as a corresponding peak. The area of the phenol peak was calculated by triangulation and was taken equal to its height times its width at mid-height, and the concentration of phenol was determined from an appropriate calibration curve. A series of calibration curves was prepared by dissolving a precisely weighed amount of phenol in deionized water and fresh or redistilled benzene.

2. Turbidity.

Turbidities in excess of 25 units were measured by means of the Jackson candle turbidimeter as outlined in Standard Methods (5, p.312). Turbidities less than 25 units were measured by means of the Hach laboratory turbidimeter (model 1860*).

3. pH.

pH was determined using a Beckman Zeromatic pH meter** which was calibrated before use with a phosphate buffer solution.

4. Water Characterization.

In order to evaluate the quality of the river waters used in the natural water system studies, total and calcium hardness, alkalinity, and chemical oxygen demand were determined in several samples. Calcium and total hardness were measured by the EDTA titrimetric method (5, p.74 & 147) using Calver II and Univer II indicating powders,* respectively. Alkalinity was determined by titration with a 0.02N sulfuric acid solution using a methyl orange indicator (5, p.48). Chemical oxygen demand was measured by refluxing for

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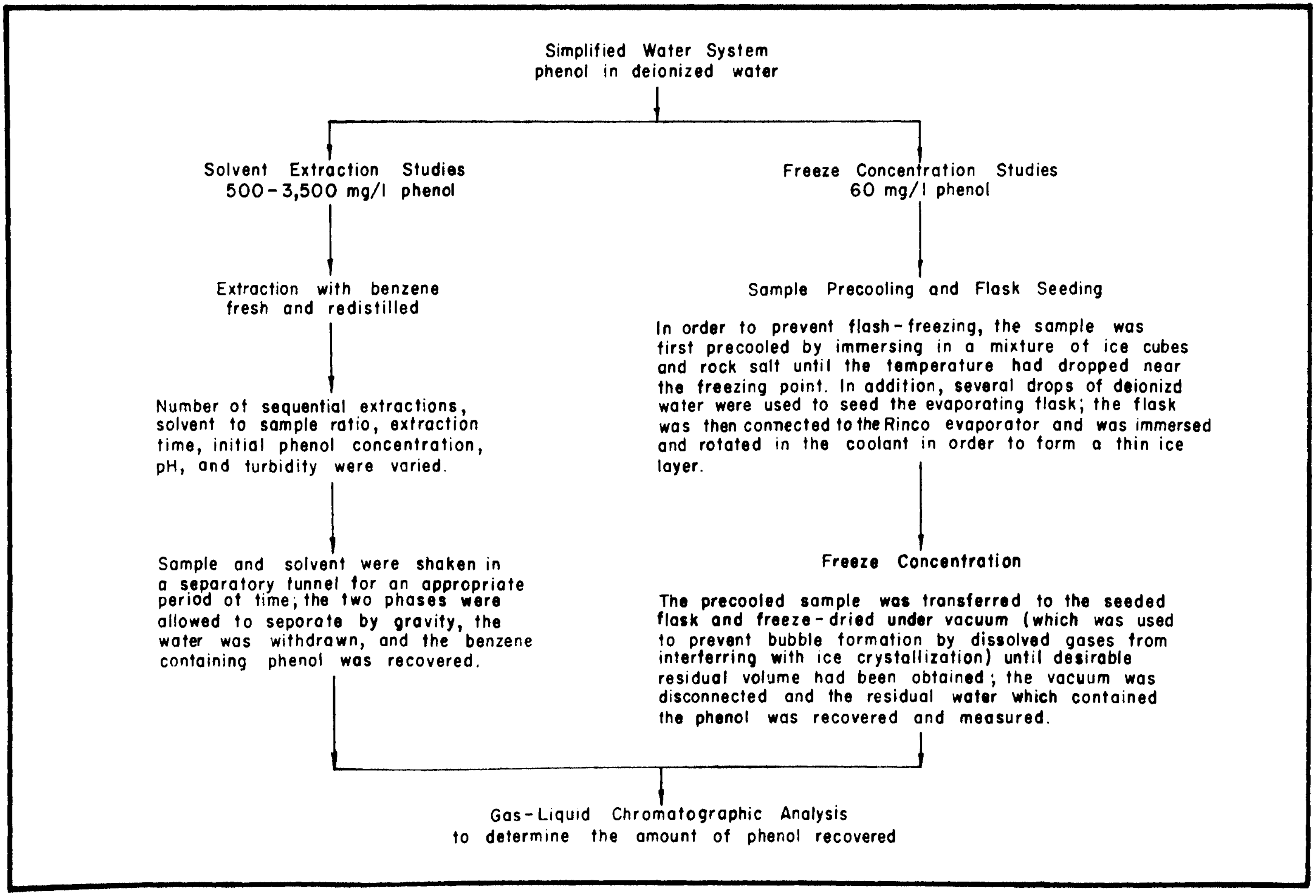
*A product of Hach Chemical Company, Ames, Iowa.

**A product of Beckman Instruments, Inc., Fullerton, California.

two hours a mixture consisting of 20 ml sample, 10 ml 0.25N potassium dichromate solution, and 30 ml concentrated sulfuric acid containing silver sulfate; cooling; and determining the excess dichromate with 0.1N ferrous ammonium sulfate solution (5, p.510).

F. EXPERIMENTAL PROCEDURES

The experimental procedures used in the simplified water system studies are presented in Figure 6 and those employed in the natural water system studies are given in Figure 7.



Simplified Water System
phenol in deionized water

Solvent Extraction Studies
500-3,500 mg/l phenol

Extraction with benzene
fresh and redistilled

Number of sequential extractions, solvent to sample ratio, extraction time, initial phenol concentration, pH, and turbidity were varied.

Sample and solvent were shaken in a separatory funnel for an appropriate period of time; the two phases were allowed to separate by gravity, the water was withdrawn, and the benzene containing phenol was recovered.

Freeze Concentration Studies
60 mg/l phenol

Sample Precooling and Flask Seeding

In order to prevent flash-freezing, the sample was first precooled by immersing in a mixture of ice cubes and rock salt until the temperature had dropped near the freezing point. In addition, several drops of deionizd water were used to seed the evaporating flask; the flask was then connected to the Rinco evaporator and was immersed and rotated in the coolant in order to form a thin ice layer.

Freeze Concentration

The precooled sample was transferred to the seeded flask and freeze-dried under vacuum (which was used to prevent bubble formation by dissolved gases from interferring with ice crystallization) until desirable residual volume had been obtained; the vacuum was disconnected and the residual water which contained the phenol was recovered and measured.

Gas-Liquid Chromatographic Analysis
to determine the amount of phenol recovered

Figure 6. Experimental Procedures – Simplified Water System Studies

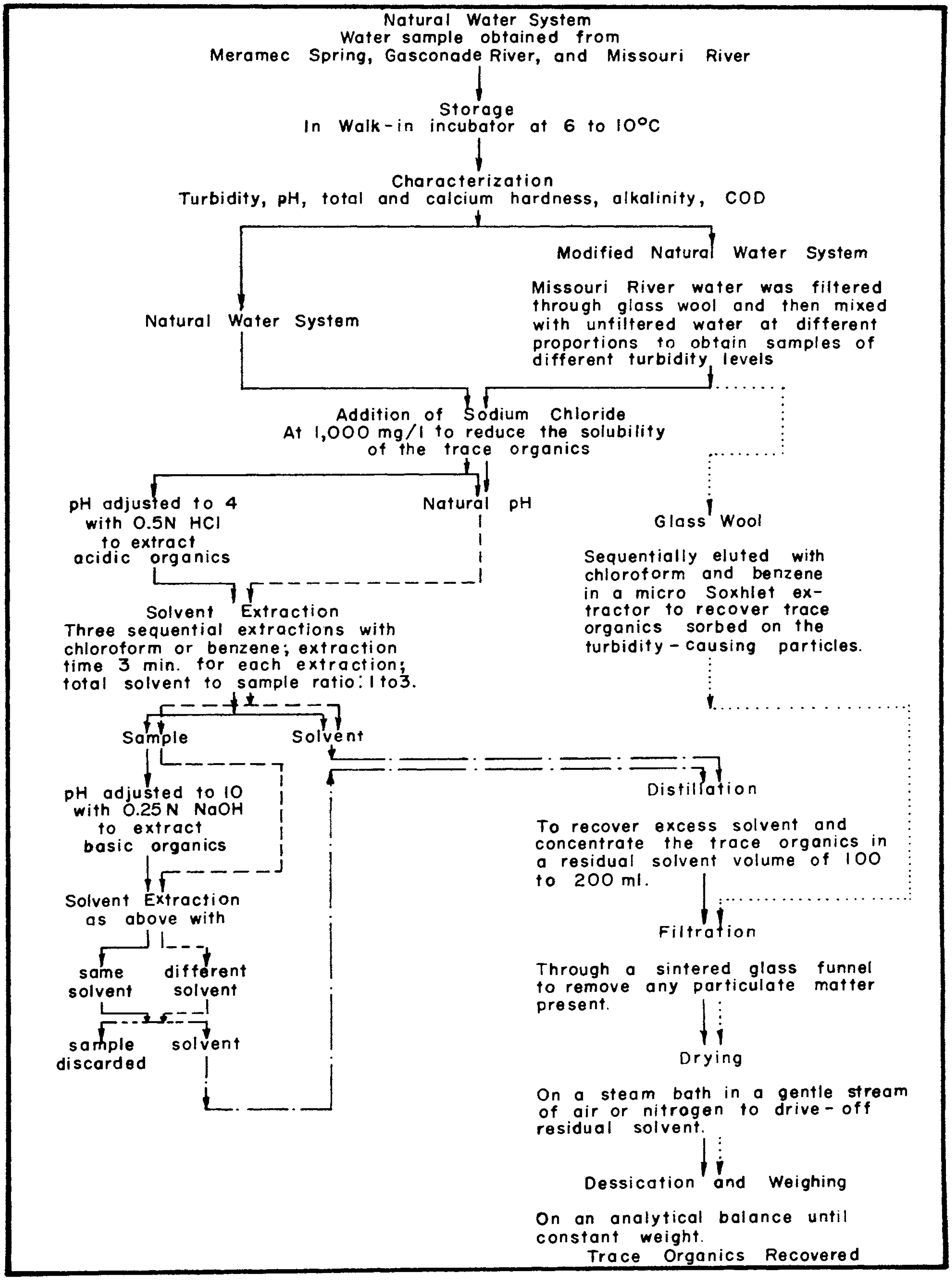


Figure 7. Experimental Procedures — Natural Water System Studies

IV. PRESENTATION OF RESULTS

This investigation was conducted to evaluate the use of solvent extraction and freeze concentration in recovering organic micropollutants from water. The work was performed using simplified and natural water systems and the results are accordingly presented in two parts.

A. SIMPLIFIED WATER SYSTEM STUDIES

The simplified water system consisted of known concentrations of phenol in deionized water and was used to determine the effect of several variables on the two recovery methods. A summary of the simplified water system studies is presented in Table II. Variables investigated in the solvent extraction work were the number of extractions, solvent to sample ratio, extraction time, initial organic concentration, pH and turbidity, and those used in the freeze concentration study were the volumetric concentration and flash freezing. Batch type solvent extraction using fresh or redistilled benzene and batch type freeze concentration were employed.

The effect of the number of extractions and of the solvent to sample ratio is shown in Figures 8 and 9. Recovery efficiencies obtained with three sequential extractions, each with one-third of the total volume of solvent, are compared with efficiencies obtained with a single extraction using the same total volume of solvent. Solvent to sample ratios ranging from 0.1 to 2.0 were employed; the initial phenol concentration was 2,000 mg/l and extraction time was one minute. Figure 8 presents the recoveries obtained with fresh benzene, while Figure 9 presents the recoveries obtained with redistilled benzene. On the basis of the same solvent to sample

Table II

Summary of Simplified Water System Studies

Recovery Method	Type of Study	Sample Volume ml	Solvent (Benzene) Used	Solvent to Sample Ratio	Extraction or Freezing Time min.	Number of Extractions	Initial Phenol Concentration mg/l	Turbidity units	pH units
Solvent Extraction	Number of Extractions	300	Fresh & Redistilled	0.1-2.0*	1	1 & 3**	2,000	0.2	5.6
	Solvent to Sample Ratio								
	Fresh vs. Redistilled Solvent								
	Extraction Time	100	Fresh	1.0	0.5-5.0#	1	2,016		
	Initial Phenol Concentration	300	Redistilled	0.3 & 1.0	1		500-3,500##	0.1-0.2	5.6-4.1
	pH Value			1.0		3	2,016	0.2	1-11+
	Turbidity	100	Fresh			1	1,000	0.3-1,250++	--
Freeze Concentration	Volumetric Concentration	500	N/A	N/A	23-57	N/A	60	0.1	5.8
	Flash Freezing								

*Solvent to sample ratios of 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, and 2.0 were used.

**Both fresh and redistilled benzene were used to perform either one or three sequential extractions using the same solvent to sample ratio.

#Extraction times of 0.5, 1, 2, 3, 4, and 5 min. were used.

##Initial concentrations of 500, 1,000, 1,500, 2,000, 2,500, and 3,500 mg/l were used.

+pH values of 1, 3.1, 5, 7.5, 9, and 11 units were used.

++Turbidities of 0.3, 60, 150, 225, 300, 560, 960, and 1,250 units were used.

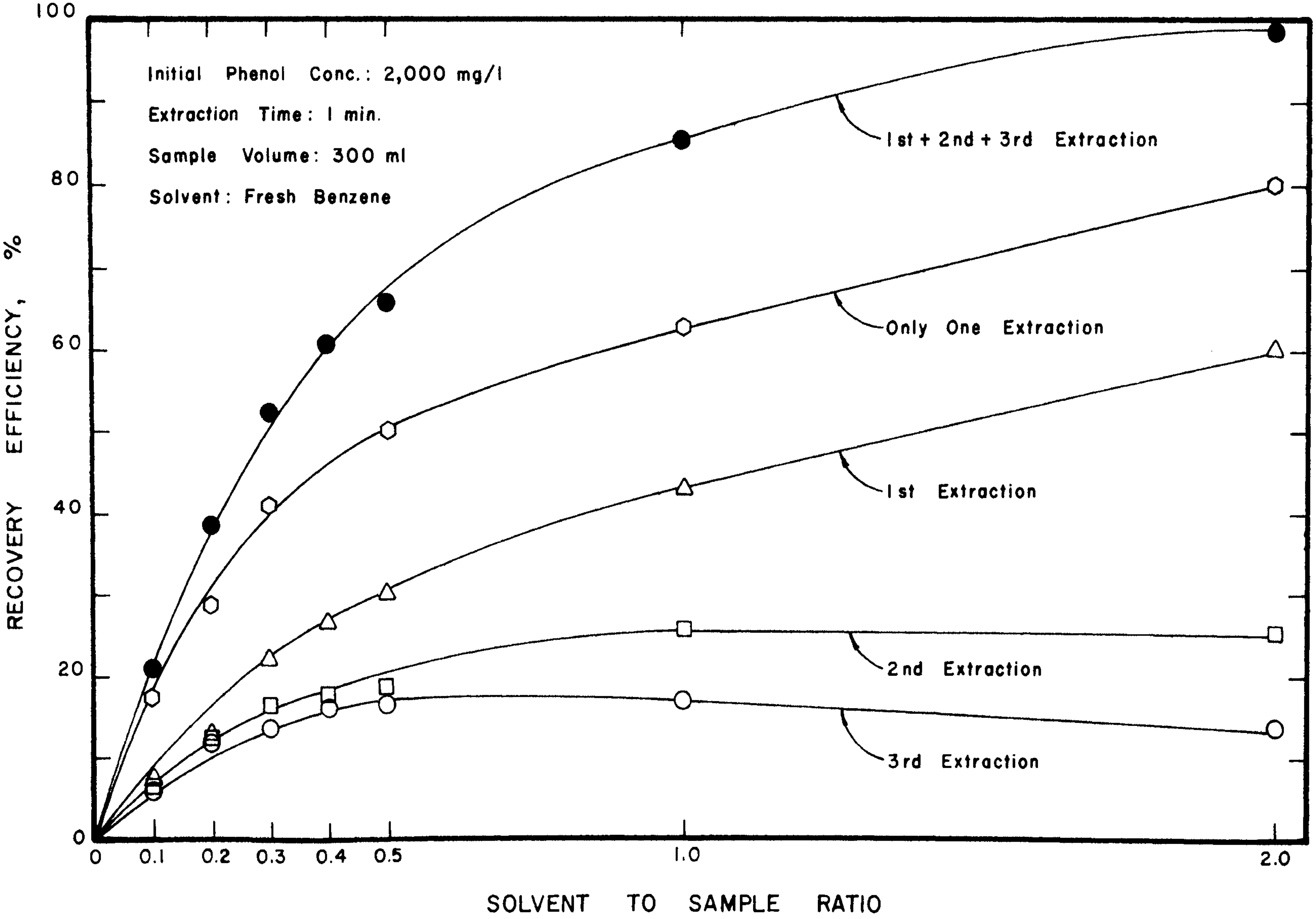


Figure 8. Solvent Extraction Studies in a Simplified Water System – Effect of Number of Extractions and Solvent to Sample Ratio (Fresh Benzene Used)

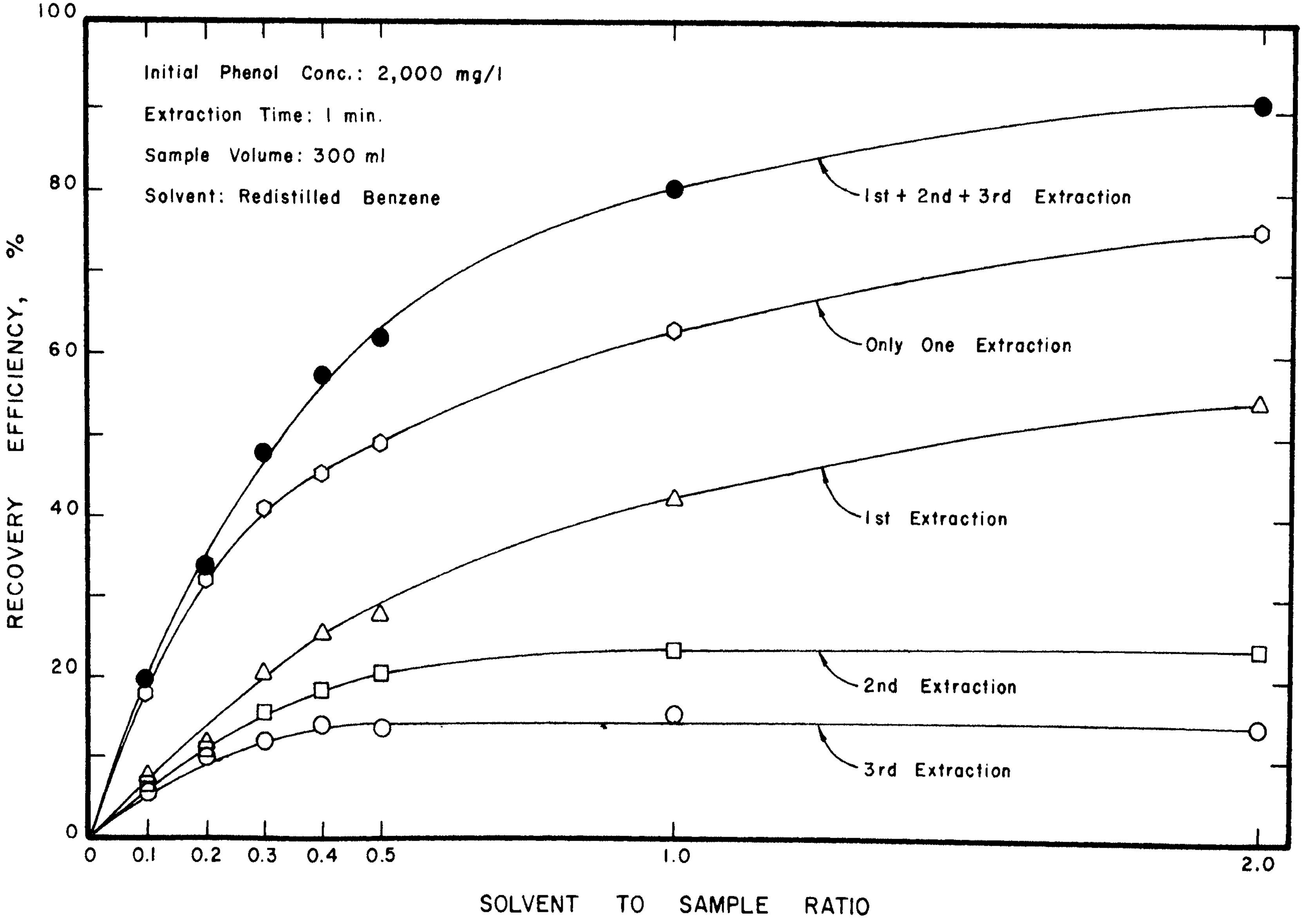


Figure 9. Solvent Extraction Studies in a Simplified Water System - Effect of Number of Extractions and Solvent to Sample Ratio (Redistilled Benzene Used)

ratio, three extractions were more effective than one extraction, and recovery efficiencies continued to improve with higher ratios. Fresh benzene was slightly more efficient, and this was particularly true during the first extraction.

The effect of extraction time was studied using a single extraction, a solvent to sample ratio of one, and an initial phenol concentration of 2,016 mg/l. The results are plotted in Figure 10. When extraction time was varied from 0.5 to 5 minutes, the recovery efficiency increased from 40 to 50 percent; however, the recoveries obtained with extraction times between 1 and 4 minutes were essentially the same and approximately equal to 45 percent.

In order to determine the effect of the initial concentration, phenol solutions containing from 500 to 3,500 mg/l of this chemical were extracted with redistilled benzene. One extraction for a period of one minute was performed using solvent to sample ratios of 0.3 to 1.0, and the results are shown in Figure 11. As the initial concentration increased up to about 2,000 mg/l, the recovery efficiency decreased, but remained essentially constant at higher concentrations. Approximately 30 to 25 percent more phenol was recovered with the higher solvent to sample ratio, and this is in agreement with the results obtained in previous studies (Figure 9). It should be pointed out, however, that the organic concentrations used in the simplified water system were much greater (500 to 5,000 times) than would be expected in natural water; consequently, the effect of the initial concentration and the solvent to sample ratio would not be as significant.

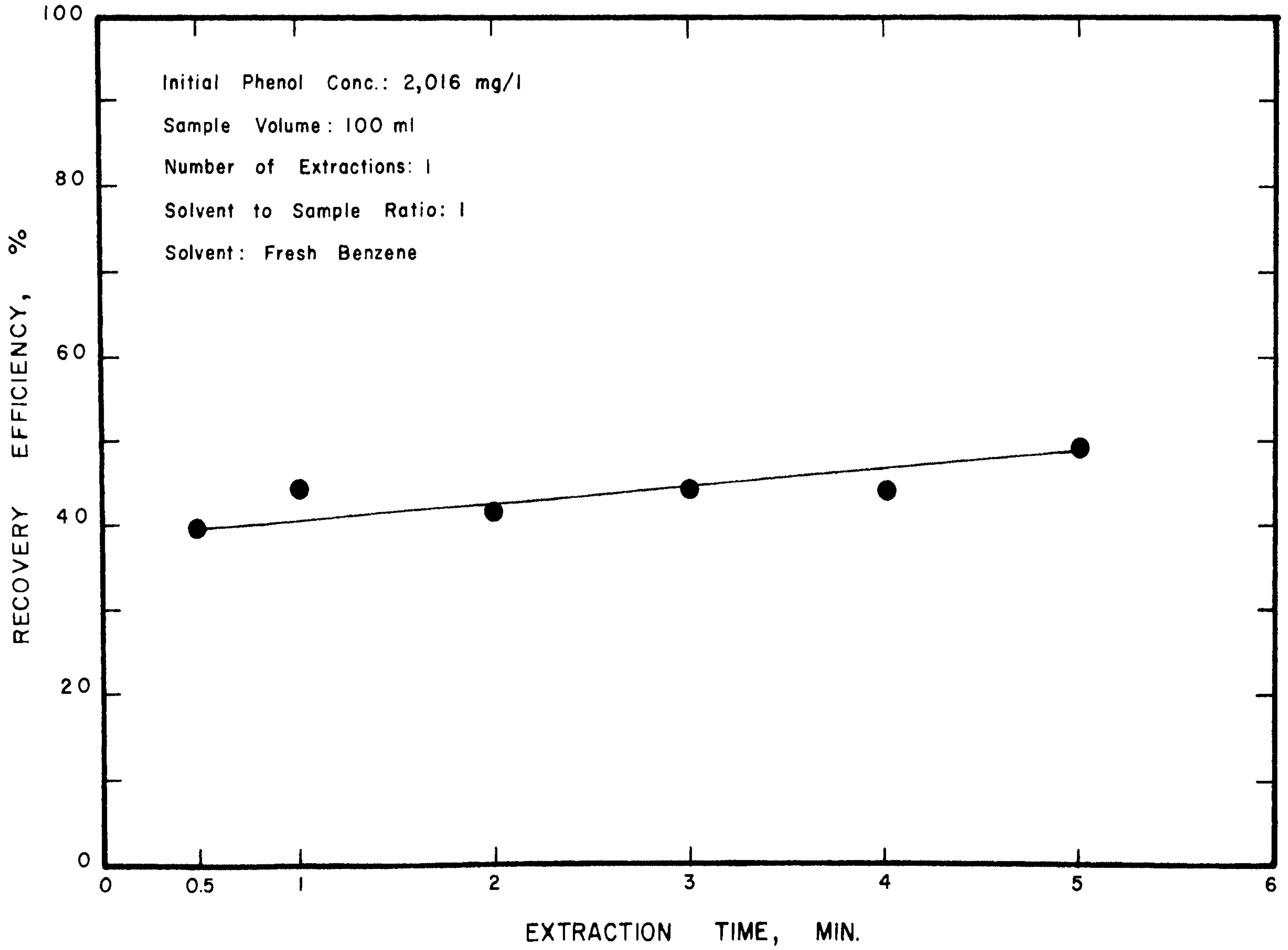
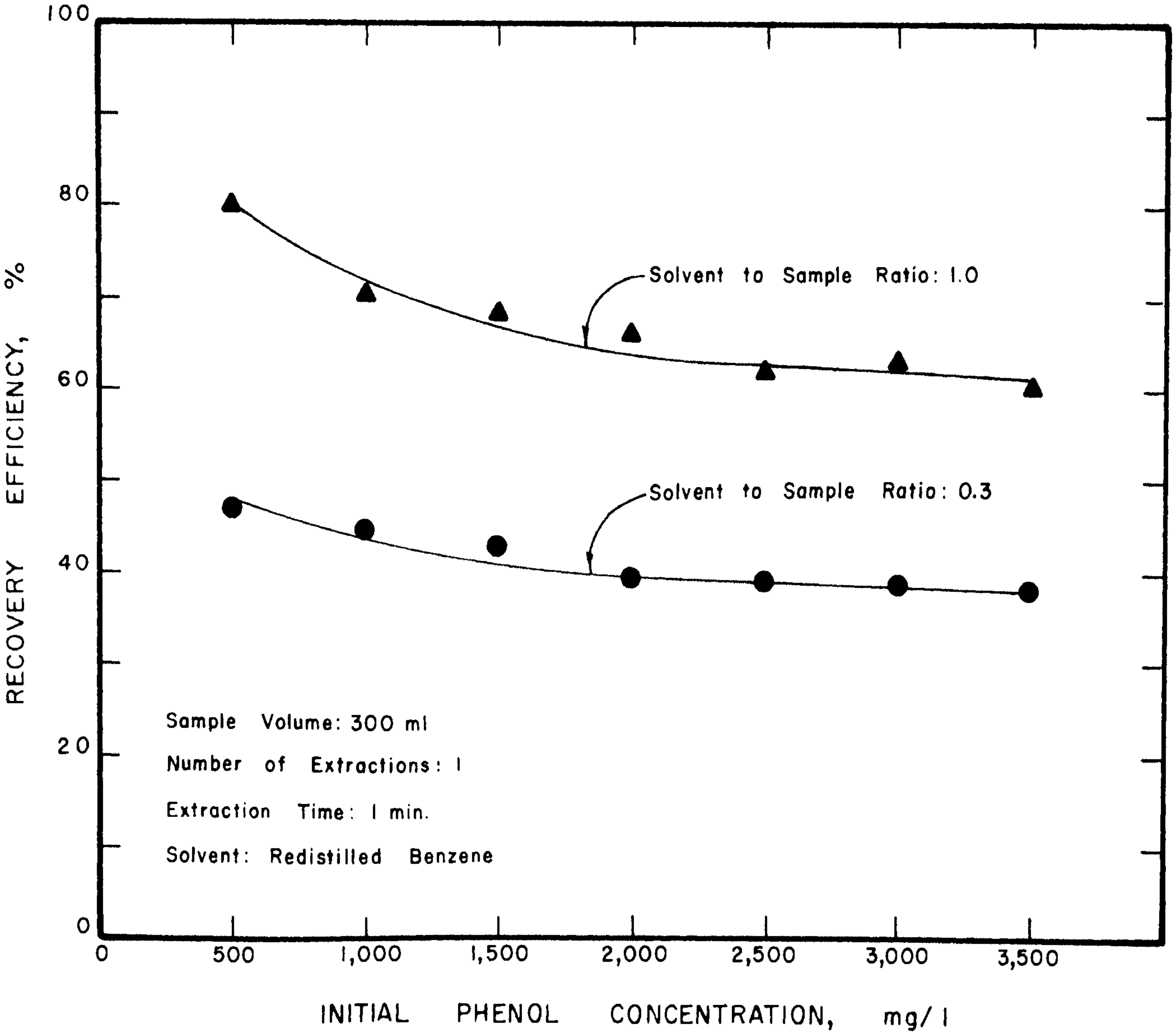


Figure 10. Solvent Extraction Studies in a Simplified Water System – Effect of Extraction Time



Sample Volume: 300 ml

Number of Extractions: 1

Extraction Time: 1 min.

Solvent: Redistilled Benzene

Figure 11. Solvent Extraction Studies in a Simplified Water System – Effect of Initial Phenol Concentration

The pH at which the water is extracted has been reported in the literature to play an important role in the solvent extraction method. Adjustment of pH to an acidic (pH 3 to 4) and a basic (pH 10 to 11) value has been recommended (6,20) to allow extraction of both acidic and basic compounds, as well as neutral. The pH of a solution containing 2,016 mg/l phenol was adjusted from 1 to 11 units by dilute hydrochloric acid and sodium hydroxide solutions. Three sequential extractions were performed using a total redistilled benzene volume equal to the sample volume and an extraction time one minute. When the pH varied from 1 to 7.5 units (Figure 12), no appreciable change in recovery efficiency could be noted; however, when the pH exceeded 7.5 units, the efficiency dropped rapidly and was less than 15 percent at pH 11. In addition, when extraction was performed at pH values of 9 and 11, it was difficult to distinguish the interface between benzene and water because of an emulsion; this problem was more intense at pH 11.

To evaluate the recovery of trace organics from turbid water by the solvent extraction method, finely ground Grundit clay was added to a 1,000 mg/l phenol solution to give turbidities ranging from 60 to 1,250 units. The samples were extracted with fresh benzene (solvent to sample ratio of one) using one extraction for one minute, and the resulting recoveries were as follows:

Turbidity, units	Phenol Recovery, %
0.3 (no clay added)	82
60	80
150	78
225	77
300	77
560	76
960	74
1,250	73

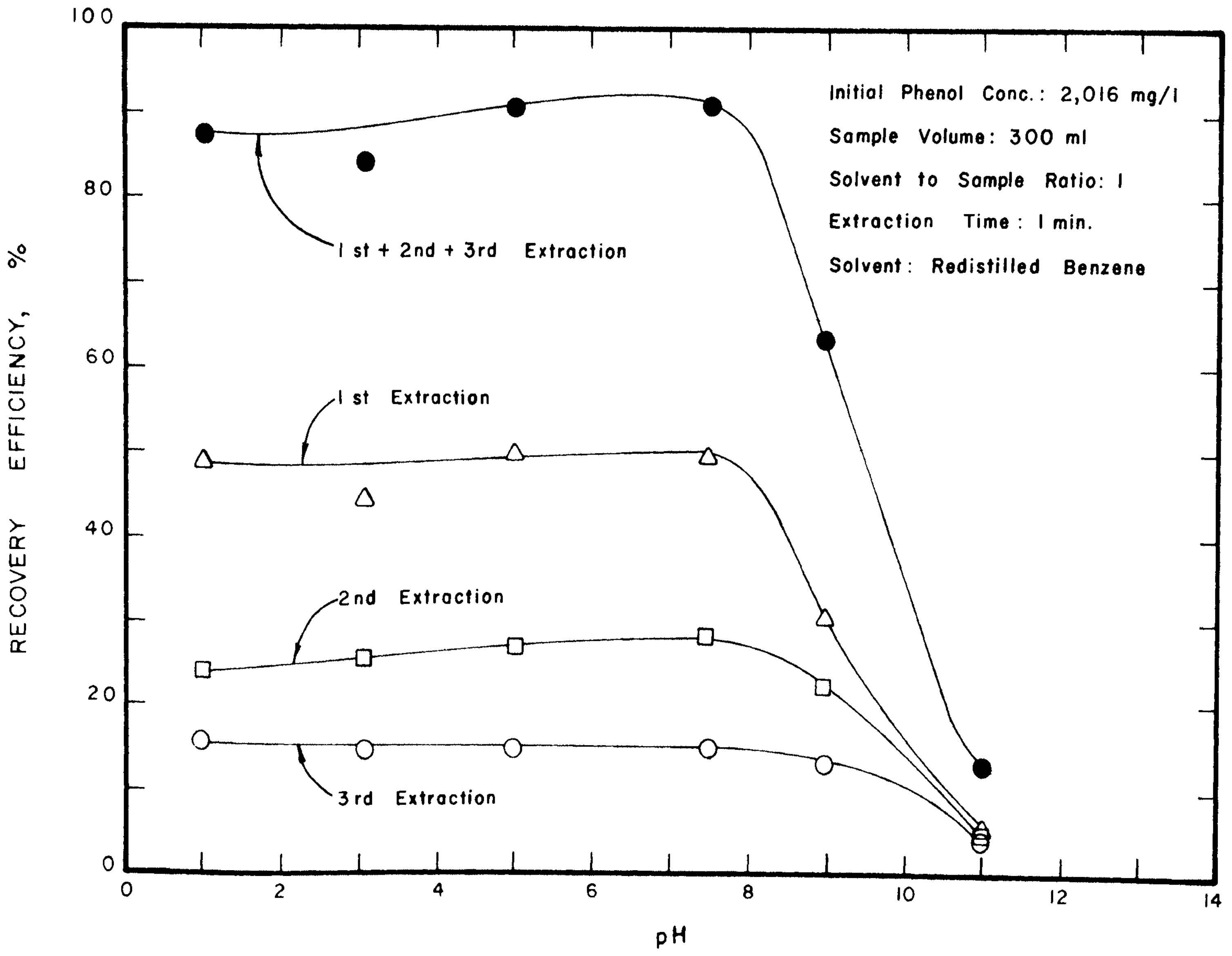


Figure 12. Solvent Extraction Studies in a Simplified Water System – Effect of pH

The effect of turbidity was not found to be as significant as was expected; however, the concentration of phenol was quite high relative to the concentration of trace organics in natural water, and it is possible that the clay did not have enough adsorptive capacity to retain an appreciable amount of phenol.

The scope of the freeze concentration studies was more limited, and involved primarily an investigation to determine the relationship between volumetric concentration and recovery efficiency and evaluate the effect of flash freezing. Flash freezing occurred when an overcooled sample froze in a very short period of time resulting in the entrapment of phenol and reducing the recovery efficiency. A series of 500 ml volumes of a phenol solution containing 60 mg/l were frozen in round-bottom evaporating flasks which were immersed in a mixture of ice cubes and rock salt (-6 to -7.5°C) and rotated by a Rinco vacuum evaporator. In order to overcome the problem of flash freezing, the sample was precooled (0 to 6°C) and the flask was preseeded; although this technique was successful most of the time, flash freezing still occurred occasionally. The results of the freeze concentration studies are presented in Figures 13 and 14. In the absence of flash freezing, almost 100 percent phenol recovery was obtained when the volumetric concentration ratio ranged from 6 to 9, and recovery decreased at lower and higher ratios. In general, phenol recovery was quite good up to a volumetric concentration of 17 fold; however, flash freezing could significantly reduce the recovery efficiency.

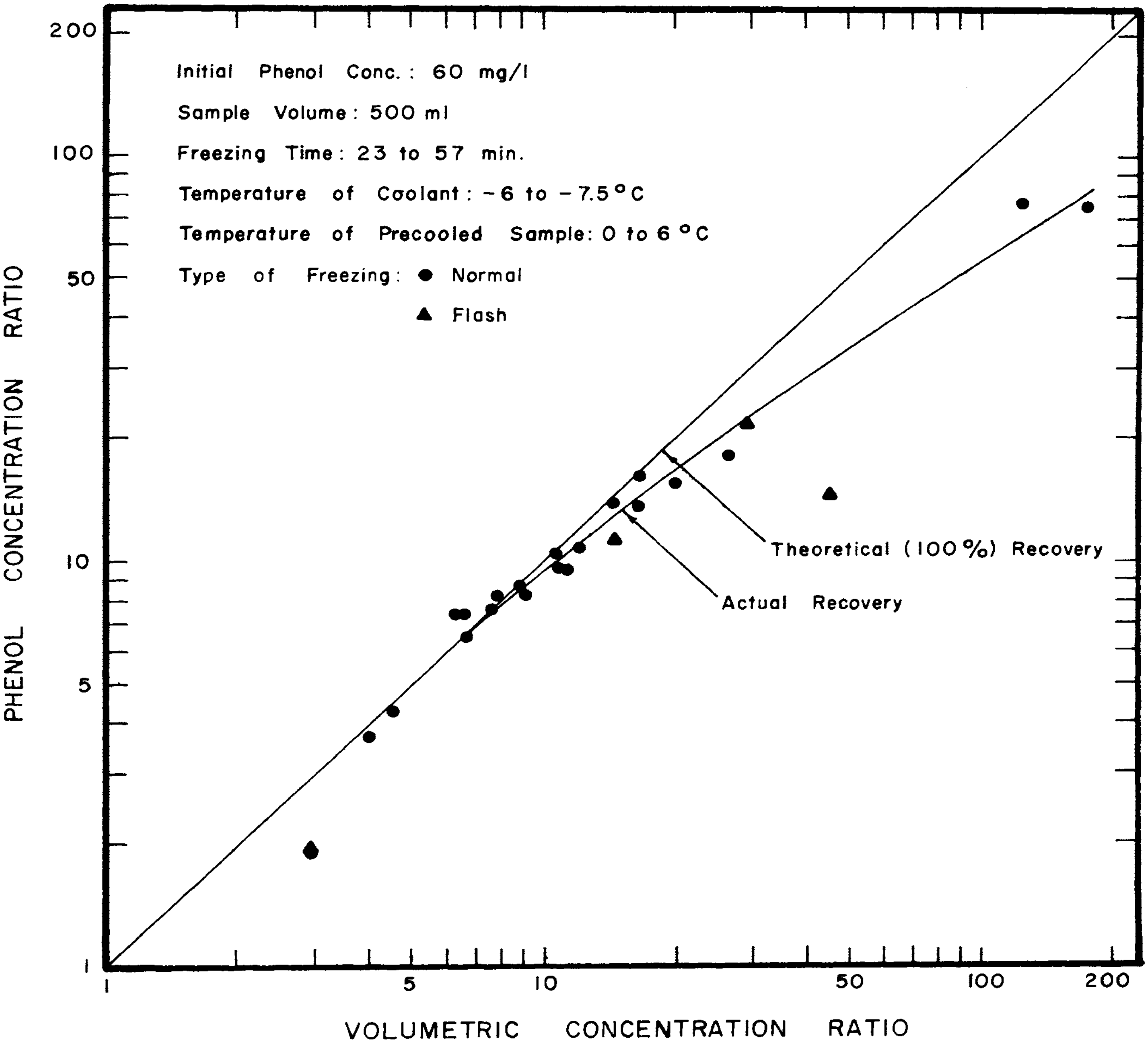


Figure 13. Freeze Concentration Studies in a Simplified Water System — Effect of Volumetric Concentration

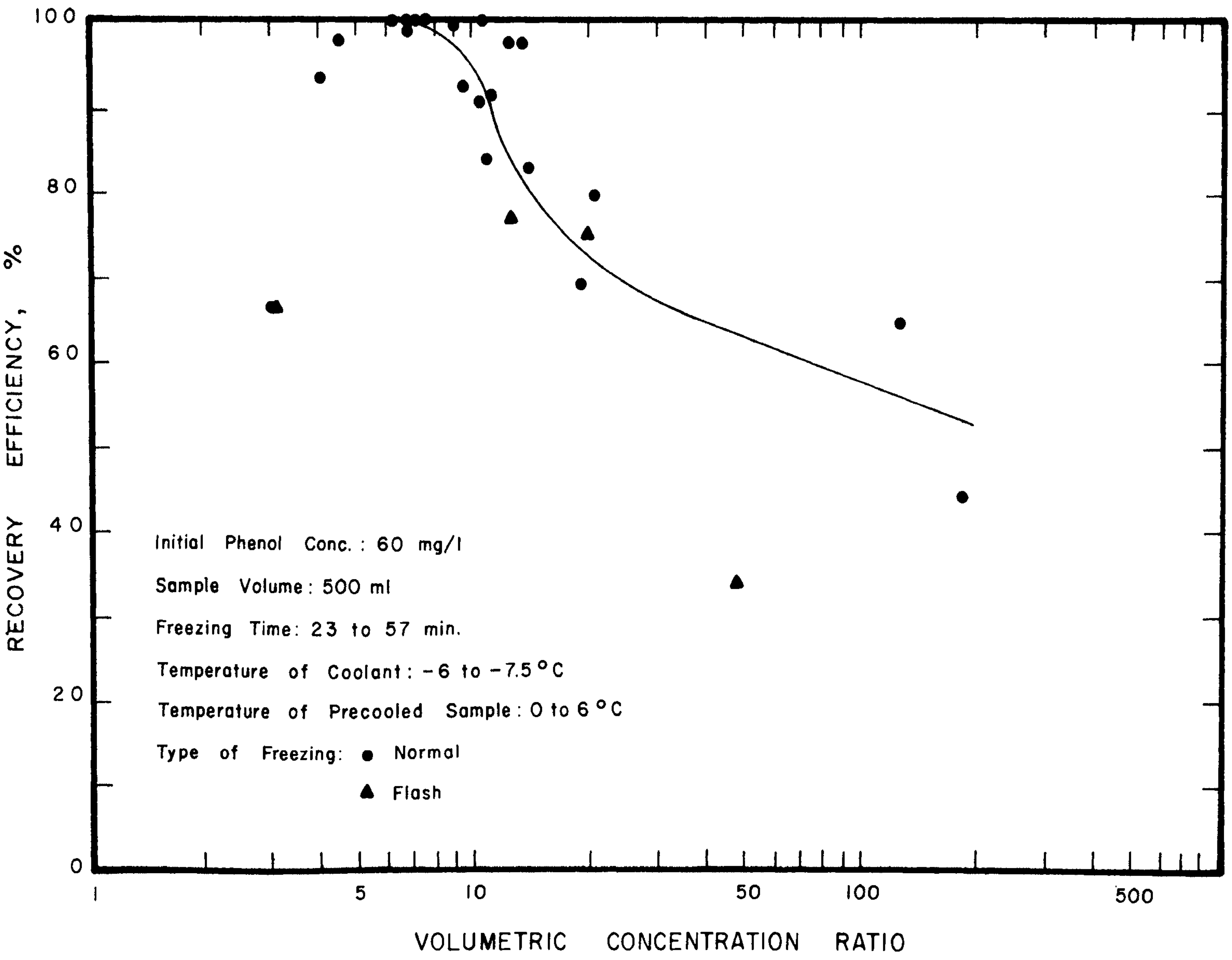


Figure 14. Freeze Concentration Studies in a Simplified Water System – Recovery Efficiency

B. NATURAL WATER SYSTEM STUDIES

Spring and surface water samples for these studies were collected at Meramec Spring, Gasconade River near Jerome, and Missouri River in Jefferson City. The location of the three sampling sites is shown in Figure 2 (p.21) and available flow and water quality data are given in Table III.

On the basis of the results of the simplified water system studies and information presented in the literature, the following conditions were employed in the solvent extraction of the natural water systems:

Solvent: redistilled chloroform or benzene
pH: natural and adjusted to 4 and 10
Number of sequential extractions: three per sample
Total solvent to sample ratio: 1 to 3
Extraction time: three minutes for each extraction

In addition, sodium chloride at a concentration of 1,000 mg/l was added to the samples before extraction in order to decrease the solubility of the organics in water.

The extraction studies performed, and the concentrations of trace organics obtained are presented in Table IV. Initially, following the removal of solvent by distillation all extracts were dried on a steam bath at 46±1°C in a stream of air in order to remove the residual solvent. However, after drying, the benzene extracts seemed to be viscous in appearance and their concentration seemed to be out of proportion compared to the chloroform extracts. Because of the relatively high boiling point of benzene (80.1°C), it was thought that the drying procedure employed was not sufficient for the benzene extracts. Additional drying was, therefore, provided by placing the vials just above the steam in the bath where the temperature was maintained at

Table III

Natural Water System Studies
Flow and Water Quality Data

Source	Date of Sampling	Discharge* cfs	Average Velocity* fps	pH units	Turbidity units	COD mg/l	Alkalinity mg/l ($CaCO_3$)	Hardness mg/l ($CaCO_3$)	
								Total	Calcium
Meramec Spring	8/06/68	110		7.2					
	8/20/68	105		7.2					
	2/18/69	140		7.3					
	2/27/69	195		7.2					
Gasconade River	9/17/68	683		8.2					
	2/09/69	4,420		7.8	10	30.3	122	126	76
Missouri River**	10/24/68	65,000	4.2	7.6	800				
	11/11/68	48,500	3.45	8.2	150	30.0	148	220	148
	11/22/68	52,000	4.05	7.9	10	25.0	146	216	152
	12/11/68	40,000	3.3	7.6	650	32.0	140	210	145
	3/06/69	84,000	4.2	7.8	600	23.0	143	205	142

*Data were obtained from the U.S. Geological Survey, Water Resources Division, Rolla, Missouri.
**Flow data were obtained at the Boonville Station, Boonville, Missouri.

Table IV

Natural Water System Studies
Solvent Extraction Data

Location	Date	Water Extracted			Solvents Used	Extract, μg/l							Total
		Volume liters	Turb. units	pH units		pH 4		Natural pH			pH 10		
						$CHCl_3$	C_6H_6	$CHCl_3$	C_6H_6	$CHCl_3$	$CHCl_3$	C_6H_6	
Meramec Spring	7/24/68	72	---	4/10	$CHCl_3$	423.6					91.7		515.3
	7/27/68					81.9					441.7		523.6
	7/31/68					338.9					222.2		561.1
	8/06/68				C_6H_6		120.8					152.8	273.6
	8/20/68	36					161.1					155.6	316.7
	2/18/69	54	8.5	natural	$CHCl_3/C_6H_6$			96.3	194.4				290.7
					$C_6H_6/CHCl_3$				131.5	68.5			200.0
	2/27/69	36	7.5	4/10	$CHCl_3$	50.0					25.0		75.0
					C_6H_6		97.2					119.4	216.6
Gasconade River	9/17/68	72	---	4/10	C_6H_6		376.4					327.8	704.2
	2/19/69	27	10.0	natural	$CHCl_3/C_6H_6$			44.4	437.0				481.4
					$C_6H_6/CHCl_3$				66.7	51.9			118.6
		18		4/10	$CHCl_3$	91.7					45.8		137.5
		24			C_6H_6		72.2					45.8	128.0
Missouri River	10/24/68	90	800	4/10	C_6H_6		334.4					162.2	496.6
	11/11/68	54	150		C_6H_6		98.1					1,694.4	1,792.5
			4*		C_6H_6		211.1					629.4	840.5
	11/22/68	36	10		C_6H_6		86.1					1,291.7	1,377.8
			1.5*		C_6H_6		208.3					336.1	544.4
		18			$CHCl_3/C_6H_6$	216.7	161.1				66.7	38.9	483.4
	12/11/68	36	650	natural	$CHCl_3/C_6H_6$			466.7	605.6				1,072.3
					$C_6H_6/CHCl_3$				469.4	83.3			522.7
				4/10	$CHCl_3$	175.0					452.8		627.8
					C_6H_6		372.2					77.8	450.0
	3/06/69	18	600	natural	$CHCl_3/C_6H_6$			182.2	361.1				543.3
					$C_6H_6/CHCl_3$				294.4	72.2			366.6
		18/9**		4/10	$CHCl_3$	155.7					144.4		300.1
		18			C_6H_6		155.6					50.0	205.6
		18***	450#	natural	$CHCl_3/C_6H_6$			111.1	816.7				927.8
			300#					88.9	794.4				883.3
			150#					238.9	172.2				411.1
		18	1*					116.7	127.8				244.5
		45##	Glass Wool					91.1	71.1				162.2

*The water was filtered through glass wool before extraction.

**One-half of the sample extracted at pH 4 was lost, consequently only 9 liters were extracted at pH 10.

***Modified water system prepared by mixing river water with river water filtered through glass wool.

#13.5, 9, and 4.5 liters of river water (turbidity 600 units) were mixed with 4.5, 9, and 13.5 liters of filtered river water (turbidity 1 unit) to give final turbidities of 450, 300, and 150 units, respectively.

##Glass wool, through which 45 liters of river water had been filtered, was sequentially extracted with chloroform and benzene, using a Micro Soxhlet extractor.

90±2°C, and to prevent any oxidation of the organics at the higher temperature, the stream of air was replaced by a stream of inert nitrogen gas. Before this procedure was adopted, an infrared study was made of one extract to assure that no qualitative changes occurred during the prolonged drying process, and the results are shown in Table V and Figure 15. Since no difference could be detected in the infrared spectra, it was concluded that the benzene extracts were not qualitatively altered during the additional drying.

The concentration of solvent extracts recovered from the three sources is graphically presented in Figure 16. Samples were sequentially extracted with either chloroform or benzene at pH 4 and 10, and with chloroform and benzene or benzene and chloroform at the natural pH. In general, the chloroform/benzene extracts were larger than the benzene/chloroform extracts, and the total chloroform extracts obtained with pH adjustment were greater than the corresponding total benzene extracts. The amount of trace organics recovered from all three sources varied widely with the season of the year.

In addition, as shown in Figure 17, in the case of Missouri River water turbidity had a significant effect on recovery; the concentration of trace organics was lower when the river water turbidity was relatively high (600 to 800 units on October 24 and December 11, 1968, and on March 6, 1969) and higher when the turbidity was lower (150 units on November 11, and 10 units on November 22). One of the main difficulties encountered was an emulsion which formed between the water and solvent when turbidity was present and which became more intense at higher turbidities. Although a centrifuge was used to

Table V

Evaluation of Benzene Extract Drying at 90±2°C in a Nitrogen Atmosphere*

Infrared Spectrum	Total Drying Time hours	Extract, grams				Weight Loss % of Initial
		Weight at End of Drying	Used for Infrared Analysis	Remaining Weight	Adjusted Weight	
Initial	0**	0.1454	0.0087	0.1367	0.1454	--
First Trial	35	0.1160	0.0110	0.1050	0.1234[#]	15.1[##]
Second Trial	73.5	0.0904	--	0.0904	0.1062	13.9
	78.5	0.0890	0.0094	0.0796	0.1046	1.5
Final	112.5	0.0746	--	0.0746	0.0980	6.3
	121.5	0.0735	--	0.0735	0.0965	1.5
	149.5	0.0714	--	0.0714	0.0937	2.9
	175.5	0.0703	--	0.0703	0.0923	1.5
	190.5	0.0685	--	0.0685	0.0899	2.6
	195.5	0.0683	0.0061	0.0622	0.0896[+]	0.3

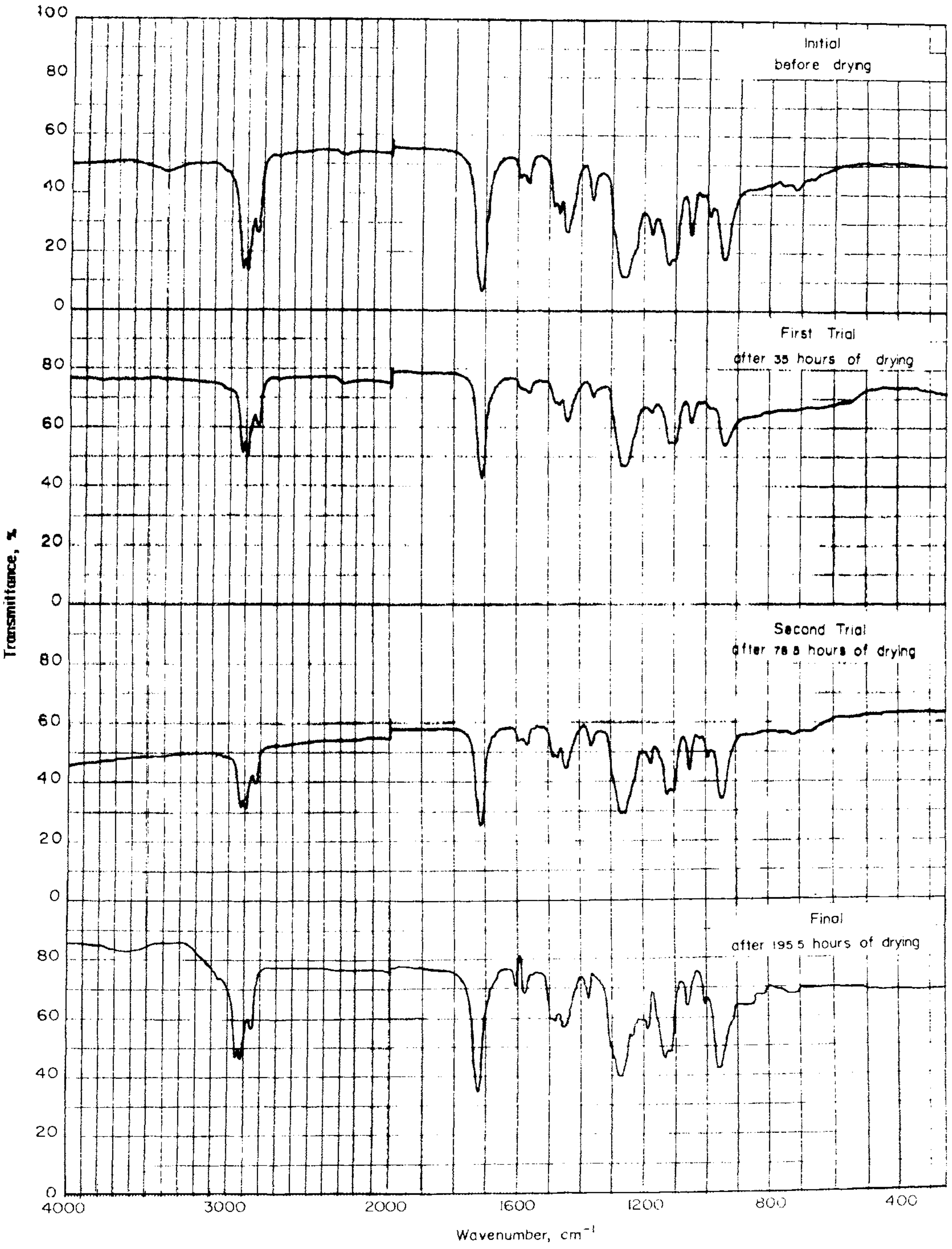
*Test sample extracted from Missouri River water collected 11/11/68; pH adjusted to 10.

**Sample had already been dried to apparent constant weight at 46±1°C on a steam bath in a gentle stream of air; drying continued at 90±2°C in the bath in a stream of nitrogen.

[#] Determined as: 0.1454 x (1-0.151) = 0.1234 grams.

[##] Determined as: [(0.1367-0.1160) ÷ 0.1367] x 100 = 15.1%.

[+] Total weight loss: [(0.1454-0.0896) ÷ 0.1454] x 100 = 38.4%.



Sample: Missouri River water collected 11/11/68, pH adjusted to 10
Scanning speed: Upper two spectra – fast, lower two spectra – slow
Gain setting: 2.3 Slit override setting: 1.0
Mode: Double beam vs KBr Cell: KBr pellet

Figure 15. Infrared Spectra of Benzene Extract During Drying at 90±2°C in a Nitrogen Atmosphere

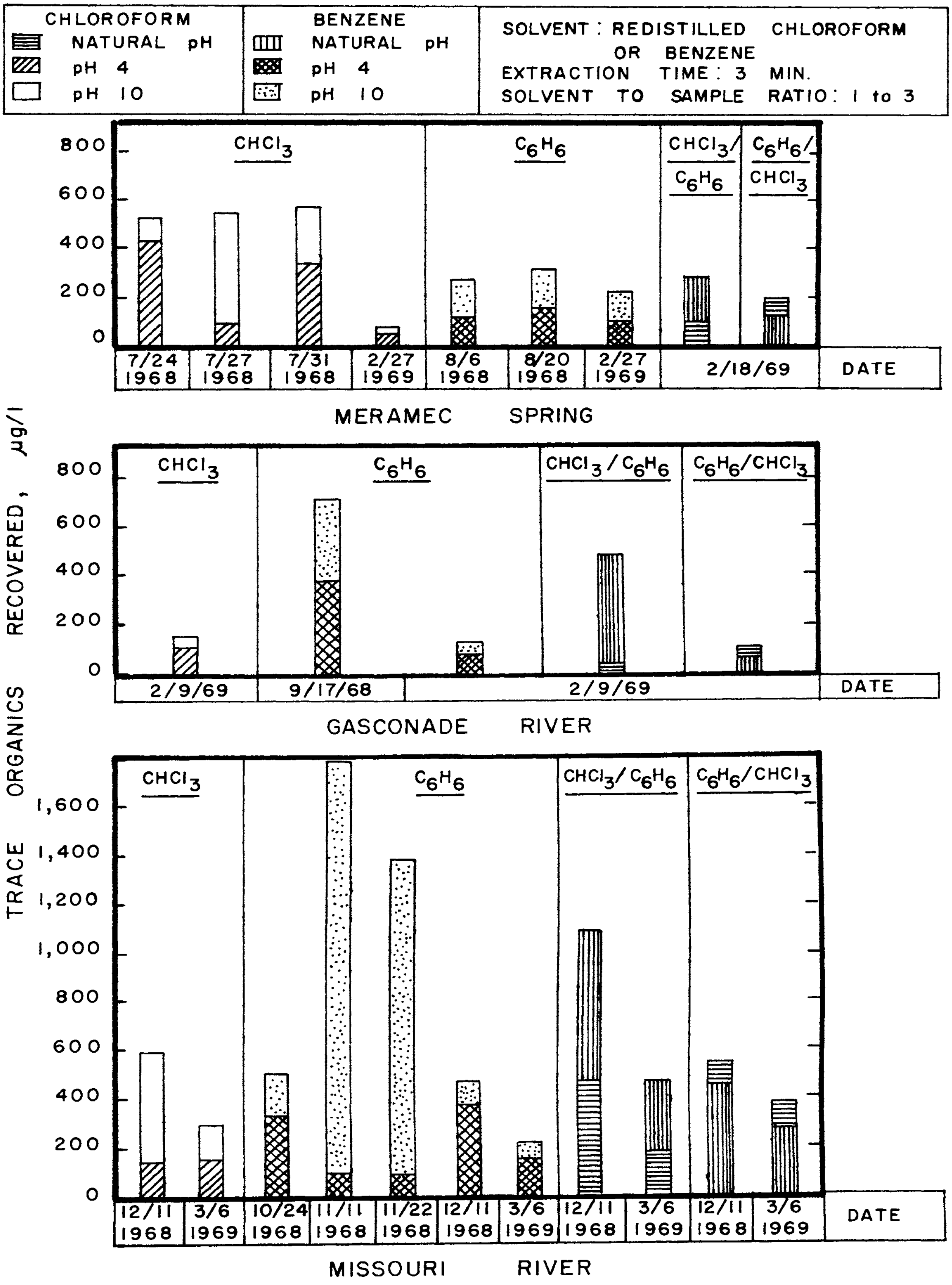


Figure 16. Solvent Extraction Studies in Natural Water Systems

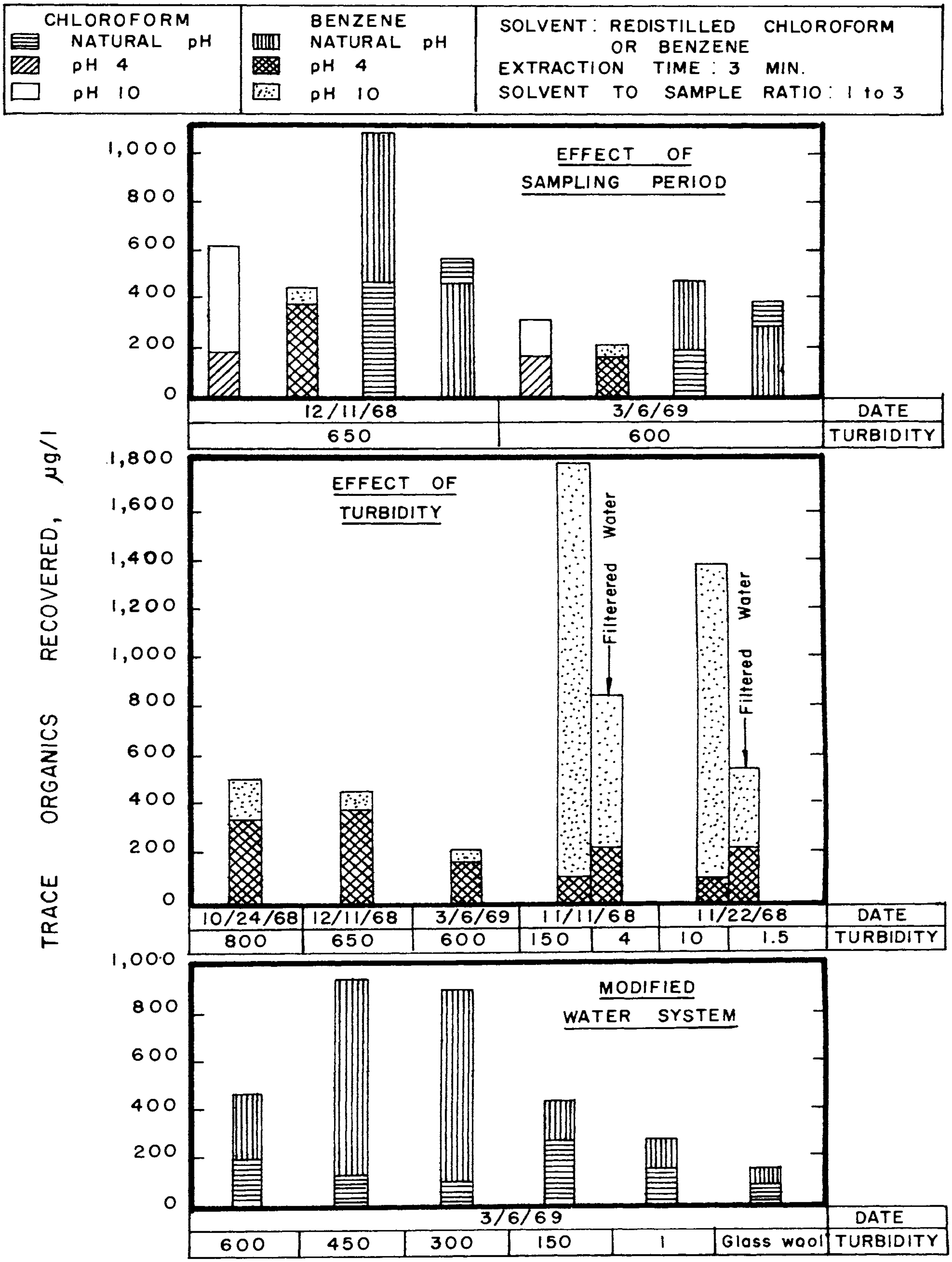


Figure 17. Solvent Extraction Studies in Missouri River Water

separate the two phases, part of the solvent still remained entrapped in the emulsion resulting in a reduced recovery efficiency.

In order to evaluate further the effect of turbidity, a modified water system was used and was prepared by mixing Missouri River water containing 600 units of turbidity with turbidity-free water obtained by passing river water through glass wool. As indicated in Figure 17, maximum recovery of trace organics was obtained when the turbidity was 300 to 450 units, and recovery decreased at lower turbidity and when the raw water was extracted. The glass wool which had been used to filter the river water, together with the turbidity material retained, was solvent extracted with chloroform and benzene using a micro Soxhlet extractor. The amount of organics recovered from the glass wool (91.1 µg/l chloroform and 71.1 µg/l benzene extract) was used to adjust the concentration of the extracts obtained at different turbidity levels and the results were as follows:

	Extracts, µg/l		
Turbidity*	Chloroform	Benzene	Total
600	182.2	361.1	543.3
450	133.9	834.5	968.4
300	134.5	829.9	964.4
150	307.2	225.5	532.7
1	207.8	198.9	406.7

---

*Volumes of 13.5, 9, and 4.5 liters of river water (turbidity 600 units) were mixed with 4.5, 9, and 13.5 liters of filtered river water (turbidity 1 unit) to give final turbidities of 450, 300, and 150 units, respectively.

V. DISCUSSION OF RESULTS

The primary purpose for using the simplified water system was to evaluate the effect of many variables on the solvent extraction process and to serve as a guide for the natural water system studies. Phenol was used as the organic component of the simplified water system because phenolic substances are the end products of natural, as well as domestic and industrial activities, and are present in almost all natural waters. High-strength phenol solutions were used in this study so that phenol concentration could be quickly and accurately determined by means of gas chromatographic analysis. These concentrations were many times greater than the concentration of trace organics in natural waters, and this should be taken into consideration when using the results of the simplified studies to guide the development of the natural water studies. An additional limitation resulting from the use of the gas chromatograph to determine phenol was the fact that benzene was the only solvent which could be employed in the studies, since chloroform might have damaged the detector of the chromatograph.

Because of time requirements, the number of extractions that must be performed on a sample in order to obtain optimum efficiency is an important consideration in solvent extraction. Recovery efficiency was significantly improved when three sequential extractions rather than a single extraction were made. When solvent to sample ratios in the range of 0.1 to 2.0 were used and three extractions were made, the efficiency increased from 18.8 percent at a ratio of 0.1 to 34.5 percent at a ratio of 0.2 to 0.3 and then gradually dropped to 23 percent at a ratio of 2.0. Another practical consideration, especially when large samples are extracted, is the volume of solvent required. As was expected, the phenol recovery efficiency increased with higher solvent to sample ratios; a ratio of 2.0 was necessary to recover more than 90 percent of the phenol, while a ratio of 0.3 recovered only about 50 percent. The higher phenol concentration was, however, at least partly responsible for the low recovery at lower ratios. This was demonstrated when phenol solutions containing from 500 to 3,500 mg/l were used and one extraction was performed. At a solvent to sample ratio of 0.3, the efficiency dropped from 47 to 39 percent as the concentration increased; it dropped from 80 to 60 percent when a ratio of 1.0 was employed. Considering that these phenol concentrations were at least 500 to 5,000 times greater than the levels of trace organics reported in surface and subsurface waters, a lower solvent to sample ratio could be expected to provide satisfactory recoveries. Because of these considerations, a ratio of 0.33 (1 to 3) and three sequential extractions were selected for the natural water system studies.

The pH at which the sample was extracted had a very significant effect on phenol recovery. When the pH was adjusted within an acidic range (1 to 7.5) almost 90 percent recovery was obtained, but when the pH was adjusted within an alkaline range (9.5 to 11) the recovery decreased sharply to less than 15 percent at pH 11. Adjustment of the pH is therefore important, especially in natural water where different types of organics would be present, in order to assure more complete recovery of acidic and basic organics.

Other investigators have used comparable extraction conditions. Use of a solvent to sample ratio of 1 to 10 to extract with chloroform

Missouri River water at pH values of 2, 7 and 11 has been reported by Skrinde and Tomlinson (12), while a ratio of 1 to 3 and pH adjustment to 4 and 10 were employed by Caruso, et al. (20) in lake and stream surveys using diethyl ether as the solvent. After the experimental portion of this investigation had been completed, a tentative method was proposed at the 72nd annual meeting (June 1969) of the American Society for Testing and Materials (6). This method recommended three serial extractions, a total solvent to sample ratio of 1 to 12, and sequential pH adjustment to neutral, acidic (pH 3), and alkaline (pH 11) ranges.

Solvent extraction studies using natural water systems were conducted over a nine month period (July 1968 to March 1969) to determine seasonal variations in the concentration of trace organics. Three sources, Meramec Spring, Gasconade River and Missouri River, were selected to represent surface and subsurface waters and different pollutional levels and to allow comparison of the results to those obtained in previous investigations (10,12,38).

Significant changes in concentration were observed between the summer and winter season at Meramec Spring; the total chloroform and benzene extracts (pH 4 and 10) averaged 533.3 and 295.1 µg/l, respectively, in the summer, but were only 75.0 and 216.6 µg/l in the winter. A similar situation was found in Gasconade River water where the total benzene extracts (pH 4 and 10) varied from 704.2 µg/l in the fall to 128.0 µg/l in the winter.

Of the two solvents used, chloroform appeared to be the more efficient in recovering trace organics. This was true when chloroform and benzene were both used to extract the same sample at natural pH, and the chloroform/benzene extracts were always greater than the benzene/chloroform extracts. It was also true when chloroform or benzene were individually used to extract a sample at the two adjusted pH values; the total chloroform extracts were in most cases greater than the total benzene extracts.

The effect of turbidity was not conclusively established. In a simplified water system study where turbidities ranging from 0.3 to 1,250 units were applied, the recovery efficiency decreased from 82 to 73 percent. In Missouri River water, the effect of turbidity appeared to be more significant and lower concentrations of trace organics were generally recovered when the turbidity was higher, although other factors could have also been responsible for the lower recoveries. Thus, when all the different extracts are considered, the lowest concentrations were obtained on October 24 and March 6; the river water at those two days had a high turbidity (800 and 600 units, respectively) but also a high flow (65,000 and 84,000 cfs, respectively). A turbidity of 650 units was also noted on December 11, yet the concentration of trace organics recovered, especially the chloroform/benzene extracts, was relative high; the river flow at that time was only 40,000 cfs, the lowest observed during any sampling period. Therefore, it appears that dilution with runoff, which would normally be accompanied with a high river turbidity, was responsible for the lower recoveries.

In order to eliminate other factors so that the effect of turbidity alone could be determined, a modified Missouri River water was used and consisted of a series of samples of different turbidities which were prepared by mixing river water with glass wool-filtered river water. The results of this study were again not entirely conclusive. When the turbidity was reduced from 600 to 450 or 300 units, the chloroform/benzene materials recovered by extraction at natural pH increased from 543.3 to an average of 966.4 µg/l; however, when the turbidity was further decreased to 150 and 1 unit, the concentration of the extracts decreased to 532.7 and 406.7 µg/l, respectively. It is believed that turbidity has two effects; the formation of an emulsion which would tend to give lower recoveries because of the entrapping of solvent, and the sorption of organics on the turbidity-causing particles. Removal of turbidity would reduce emulsion problems, but also would remove some of the organics present. This was noted, in addition to the modified water system study, on two other occasions, November 11 and 22, when the removal of turbidity by filtration through glass wool significantly reduced the concentration of trace organics recovered. Although an attempt was made to compensate for this by solvent extracting the glass wool and particulate matter, it is possible that all materials could not be desorbed and consequently the corrections made could be inadequate.

In order to evaluate the results of this study, the concentrations of trace organics obtained were compared, whenever possible to data reported in the literature. The 96.3 µg/l chloroform extract obtained from Meramec Spring water in the winter of 1969 compared favorably with the 43.7 and 92.2 µg/l total carbon chloroform extracts recovered at the same location by Smith (38) who used three activated carbon filters in series in two runs made in the winter of 1965. The 155.7 to 216.7 µg/l range of chloroform extracts obtained by extraction of Missouri River water at pH 4 was considerably higher than the

67.5 µg/l carbon chloroform extract obtained by Myrick and Ryckman (10) by extraction of acidified (pH 3.5) Missouri River water at St. Louis; however, the water had already been passed through another activated carbon column at natural pH. Skrinde and Tomlinson (12) have reported that chloroform extraction of three Missouri River water samples at pH values at 2, 7 and 11 yielded average trace organics concentrations of 883, 637, and 490 µg/l, respectively; these would compare with average concentrations of 182 and 324 µg/l obtained in this study by extraction with chloroform at pH 4 and 7.7. These data cannot of course be compared without taking into consideration that they were obtained by different investigators, at different locations, and over a period of about eight years.

Carbon adsorption and solvent extraction are the methods which have been most widely used for the recovery of trace organic pollutants from water. On the basis of the limited information presented, solvent extraction seems to be more efficient than carbon adsorption. Therefore, it would be highly desirable that research be conducted to directly compare the two methods. Work in progress at the University of Missouri-Rolla by Wagher (41), who is attempting to evaluate the carbon adsorption method by parallel solvent extraction studies, could answer this question more fully.

In summary, the important considerations in the solvent extraction method were the proper selection of the solvents and the solvent to sample ratio. A greater yield could be obtained by the adjustment of the pH, the sequential extraction with a combination of the solvents, and the partial removal of turbidity in order to reduce the effect of emulsion formation. It would be a tedious and time-consuming job to obtain a sufficient quantity of organic matter, as would be needed for characterization and identification work, using batch type solvent extraction. Therefore, a continuous flow type solvent extractor needs to be developed, and this is recommended as an area for future investigation.

A preliminary study of the freeze concentration method using a simplified water system was also undertaken in this study. Freeze concentration is another method which can be used for the recovery of organic micropollutants, and offers the advantage that it is a direct concentration technique which limits the possibility of biological, chemical, or physical alteration of the organics. Precautions should be taken to avoid flash freezing; this might be accomplished by precooling the sample and preseeding the flask. The results of this study showed that the maximum recovery was obtained when the volumetric concentration ratio ranged from 6 to 9, and recovery decreased at lower and higher ratios. Freeze concentration is another area where additional work is needed in order to determine the fundamental requirements of the process and evaluate its practical application in the field of trace organic pollutants.

VI. CONCLUSIONS

From the results obtained in this investigation, the following conclusions may be drawn:

1. The proper selection of the solvents and the solvent to sample ratio were the most important factors in the solvent extraction method; the number of sequential extractions and pH adjustment were two other important variables.
2. At the natural pH, serial extraction with chloroform and benzene yielded a larger recovery of trace organics than sequential extraction with benzene and chloroform; at adjusted pH values (4 and 10) extraction with chloroform yielded a greater recovery than extraction with benzene.
3. The concentration of trace organics in spring and river water was subject to significant seasonal variation.
4. The presence of turbidity in the water appeared to have an effect on the recovery efficiency, however, a definite correlation between the turbidity level and the recovery efficiency was not conclusively established.
5. The efficiency of phenol recovery by freeze concentration depended on the volumetric concentration ratio, and almost complete recovery was obtained at ratios ranging from 6 to 9.

VII. RECOMMENDATIONS FOR FUTURE INVESTIGATION

Solvent extraction and freeze concentration are two relatively new techniques in the field of recovering trace organic pollutants from natural waters. Although a tentative solvent extraction method has been recently adopted by the American Society for Testing and Materials, the following areas where additional investigation would be desirable have been identified during the course of this study.

1. Solvent extraction on the basis of limited data appeared to be more effective than carbon adsorption which is the standard recovery method in the field of organic micropollutants; the parallel application of the two techniques under actual field conditions would make possible the direct evaluation of the two methods.
2. Batch type solvent extraction was a tedious and time-consuming operation, especially when the quantity of extracts desired required the extraction of large volumes of water; the development of a continuous flow solvent extraction unit would eliminate the limitation of sample size and would save a lot of labor and time.
3. Freeze concentration to date has been primarily used as a method for concentrating trace organics in water for instrumental qualitative analysis; inorganic impurities in the water would prevent the direct quantitative recovery of the organics present in the concentrate and a method should be developed to accomplish this task.

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