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Gas chromatographic determination of water in organic compounds and of organic compounds in water after steam distillation

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Gas chromatographic determination of water in organic compounds and of organic compounds in water after steam distillation

by

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DEDICATION

This work is dedicated to the
three most important people
in my life; mom, dad and
Meri. Their guidance,
support and love are
the things I value
the most of all.

GENERAL INTRODUCTION

Gas chromatography (GC) is one of the most common methods of obtaining either quantitative or qualitative (or both) information about a sample. Excellent separating ability and high sensitivity are two of the main reasons why GC has caught on in many areas of science, as well as chemistry. Several methods of analysis are written strictly around the use of GC for a wide variety of determinations.

Modern GC involves the use of flexible fused-silica capillary columns, sensitive detectors, and many modes of sample introduction. Fused-silica columns are available with several types of stationary phases. Most of these phases are now chemically bonded to the wall of the column to reduce column bleeding and increase column lifetime. There are numerous detectors that can be used for all types of GC determinations. The most popular is the flame ionization detector because of its sensitivity and large linear dynamic range.

Commercial vendors offer instruments that can perform many different analyses or one that is tailor fitted for a specific need. Because of the flexibility that GC can provide, most laboratories have at least one gas chromatograph. Therefore, methods that involve analysis by GC can be used by a large number of people.

This dissertation is divided into three sections, the last two being related to each other but not to the first. All three require the use of gas chromatography to provide separation and quantitative information of analytes.

The first section is a gas chromatographic method for indirect determination of water in organic compounds using a flame ionization detector. A reaction of 2,2-dimethoxypropane with water is utilized and the amount of the product, acetone, is determined. The solid acid catalyst, Nafion, is used to give a reaction time of under 5 minutes.

The second section describes a sample preparation method for organic compounds in water. Simple steam distillation is shown to be useful for a large variety of compounds with vastly different functionalities and boiling points. Once the distillation is completed, a portion of the condensate is injected into a GC for separation and quanitative information. Many different boiling modifiers were examined with varying degrees of success.

The third and final section uses the distillation apparatus from section two, but also incorporates solid phase extraction (SPE) at the condensate collection step. A simple Teflon interface is described that allows for the determination of samples in the part-per-billion range. The extracting resin is washed clean of analytes with an organic solvent and a portion of this wash is introduced into a gas chromatograph.

The use of gas chromatography is essential to each of the sections and this is the underlying requirement that incorporates these together in this dissertation.

SECTION I. GAS CHROMATOGRAPHIC DETERMINATION OF WATER IN ORGANIC COMPOUNDS USING 2,2-DIMETHOXYPROPANE AND A SOLID ACID CATALYST

INTRODUCTION

The determination of the amount of water in organic and inorganic compounds is a common problem encountered in all areas of science. There have been many gravimetric, distillation, chromatographic, electronic, spectroscopic, nuclear, and titrimetric methods for this determination. Unarguably, the most common method for the quantitative determination of water is the Karl Fischer titration. This titration makes use of the reaction:

$$2\ H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI \qquad (1)$$

Unfortunately, the products of this reaction can further react with one another to form more iodine. When an organic base like pyridine is added, this problem is eliminated and the reaction proceeds in steps in methanol (1):

$$I_2 + SO_2 + 3\ pyr + H_2O \rightarrow 2\ pyr : HI + pyr : SO_3 \qquad (2)$$

$$pyr : SO_3 + CH_3OH \rightarrow pyr : HSO_4CH_3 \qquad (3)$$

A Karl Fischer reagent containing iodine, sulfur dioxide, and pyridine dissolved in methanol is commercially available from vendors. Also a pyridine free reagent is available.

Since the Karl Fischer titration is based upon an oxidation-reduction reaction, species with such potential that are present can

cause severe problems. A complete discussion of interferences is available (2). Also, the endpoint of the titration is not easily determined visually. Even small differences in the lighting of a room can give a different appearance for the endpoint and procedures using special light sources have been described. Electrochemical detection is commonly used and is more sensitive. These detectors can be very costly and are usually dedicated for this special titration.

Recently, there have been a few liquid chromatographic methods for the determination of water that have been published. Stevens et al. (3) showed that conductometric detection could be applied for the direct determination of water as low as 2.5 ppm. Methanol with a small amount of sulfuric acid served as the eluent. When an organic sample with water is injected, the water is separated and causes the sulfuric acid to ionize. It is this ionization that gives a response in the conductivity detector. The method is easy to use and fast, but the response factors vary widely for different ranges of water concentration. Fortier and Fritz (4) have described a method that uses spectrophotometric detection for the water separated. A cation exchange column in the Li^+ form is used for the separation, followed by a catalytic column containing cation exchange resin in the H^+ form. Detection is based on the effect of water on the equilibrium between cinnamaldehyde and its acetal. A mixture of methanol and acetonitrile served as the eluent and detection was performed at 310nm. Excellent results were obtained for over 3 orders of magnitude of water concentration and detection limits were in the low ppm range. This method has been significantly improved in new work by Chen and Fritz

(5). Here a similar detection scheme is employed at 300 and 310 nm. A single column is used and a complete determination takes less than 2 minutes. A complete theoretical description is presented and the concentration of water in several samples is listed.

Perhaps the second most common method for the determination of water is gas chromatography (GC) with thermal conductivity detection (TCD). A TCD is capable of detecting water directly at concentrations as low as 1 ppm. Until recently, these detectors were only compatible with packed columns and had very large cell volumes. The water had to be well separated from any other component because of peak spreading in the detector. Also, most packed columns give only marginal separation and peak tailing is often a problem with water.

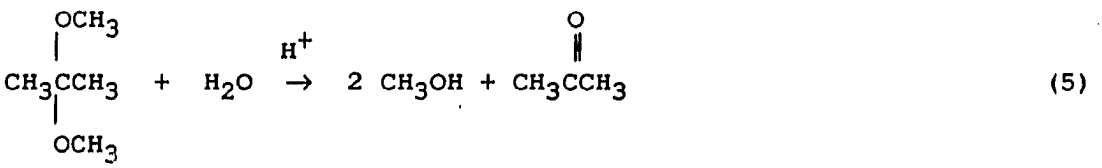
Direct analysis can also be performed using an electron capture detector (ECD). Work by Scholz and Ballschmiter (6) shows that the ECD can detect a minimum of 15 ng of water absolute and the response is linear from 7 to 150 µg/ml. Upon first inspection, these results seem quite impressive, but not when typical chromatographic conditions are considered. Using capillary columns, a split ratio of 100:1, and a 1 µl injection, the detection limit would only be 0.15%.

In 1988, a far-UV detector for GC was commercially introduced (7,8). This detector operates at 124 nm where almost all compounds except the noble gases absorb. Presently, this detector is available for use with packed columns and many improvements need to be made. The detection limit for water is in the low ppm range and good linearity is obtained from 10 to 180 ppm.

Presently, most GC units are sold with a flame ionization detector. This detector is not only sensitive, but also has a linear response for up to 8 orders of magnitude and is almost universal. Although the newer thermal conductivity detectors are compatible with capillary columns, it is unlikely they will gain wide scale use. The FID is still more sensitive and has a much larger linear response range.

Several requirements were set before the development of a method that would determine the amount of water in a sample. First, the method should utilize modern, non-dedicated instrumentation that is common to this and other laboratories. Second, this method should be developed to the point where it could be used quickly, routinely and easily by unskilled hands. Third, the cost of an analysis should be minimal. Last, the method should be accurate and applicable for a wide range of samples containing vastly different amounts of water.

This method makes use of the reaction involving 2,2-dimethoxypropane and water to form acetone and methanol in the presence of an acid catalyst and is shown below:



$$CH_3C(OCH_3)_2CH_3 + H_2O \xrightarrow{H^+} 2\ CH_3OH + CH_3COCH_3 \qquad (5)$$

The amount of acetone or methanol is easily determined by gas chromatography (GC) with flame ionization detection (FID). Using GC with FID is a powerful, useful tool that is common to a majority of laboratories.

The reactant, 2,2-dimethoxypropane (DMP), is very inexpensive and is commercially available from several vendors. Its analytical use as a drying agent was first described by Erley (9). Non-volatile samples containing water were treated with DMP before infared analysis and the volatile products from the reaction were allowed to evaporate. Since the sample is not heated to drive off the water, no thermal degradation occurs. Kalasinsky et al. (10) developed a system that uses an acidified solution of DMP as a post-column reactor for reverse-phase high performance liquid chromatography. Diffuse reflectance infared analysis on potassium chloride powder was used as the detection system. Since the water is reacted and eliminated before detection, the powder substrate is not altered from dissolution. The reactivation of silica columns is important to maintain good peak shape in normal phase high performance liquid chromatography. Bredeweg et al. (11) used DMP to react with water and reactivate the silica columns. A solution containing DMP and glacial acetic acid was made in hexane and passed through the silica column. Excellent peak shapes were obtained that compared closely to those of a new column. Riederer and Schonherr (12) studied the ability of DMP as a drying agent for ether. Ether is used to extract methyl esters of hydroxy fatty acids from water. These esters need to be converted to their trimethylsiloxy derivatives in anhydrous conditions before analysis. DMP was shown to be superior to $CuSO_4$, $CaCl_2$, and Na_2SO_4 for drying the saturated ether extract and the water could be reduced to as low as 0.004% in fifteen minutes.

Critchfield and Bishop (13) determined the amount of water in organic solvents and inorganic hydrates using DMP with methanesulfonic

acid as the acid catalysis. The amount of acetone generated is determined using infared absorption of the carbonyl band at 5.87 microns. Detection limits as low as 0.05% water are claimed. Since this method is based upon the determination of the infared absorption of the carbonyl group of acetone, other carbonyl compounds interfere severely.

The first work involving DMP and subsequent determination of the products by GC was demonstrated by Hager and Baker (14). Here, a packed column was employed and a thermal conductivity detector detected the amount of acetone generated. Methanesulfonic acid was used as the catalyst making this method impractical with modern fused silica capillary columns. Strong acids attack fused silica and cause the column to break. Although only one sample was used and almost no other information was provided, the authors claim the method is useful for water determinations from 0.03 to 5.0%. Martin and Knevel (15) examined the theoretical considerations as well as the actual analysis of samples. Again, packed columns, methanesulfonic acid, and a thermal conductivity detector were used in the determinations. A usable, practical analytical procedure was described and comparisons to the Karl Fischer titration were presented. Again, the water in only two samples, ethanol and dioxane, was determined.

Blanco et al. (16) used DMP for the determination of water in Nitroglycerin-Nitrocellulose pastes. Packed columns and a flame ionization detector were used with methanesulfonic acid as the catalyst. Samples containing 4 to 25% water were determined, but no detection

limits were given. This experimentation was not extended to other samples or samples containing smaller amounts of water.

The drawback to each of the methods using DMP and GC has been the use of methanesulfonic acid. This acid will destroy modern fused silica columns and contains a carcinogen that is added as a stabilizer. Nafion is solid acid resin that has the structure shown in Figure 1. This resin contains a sulfonic acid group adjacent to a carbon that contains two fluorine atoms. These electron-withdrawing atoms make this a very strong acid. It is classified as a "superacid" and is considered the polymer equivalent of triflic acid. Since this resin is a solid and does not dissolve in any solvents at standard pressures, it is ideal for use with DMP in the determination of water in organic compounds because it is easily separated prior to sample introduction into a gas chromatograph. Therefore, capillary columns can be used without difficulties.

The catalytic qualities and the use of Nafion in organic synthesis has been reviewed (17-19). Generally, Nafion has a perfluorinated backbone making it highly resistant to attack from strong oxidizing and reducing agents. Unlike Teflon, the polymer is permeable to many cations and polar compounds but impermeable to anions and non-polar species. Nafion can be purchased from Aldrich Chemical Company or C. G. Processing Company in a variety of particle sizes.

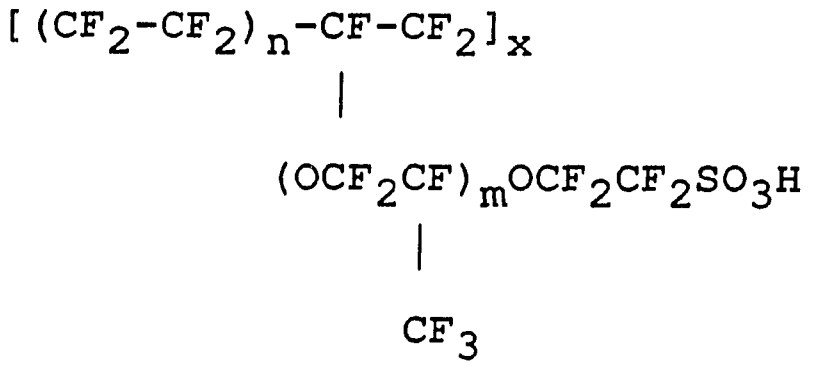


Figure 1. Structure of Nafion 1100 EW. For this resin, n = 5-13.5, m = 1, 2, 3, ..., and x = 1000

EXPERIMENTAL SECTION

Glassware and Apparatus

The reactions were carried out in 5-ml micro-reaction vessels with Teflon lined septa (Supelco, Glass Co., Bellefonte, PA). A shaker (Burrell Corp., Pittsburgh, PA) was used to agitate the reaction vessels and mix the reactants.

Reagents and Chemicals

The reactant, 2,2-dimethoxypropane, was purchased from either Eastman Kodak Chemical (Rochester, NY) or Aldrich Chemical (Milwaukee, WI). Nafion 1100 EW was obtained in the 60-100 mesh size from C. G. Processing Inc. (Rockland, NY). Amberlyst-15 resin was obtained from Rohm and Haas (Philadephia, PA). Both resins were dried under vacuum at 110^{o}C for three hours before use. Distilled water was further purified with the Barnstead Nanopure II water system before use. The reagents and solvents used were reagent grade or better. All reagents and chemicals were "blanked" before use.

Gas Chromatography

A Hewlett Packard 5790A gas chromatograph equipped with a flame ionization detector was used. Split injections were made using a split ratio of 80-100:1. The ratio was held constant during a series of experiments. The split injection liner was packed with a small amount of 80-100 mesh silanized glass beads to prevent the collection of non-

volatile compounds on the column. These beads were changed periodically and the injector was held at 150°C. Two different carrier gas flow rates were used in this work. Initially, a flow of 2.5 ml/min of zero grade He was used with an oven profile of 5.2 minutes at 40°C. Acetone elutes first followed by 3-methylpentane, the internal standard, with retention times of 3.6 and 5.2 minutes respectively. Later, it was found that a flow rate of 5.0 ml/min and an oven profile of 2.2 minutes at 40°C provided adequate resolution and decreased the analysis time. The retention times of acetone and 3-methylpentane with the faster flow rate are 1.8 and 2.6 minutes respectively. In both cases, the oven temperature was stepped to 220°C after the initial hold. This rapid temperature increase removes any later-eluting compounds that may interfere with the next run and takes only 5 minutes to complete. The flame ionization detector was held at 250°C.

The column was a 30 meter x 0.53 mm J+W DB-5 Megabore with a film thickness of 1.5 microns. The 0.53 mm columns have several advantages over the traditional capillary columns with smaller diameters of 0.20-0.32 mm. First, thicker stationary phases can be coated on wider bore columns. This allows for larger sample loading and longer retention of early eluting peaks without sacrificing resolution. Second, faster linear flow rates are possible permitting lower elution temperatures.

Reactant Solution

A reactant solution was prepared in a dry 100-ml volumetric flask using a 5-ml aliquot of DMP, the reactant, and a 1-ml aliquot of 3-methylpentane, the internal standard, and diluted using pure solvent.

The solution was stored in the flask which was fitted with a septum. This solution permitted a simple one-step addition of the chemicals needed for an analysis. Both dimethylformamide and ethyl acetate were used as the solvent without any complications.

Standardization

Internal standardization is used to quantify the amount of acetone generated in the reaction. This method allows for small differences in the volume injected. This is particularly useful with GC since the injection volume is typically 1 µl or less. First, the reactant solution is chromatographed to determine the amount of acetone intially present. Second, 10 µl of acetone was added and the solution was chromatographed again. By subtracting the initial acetone a response factor can be calculated. Since the oven temperature is the only parameter that is changed throughout a series of experiments , this factor varies only very slightly throughout the day. Therefore, this procedure only needs to be done periodically.

Procedure

At least 12 mg of Nafion resin was weighed into a microreaction vessel and then capped. Next, 1 ml of the reactant solution was added to the vessel via syringe. Transfers via syringe are easy and minimize the uptake of water from the atmosphere. The vessel was shaken for a specific length of time, usually 5 min, and then a 1-µl aliquot was injected into the GC. The area of the acetone peak (relative to the internal standard) represents the water blank of the system. Next, a

specific amount of liquid sample was introduced via syringe or solid was added to the reaction vessel. The mixture was shaken again for the specific length of time and a 1-µl aliquot is injected into the GC.

A ratio of the peak area of acetone to internal standard is calculated for both runs. The ratio of the blank is subtracted from the ratio of the sample to yield the relative response of acetone generated from the reaction of water in the sample. Using the response factor previously determined for acetone, a value for the absolute amount of acetone is found. The amount of acetone is used to determine the amount of water using the stoichiometry of the reaction and the molecular weights of acetone and water. The following equations show how this is done:

$$R_W = \frac{W_A \quad \text{Weight of acetone}}{W_{IS} \text{ Weight of Internal Standard}} \tag{5}$$

$$R_A = \frac{A_A \text{ Peak area of acetone}}{A_{IS} \text{ Peak area of internal standard}} \tag{6}$$

$$F = \frac{R_W}{R_A} \quad F \text{ is the response factor for acetone} \tag{7}$$

$$W_A = F \times W_{IS} \times R_A \tag{8}$$

$$W_W = \text{Weight of water} \tag{9}$$

$$W_W = W_A \times \frac{1 \text{ Mole of water}}{1 \text{ Mole of acetone}} \times \frac{\text{M.W. of water}}{\text{M.W. of acetone}} \tag{10}$$

RESULTS

Time of Reaction

It is important that the time for complete reaction to occur be as short as possible. Ideally, this time should be 10 minutes or less, so that many samples can be analyzed in a short period of time. To determine the time for the reaction to reach completeness an actual sample determination was carried out. The reaction vessel containing 1 ml of the reactant solution, 2 ml of sample (ethyl acetate) and 12 mg of Nafion was shaken and aliquots were taken at various time periods for gas chromatographic analysis. Figure 2 shows that the acetone peak reaches its maximum area after 5 minutes and remains constant for 45 minutes. It is apparent that the reaction is complete in a short period of time. For all proceeding experiments, 5 minutes was chosen as optimum time for the determination of water.

A similar experiment was performed using 12 mg of Amberlyst 15 cation-exchange resin in place of Nafion as the acid catalyst. The curve in Figure 3 shows that a reaction time of at least 25 minutes is required for acetone to reach its maximum area and form a plateau. In other words, Amberlyst 15 will catalyze the reaction but in a much longer period of time. This study shows that Nafion is a superior catalyst for this reaction.

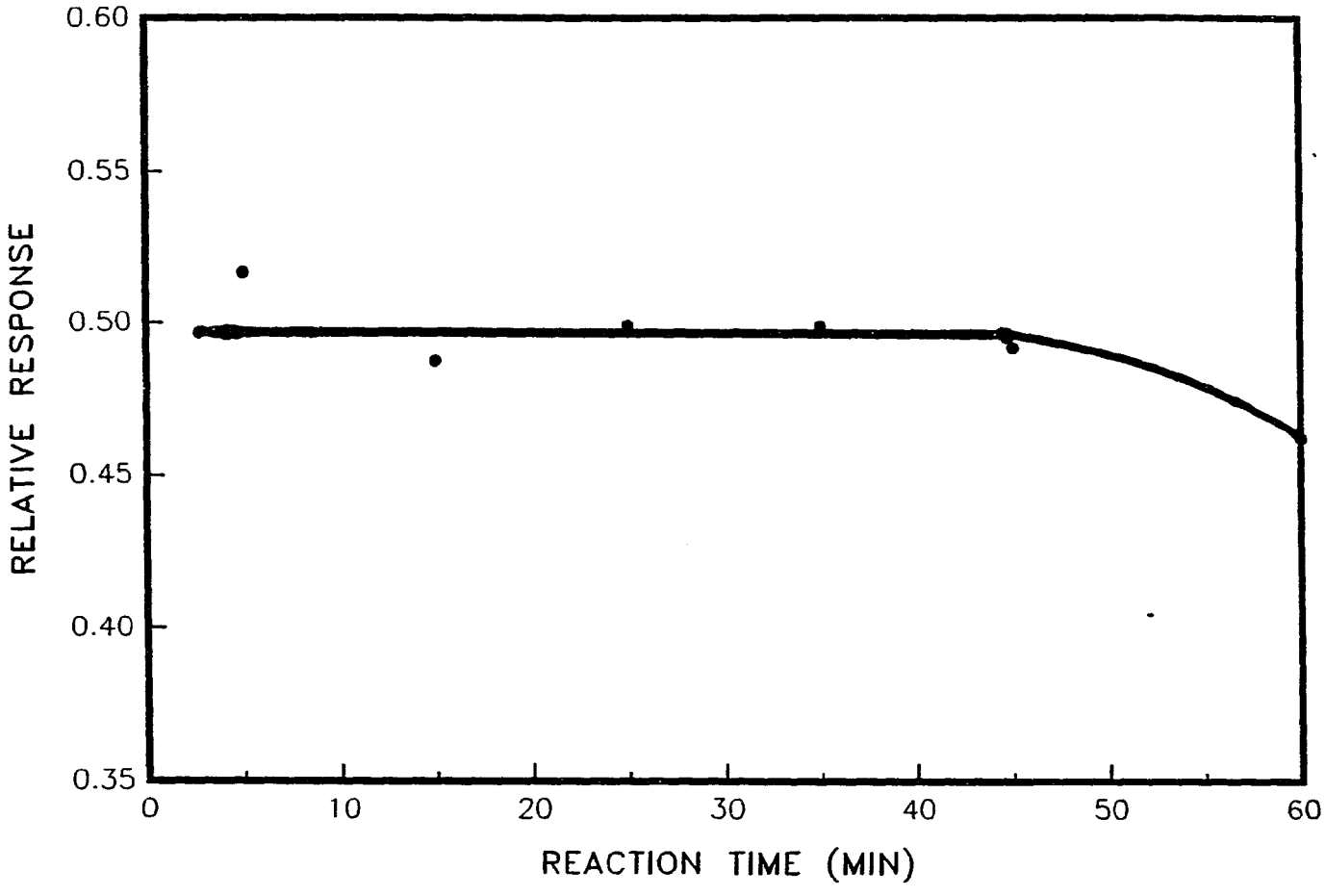


Figure 2. Plot of the relative response of acetone generated in the reaction vs. the time of reaction. 12 mg of Nafion was used to catalyze the reaction

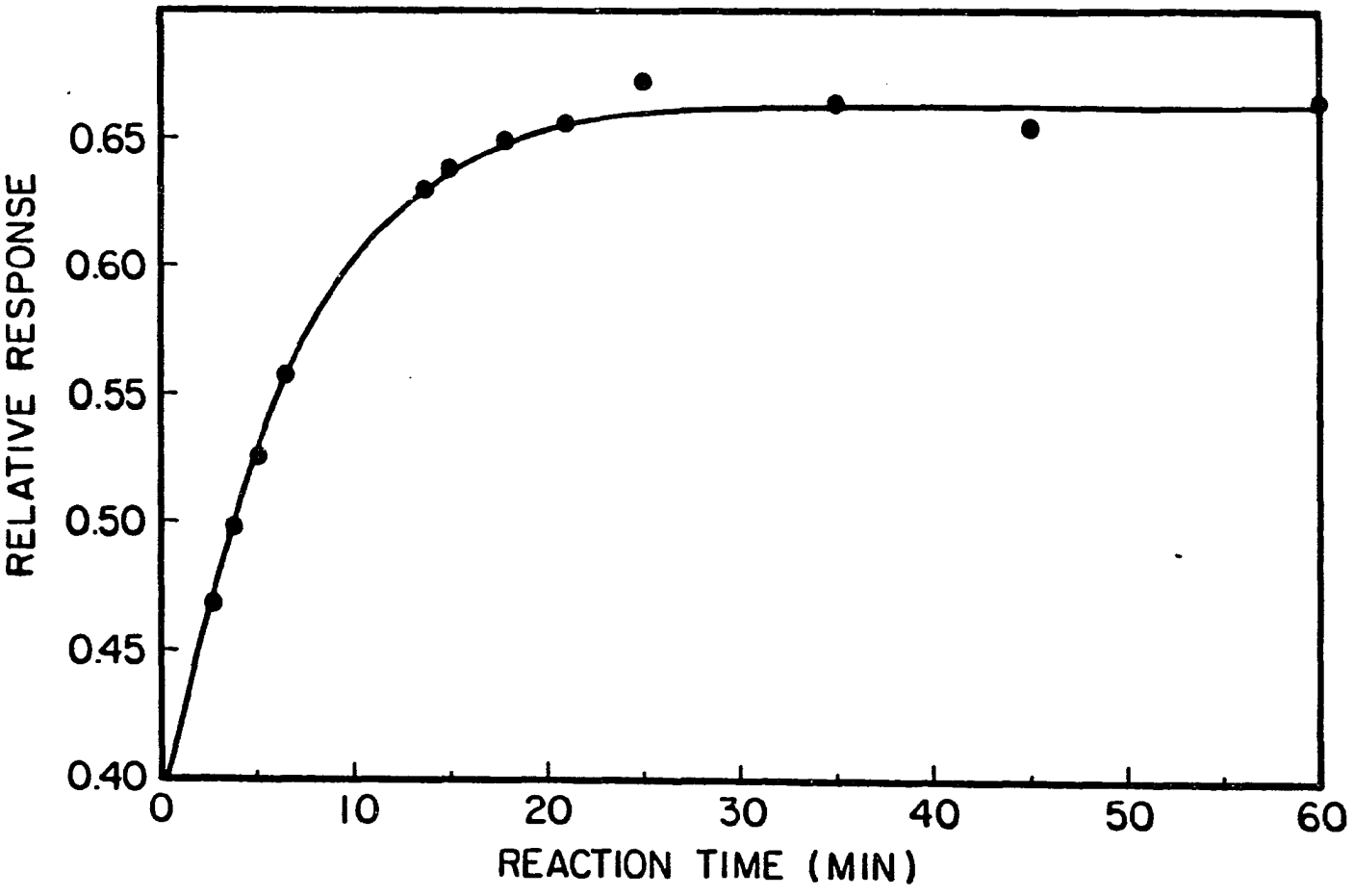


Figure 3. Plot of the relative response of acetone generated in the reaction vs. the time of reaction. 12 mg of Amberlyst-15 was used to catalyze the reaction

Amount of Catalyst

The same reaction conditions were carried out as above except the amount of Nafion was varied. It was determined that a minimum of 6 mg of Nafion resin was needed to attain the maximum area of the acetone peak in 5 minutes (Table I). The differences in the relative peak areas of acetone in Table I are due to the amount of water found in the resin. For all remaining determinations of water at least 10 mg of Nafion was added as the catalyst. This extra amount ensured reaction completeness with samples containing more water.

Calibration Curves

It is necessary to know the range over which water can be determined and whether the formation of acetone is linear over this range. Since a reaction is taking place, there is always the possibility of side reactions or the loss of acetone by evaporation or some other means. A non-linear response would indicate such behavior.

A 2-ml sample of dried ethyl acetate was added to the micro-reaction vessel which contained the 1-ml of reactant solution and 12 mg of Nafion resin. The amount of water was determined after 5 minutes of shaking as before. Then a small amount of water was added via a 0.5-µl syringe and the amount of water from this spike was determined chromatographically. This procedure was continued until there was no further increase in the amount of acetone generated from the reaction. The response is linear (Figure 4) up to about 0.275% water (v/v). At this point all of the DMP

Table I. Amount of Nafion required to catalyze the reaction. Nafion resin was added to a 2 ml sample of ethyl acetate. The mixture is shook for the designated time, sampled and analyzed by GC. The relative response of acetone was determined for each sampled time

	Relative response of acetone generated		
Amount of Nafion (mg)	Time of reaction (min.) 5	15	25
11.7	0.516	0.487	0.499
9.7	0.477	0.463	0.474
5.7	0.425	0.424	0.413
2.2	0.226	0.351	0.384

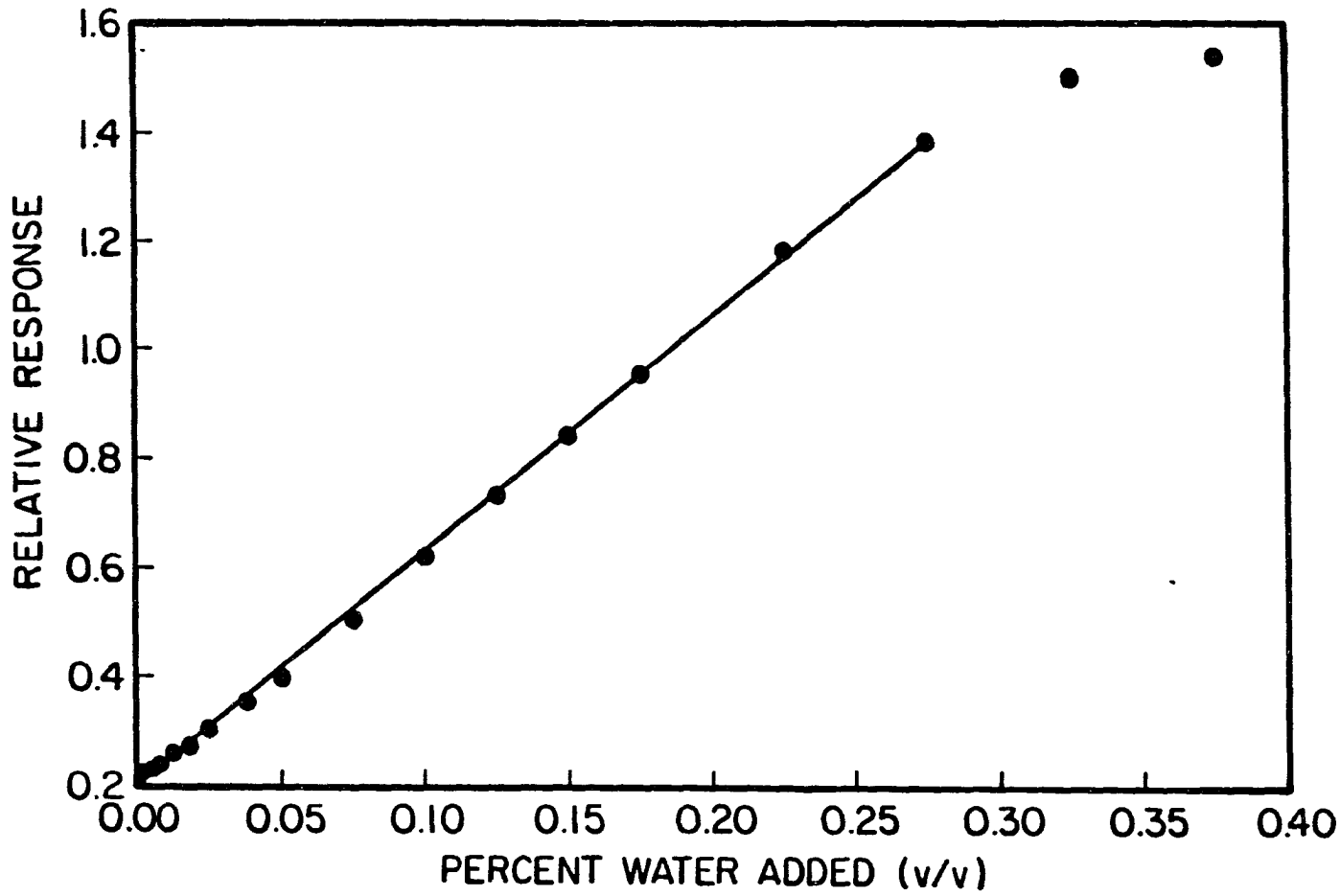


Figure 4. The relative response of acetone generated from the reaction when additional amounts of water are added to a 2 ml sample of ethyl acetate

is consumed and the formation of acetone ceases. This point agrees closely with the point that can be calculated from the amount of DMP initially added to the reactant solution. The correlation coefficient for the linear portion of the curve is 0.9995. Since this line represents a series of standard additions, the amount of water can be determined in the 2-ml sample using this plot. This is done by extrapolating the line to zero response and subtracting the intital blank. This value 0.047% (v/v) agrees closely with 0.045% found using the internal standardization method previously described.

A similar series of experiments was performed with samples containing higher percentages of water. This is done be reducing the size of the sample to be determined. In this case a 0.20-ml sample of ethyl acetate was used and the water additions were the same volume as before. Figure 5 shows a straight-line response up to 2.75% water (v/v) in the sample, as would be expected. The correlation coefficient for the line is 0.9991. Although the experiments were not performed, it seems possible to analyze samples with very large percentages of water, even up to 100% by just reducing the sample size. Also, another reactant solution can be made that contains a larger amount of the reactant.

Since the reaction of DMP also produces methanol, its peak area can also be used for calibration. The correlation coefficent for this line is 0.9963. Similarly, the decrease in the DMP peak was monitored with a correlation coefficient of 0.9973. These last two methods would be useful for samples which have components that co-elute with acetone.

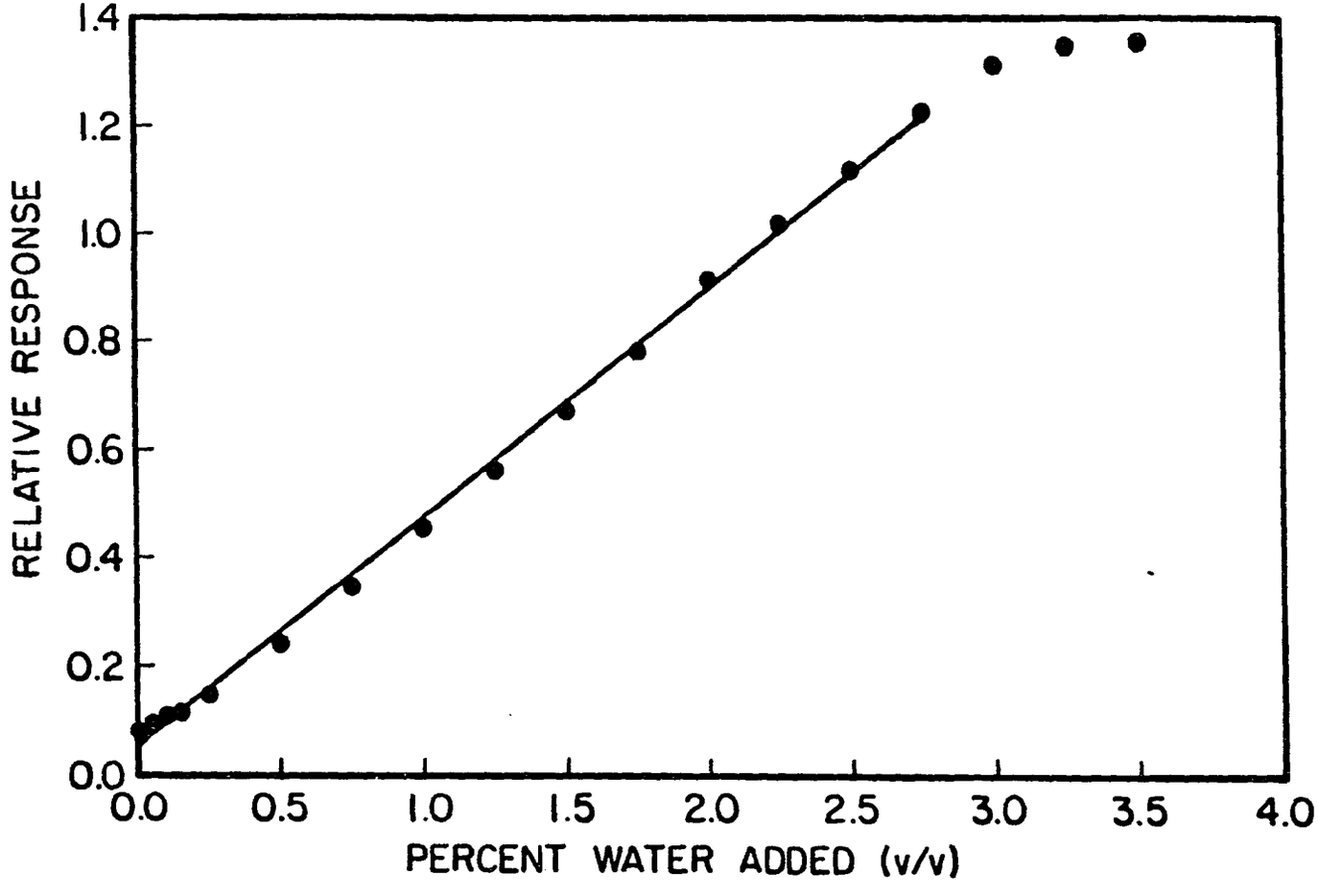


Figure 5. The relative response of acetone generated from the reaction when additional amounts of water are added to a 0.2 ml sample of ethyl acetate

Reproducibility

The reproducibility of this GC method was examined by independently determining the amount of water in six, 2-ml samples of tetrahydrofuran. The samples were taken from the same source and the water was determined in each by using the method previously described. Table II shows that the average amount of water found was 0.052% with a standard deviation of 0.0015%. This corresponds to a relative standard deviation of 2.8%. Similarly, six solutions were prepared to determine the deviation in the response factor of acetone. This relative standard deviation was 1.2%.

Limit of Detection

The limit of detection by the indirect GC procedure is apt to depend more on external forces than on the measurement method itself. Thus the detection limit depends mainly on: (a) the ability to dry the Nafion and keep it dry, the reactant solution, and the glassware and (b) on avoiding added water while transporting or weighing. It is this extra water that makes up the blank. There are larger variances associated with larger blanks which inevitably result in higher detection limits.

By careful handling and by drying the components of the reactant solution over calcium hydride and drying the Nafion at 110°C, samples containing as little as 0.001% water can be analyzed.

It should be noted that one of the aims of this work was to develop an easy to use method. A "dry" glove bag was not used because it is difficult to manipulate samples and make accurate measurements in one.

Table II. Determination of the water in six samples of tetrahydrofuran. The average amount of water is 0.052% (w/w) with a standard deviation of 0.0015%. The relative standard deviation is 2.8%

Run number	Percent water (w/w)
1	0.051
2	0.051
3	0.052
4	0.054
5	0.054
6	0.051

Comparison to a Karl Fischer Titration

The water in several organic liquids was determined both by the gas chromatographic method and the Karl Fischer titration (see Table III). The KF solution was standardized just before use and the titrations were performed in triplicate. The end point in the Karl Fischer titration wais often difficult to determine visually and in some cases precipitation occurred which made the end point even more difficult to locate. Despite these difficulties, good agreement was obtained between the percentages of water determined by the two methods.

Determination of Water in Various Samples

Several liquid and solid samples were analyzed for water by the GC method. Then a measured amount of additional water was added to each sample and the total amount of water present was determined again. The amount of water found in the sample, the amount of water added in the spike, and the amount of water determined from the spike are listed for each sample in Table IV. The excellent recoveries of added water demonstrates that the GC method gives dependably accurate results for a wide variety of samples and percentages of water.

Oxalic acid dihydrate is a solid which is not volatile in the gas chromatograph. The amount of water associated with the dihydrate as well as water sorbed onto the solid was determined without difficulties. A minimum of 28.6% (w/w) should be expected from the dihydrate. A 10-mg sample yielded 30.1% water (w/w).

Table III. Results of both the GC method and a Karl Fischer titration for the determination of the amount of water present in various organic liquids

	Percent water (w/w)	
Compound	GC method	KF titration
Ethyl Acetate	0.059	0.056
Tetrahydrofuran	0.036	0.036
Dimethylformamide	0.0075	0.0074
Methylene Chloride	0.012	0.014
Dioxane	0.489	0.479

Table IV. Determination of water in liquid and solid samples by the GC method. The water in the samples is first determined then a water spike is added and the amount of water from the spike is determined

Compound	Sample size	Percent water (w/w)	Water spikes (mg) added	Water spikes (mg) found
Liquid Samples				
Methylene Chloride	2.00 ml	0.012	0.50	0.51
Toluene	2.00 ml	0.019	0.50	0.49
Ethyl Acetate	2.00 ml	0.231	0.50	0.58
1,1,2-Trichloro-trifluoroethane	2.00 ml	0.003	0.50	0.48
"Dry" Ethyl Acetate	2.00 ml	0.006	0.50	0.43
Butanone	2.00 ml	0.408	0.50	0.58
Carbon Disulfide	2.00 ml	0.003	0.40	0.37
Anisole	2.00 ml	0.013	0.40	0.41
Tetrahydrofuran	2.00 ml	0.080	0.50	0.50
1-Propanol	0.05 ml	3.07	0.50	0.53
Solid Samples				
Oxalic Acid dihydrate	10.0 mg	30.1	0.40	0.39
Phenol	50.0 mg	0.70	0.40	0.39

Determination of Water in Ascorbic Acid

Samples containing even small amounts of ascorbic acid cannot be titrated by the Karl Fischer method. However, no difficulty is encountered using the indirect GC method. This was demonstrated in two ways. First, a 2-ml sample of dimethylformamide was analyzed for water by the GC method before and after the addition of 20.0 mg of ascorbic acid. Second, the amount of water in 20.0 mg of ascorbic acid was determined alone. In both cases, the amount of water in the ascorbic acid was 0.026% (w/w).

DISCUSSION

It might be questioned whether this method would be applicable to samples containing high-boiling or non-volatile components because of irreversible adsorption on the capillary chromatographic column. This would destroy the column in a short period of time. The experiments indicate that this was not a problem. The same column was used for all of the experiments and anaylsis. A smaller sample is injected onto capillary columns than if a packed column were used. Insertion of glass wool and silanized glass beads seems to adsorb the non-volatile sample components while allowing acetone and the internal standard to pass quantitatively onto the column. A rapid temperature rise at the end of the chromatographic run serves to remove any high-boiling compounds that might be retained by the column at 40°C.

The absolute amount of water that can be determined in the present procedure could obviously be increased by adding a larger amount of DMP to the sample. However, this would increase the blank and reduce the accuracy in samples containing a low percentage of water. If it were possible to completely dry the glassware, reactant solution, and the Nafion, samples with trace amounts of water could be analyzed. If splitless injection was employed, the limit of detection of the method under these idealized conditions would be 80-100 times lower. This is the amount thrown away when split injections were made.

Although 2,2-dimethoxypropane works well for this method, it seems feasible to use virtually any acetal, ketal, or orthoester. DMP was chosen because it is inexpensive, commercially available, and has a low boiling point compared to larger ketals.

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SECTION II. SIMPLE STEAM DISTILLATION FOR SAMPLE PREPARATION PRIOR TO GAS CHROMATOGRAPHIC DETERMINATION OF ORGANIC COMPOUNDS

INTRODUCTION

Sample preparation is often considered the weak link in a chemical analysis. Errors made at this time are carried through the rest of the analysis causing ambiguous results. This is especially true for the chromatographic determination of organic compounds in aqueous samples and other samples that contain appreciable amounts of non-volatile matter.

Solid phase resin extraction (SPE) uses a small amount of hydrophobic resin in a column to extract organic compounds from the aqueous matrix. The organics are then eluted from the column using a much smaller volume of an organic solvent. The resin is easily clogged by dirty aqueous samples and often filtration is needed prior to collection. Since many of the organic analytes are trapped in the solid material, filtration becomes a serious source of error. A complete discussion of SPE, including references can be found in SECTION III of this thesis.

Direct aqueous injection (1,2) is used in conjunction with capillary fused silica columns for gas chromatography. Here, the sample containing the organic analytes is directly injected into the GC with little or no prior sample clean-up. Sometimes filtration is required, again, causing possible sources of error. This method is limited to very clean samples. Since no concentration of the samples is performed, the analytes need to be at a level of concentration that can be quantified by the detector. Too often this is not the case.

Liquid-liquid extraction (LLE) (3-5) is a very old method for isolating organic compounds from water matrices. A non-polar organic liquid is placed in contact with the aqueous solution and mixed. The organic layer now containing the organic analytes is removed and analyzed. This can be repeated several times or in a continuous mode. Often, the extracted organics are concentrated by evaporation of the solvent. This is a problem when volatiles are present. Also, polar compounds, such as phenols, are not effectively extracted by nonpolar solvents. Many times with dirty samples, emulsions form with the solvent and it is difficult to separate the two layers. Since the solvent is evaporated, impurities are concentrated as well as the analytes.

Static head space analysis (6-9) makes use of the partitioning of the organic analytes between the water matrix and a gas held above the water. The gas is directly sampled via syringe and the amounts of the organics determined by gas chromatography. Since the amounts of the organics found in this gas are temperature dependent, strict control of the temperature is required. This method is limited to volatile compounds with boiling points below 200°C. The biggest problem with this method is standardization. Often matrix matching is needed to duplicate the sample matrix with a standard. This becomes almost impossible with messy samples such as sludge.

Dynamic head space analysis (10-18), better known as purge and trap, involves sparging of the aqueous sample with an inert gas. The gas containing the organic analytes is passed through a small resin column. The analytes are adsorbed by the hydrophobic resin while the purge gas

passes unretained. Most often, the organics are recovered by thermal desorption which causes chromatographic interferences due to artifact formation. The resin used, Tenax, has a very small surface area causing breakthrough problems. When smaller particles are used to yield more surface area, plugging of the column can occur. Habich and Grob developed a similar method (19) except the purge gas is recycled. Activated carbon is used instead of Tenax. This adsorbant is notorious for irreversible adsorption. An excellent two part review of both static and dynamic headspace is available (20,21).

Ogawa (22) developed a method which uses a heated purge and trap. Here, the aqueous matrix is heated to 80-100^{o}C and purged. The organics are collected on either Tenax or XAD-4 and removed with a small amount of organic solvent before gas chromatographic anaylsis. Recoveries were above 80% for many compounds, but much lower for polars. The major disadvantage to this method is large amounts of water vapor are produced. This resulted in a pressure build up in the system and explosions.

Simple steam distillation seems to be a worthy alternative for isolation of organic compounds from water or dirty samples prior to their separation by gas chromatography. Steam distillation has been known for a long time and a large number of papers dealing with the analytical aspects of steam distillation have been published. Many of these papers are referenced in a review article (23) and in a book (24). Unfortunately, almost none of the published papers offers a method for isolating volatile organic compounds that is simple, rapid, and achieves a significant concentration factor.

In order to achieve a better concentration factor, a liquid-liquid extraction can be performed with the distillate once it is collected. Several authors have used this off-line extraction of the condensate to study herbicide evaporation and behavior in soil (25-28). Iso-octane, petroleum ether, and hexane were used as the extracting solvent and distillation times were on the order of several hours. Kearney et al. (29) extracted 300 ml of distillate with methylene chloride to determine the amount of uptake of nitrosoamines in soybeans. The extracts were analyzed by a thermal energy analyzer. Fine et al. (30) studied the amount of nitrosamines in fish meal and bacon by a similar distillation liquid-liquid extraction procedure. Nash (31) distilled several pesticides from soil and plant tissue. About 400 ml of distillate was collected and then extracted with 10 ml of either carbon tetrachloride or 2,2,4-trimethylpentane. Although a distillation time of 2.25 hours was required, most recoveries were over 80%. Rennie (32) distilled river water to determine trace amounts of phenols. Here, 100 ml of distillate was extracted with 10 ml of hexane. The phenols were then brominated and determined as their brominated analogs using gas chromatography with electron capture detection. The level of recovery for this procedure was 90% .

Steam distillation with on-line liquid-liquid extraction methods has been worked out. In 1969, Nielson and Kryger presented an appartus for the continous extraction of the distillate based on a tube inside of a tube (33). The water is cycled back into the distillation flask and the extracting solvent can be removed by opening a stopcock. Many researchers have used this or a similar apparatus for pesticides in

fish, sediments, and water (34); chlorinated benzenes in bottom sediments (35); essential oils from water (36); phenols from soil and clay (37); 2,4-D butoxyethanol ether ester and degradation products from sediments (38); hydrocarbons from sediments (39) and; aromatic compounds from fish tissue and water (40). These procedures all require distillation times of 1-16 hours, making them impractical for routine analysis.

Donkin and Evans (41) used a simple Dean and Stark water estimator for the determination of petroleum hydrocarbons in water and mussels. Again, the condensate is extracted with a layer of organic solvent and returned to the boiling flask. A two-hour distillation time was used and recovery of compounds with boiling points up to 404°C was demonstrated. Bicchi et al. (42) used a modified system for the analysis of essential oils in two hours. Here, only 100-200 µl of pentane of hexane was used as the extracting solvent.

Excellent analytical procedures have been worked out using the Nickerson and Likens apparatus (43) or its modifications. This apparatus uses freshly distilled solvent to extract the condensate in a center area. Because of the difference in geometry of two side arms, the lighter or heavier organic solvent travels back one way and the water goes the other. Both are distilled again, continuously, and meet in the middle for extraction once more. This is continued until all or most of the extraction is complete. Maarse and Kepner (44) used this to isolate terpenes from fir needles. Yasuhara et al. (45) studied organic substances in highly polluted water using this apparatus and then injecting a portion of the extract into a gas chromatograph using mass

spectrometric detection. Lam et al. (46) studied the removal of compounds from hop essential oil. Jennings and Filsoof (47) compared this sample preparation techique with others.

In 1981, Godefroot et al. introduced a micro version of the Nickerson and Likens apparatus and used it to isolate essential oils from water, hops, pepper and flowers (48). Nunez and Bemelmans (49) used the system to isolate essential oils from water. Recoveries of 25-125% were obtained. Godefroot et al. (50) recovered pesticides and polychlorinated biphenyls from water using pentane as the extracting solvent. Janda et al. (51) isolated fatty acids from water and sludge in 60 minutes. Rijks et al. (52) and Janda and Dolezal (53) studied the theoretical aspects of this method to determine its possibilities and limitations. It was found that the limiting factor for polar and high boiling compounds was the distillation step. Therefore, Curvers et al. (54) eliminated the sample boiling step and just extracted with freshly distilled solvent. Distillations have typically taken 1-2 hours. When shorter times are used, recoveries of most phenols and high boiling compounds are low.

The aim of this work was to develop a method for the isolation of organic compounds from water using distillation that was fast (under 25 minutes), effective for polar compounds like phenol, and achieved an appreciable concentration factor. It is also desirable to have a very easy to use system that requires little or no manipulation. The modelling system is purified water that is spiked with synthetic solutions containing various compounds of interest. In this way, the

system can be evaluated and optimized for its eventual use for dirty samples that contain large amounts of non-volatile components.

EXPERIMENTAL SECTION

Glassware and Apparatus

Figure 1 illustrates the glassware used for all of the distillations. The condenser was made by the Iowa State University Chemistry Department glassblowing shop. Either 5-ml volumetric flasks or 15-ml graduated gravimetric tubes were used to collect the distillate.

Reagents and Chemicals

Distilled water was further purified with the Barnstead Nanopure II water purification system before use. All chemicals used were reagent grade or better. Solvents, including the purified water were "blanked" before use. Carborundum (GFS, Columbus, OH) boiling chips or small broken pieces of a glass frit were used to aid the boiling.

Gas Chromatography

A Hewlett-Packard 5790A gas chromatograph was used in the splitless mode. Flame ionization detection was used at 250°C. The oven temperature profile for the survey mixture and phenol mixture was 1 minute at 79°C, then 5°C/min to 210°C. For the volatile mixture, the profile was 5 minutes at 30°C, then 5°C/min to 125°C. The injector was held at 225°C except for analysis of the volatile mixture where 200°C was used. The carrier gas was zero-grade helium at 2.5 ml/min, measured at 90°C with a solution of methane in pentane. The column used was a 30 m x 0.53 mm J&W DB-5 megabore with a film thickness of 1.5 μm.

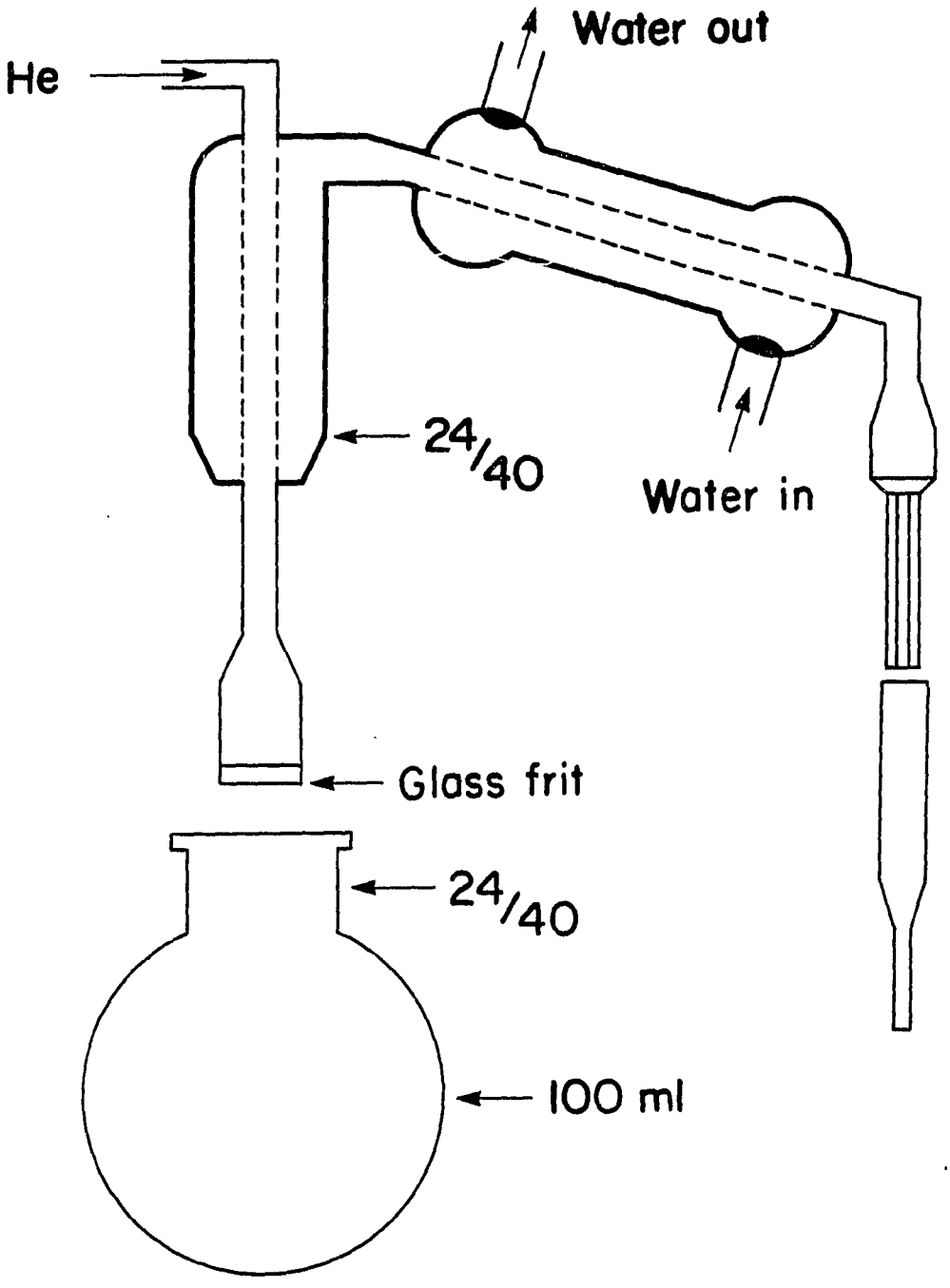

Figure 1. Illustration of the boiling apparatus for all experiments. In some cases, the tip adapter is placed on the end of the condenser

Stock Solutions of Synthetic Mixtures

For the investigations of the distillation, the following solutions were prepared:

(a) "Survey mixture": a mixture of ten compounds with various functionalities and boiling points ranging from 136 to 222°C. These were dissolved in acetone at about 100 mg/100 ml.

(b) "Survey mixture" internal standard: about 100 mg of 2-methyl-3-octanone was dissolved in 100 ml of acetone.

(c) "Phenol mixture": this mixture consisted of eight phenolic compounds ranging in boiling points between 176 and 238°C. About 100 mg of each phenol was dissolved in 100 ml of methanol.

(d) "Phenol mixture" internal standard: about 100 mg of p-ethylphenol were dissolved in 100 ml of methanol.

(e) "Volatile mixture": five volatile compounds with boiling points ranging from 78 to 145°C were mixed in acetone at 250 mg/50 ml. This solution was diluted 10-fold in acetone to make a solution at 25 mg/ 50 ml.

(f) "Volatile mixture" internal standard: 250 mg of methyl isobutyl ketone was dissolved in 50 ml of acetone and diluted in acetone 10-fold as above.

Every component of each solution was individually chromatographed to insure no overlap of peaks existed between different components. Each solution was shaken to make homogeneous mixtures.

Spiking Procedure

Approximately 50 ml of the purified water was added to the 100 ml round bottom boiling flask. To this either 50 or 100 µl of the appropriate test mixture was added via a disposable micro-pipet to make a 1 ppm solution. In some studies, a salt or an organic solvent was added to the boiling flask and the contents of the flask mixed.

Distillation Procedure

The above solution was boiled and the distillate collected in either a 5-ml volumetric flask or a 15-ml gravimetric tube. Afterwards, the glassware was cleaned by washing with acetone followed by water to remove any residual organics. The collection vessel was cooled in a water ice bath while it was being filled with distillate. In some cases, acetone was added to the vessel before boiling. The vessel containing the acetone was then cooled in an ice bath.

Standardization

After the distillation, a known volume of internal standard was added to the collection vessel and the vessel mixed. Immediately following, a portion of this solution was chromatographed. The peak areas of the components were compared to those of the internal standard and a ratio was calculated. A reference solution was made up in a similar fashion using the same type of collection vessel and the same amount of test mixture that went through the distillation. Again, the internal standard was added and a ratio of the peak areas was computed for each component. The recovery percentages were obtained by

comparison of the ratios of the two solutions. Whenever a co-distiller was added to the distillation flask and collected in the distillate, a similar amount was added to the reference solution. In this way, the reference solution mocks the actual distillate. It should be noted that this type of standardization takes into account errors associated with the entire procedure. Therefore, deviations truly reflect the whole method and does not overlook those errors made in the reference standard as is often the case. The relative standard deviation is typically less than 6% for triplicate runs.

RESULTS

Survey Mixture

Simple boiling

The survey mixture of ten organic compounds with various functional groups was added to 50 ml of water and the solution was boiled. After the collection of 5.0 ml of distillate, the internal standard was added and a portion was injected into a capillary column gas chromatograph. The peak areas of the compounds were compared to the peak area of the internal standard, as described in the experimental section. The results in Table I show good recoveries (>90%) for several of the compounds but low recoveries of the alkylbenzenes and halogenated benzenes. There are two reasons why the recoveries are low for these two types of compounds. First, the compounds may not be boiled out of the boiling flask. Second, the compounds are not being condensed.

Gas purging and salt addition

In other methods, such as purge-and-trap, purging of the water solution is effective for the removal of organics. The effect of a purge in distillation was investigated by flowing 20 ml/min of helium through the distillation apparatus before and during boiling. Column 2 of Table II shows a dramatic drop in the recovery of several compounds. This suggests that the low recoveries may be a problem of condensation.

The effect of adding a large amount of a salt to the aqueous sample was investigated by placing 7.1 grams of sodium sulfate in the flask before boiling. Recoveries shown in column 3 of Table II show an

Table I. Recovery of the survey mixture by simple boiling and collection of 5.0 ml of distillate. Boiling points are listed for reference

Component	Boiling Point (°C)	Percent Recovery
Ethylbenzene	136	30.8
Anisole	155	84.4
Cumene	153	27.6
Bromobenzene	156	53.2
Benzaldehyde	178	91.8
2-Ethyl-1-hexanol	184	97.1
o-Dichlorobenzene	175	59.2
Acetophenone	202	90.3
Menthol	217	97.7
Butyrophenone	222	94.3

Table II. Recovery of the survey mixture by gas purging with He at 20 ml/min and by the addition of 7.1 grams of sodium sulfate

Component	Percent Recoveries	
	Gas purge 20 ml/min He	7.1 grams of Na_2SO_4
Ethylbenzene	<5	19.1
Anisole	28.8	73.9
Cumene	<5	13.9
Bromobenzene	<5	37.7
Benzaldehyde	64.4	102.2
2-Ethyl-1-hexanol	99.0	96.1
o-Dichlorobenzene	<5	44.5
Acetophenone	95.5	102.5
Menthol	97.0	98.4
Butyrophenone	99.9	100.3

increase of recovery for some compounds, such as acetophenone, but low recoveries for the alkylbenzenes and halogenated benzenes. In some instances, even lower recoveries were obtained when sodium sulfate was added to the sample.

Addition of a co-distiller

A small amount of an organic solvent was added to the aqueous sample just before distillation with the aim of extracting the organic compounds out of water so that they would be distilled more readily in the organic vapor. The organic solvents benzene, toluene, and a combination of benzene and butanone were examined as co-distillers with the results listed in Table III. The recovery of most compounds of the survey solution is much better, which suggests that the co-distiller aids the distillation of the compounds from water.

The action of the co-distiller was further investigated by boiling the survey mixture for several minutes, then adding 3 ml of benzene and continuing the distillation. However, in no case were any of the survey compounds found in the fraction that was collected after the benzene was added. It was concluded from this that the benzene aids in the condensation of the survey compounds rather than promoting more complete distillation.

Another advantage of adding a co-distiller such as benzene is that the distilled compounds are effectively extracted by the benzene in the distillate. Therefore, the benzene layer of the distillate can be used for subsequent gas chromatographic analysis.

Table III. Recovery of the survey mixture by adding co-distillers to the boiling flask before distillation

Component	Percent Recoveries			
	3 ml Benzene	2 ml Benzene	3 ml Toluene	1.5 ml Butanone 1.5 ml Benzene
Ethylbenzene	98.7	93.7	-----	75.1
Anisole	87.7	92.9	80.1	91.6
Cumene	94.4	96.8	93.7	76.8
Bromobenzene	89.1	87.5	80.4	77.7
Benzaldehyde	89.1	91.2	73.4	100.1
2-Ethyl-1-hexanol	87.0	88.8	83.6	95.0
o-Dichlorobenzene	91.7	88.8	92.3	90.6
Acetophenone	75.9	81.4	61.5	82.1
Menthol	89.7	86.1	95.0	98.9
Butyrophenone	92.9	86.0	89.2	103.4

Other experiments were conducted using both benzene as a co-distiller and sodium sulfate added to the flask before distillation. The recovery of all compounds, except acetophenone, was no better than when benzene was added alone.

Collection in cold acetone

It appeared that all compounds in the survey mixture were being distilled but some were not being effectively condensed. Therefore, the tapered adapter in Figure 1 was placed on the end of the condenser. The adapter tip was placed into 1 ml of cold acetone in the receiver. This forces any non-condensed material to be bubbled through the acetone and be trapped. Acetone is miscible with water and does not interfere with gas chromatographic separation of the sample compounds. Table IV shows that most compounds were recovered near 100% with this simple modification. This further proves the point that condensation was previously the problem, not distillation.

Fast Boil

Up until this time, all experiments were carried out with a moderate amount of heat applied from a heating mantle to the boiling flask. The boiling time required to collect 5 ml of distillate is 20-22 minutes. This time can be reduced by applying more heat to the flask, adding boiling chips with a larger surface area, and insulating the top of the boiling flask. The distillate was collected in cold acetone. As can be seen in Table V, excellent recoveries are obtained and the time to collect 5.0 ml of distillate is now only 12 minutes.

Table IV. Recovery of the survey mixture by using the tip adapter and collecting in cold acetone

Component	Percent Recovery
Ethylbenzene	99.5
Anisole	99.2
Cumene	99.5
Bromobenzene	96.8
Benzaldehyde	99.5
2-Ethyl-1-hexanol	100.0
o-Dichlorobenzene	97.1
Acetophenone	90.3
Menthol	102.8
Butyrophenone	101.5

Table V. Recovery of the survey mixture using a fast boil, description of which is in text

Component	Percent Recovery
Ethylbenzene	93.7
Anisole	99.6
Cumene	91.8
Bromobenzene	95.2
Benzaldehyde	96.6
2-Ethyl-1-hexanol	101.4
o-Dichlorobenzene	94.6
Acetophenone	92.2
Menthol	100.8
Butyrophenone	98.7

There is a trade-off that is evident from this experiment. If the boiling time is reduced then a small amount of the alkylbenzenes and halogenated benzenes are not recovered. This is because when faster boiling conditions are applied there is an increase in the amount of vapor that is boiled over initially. Not all of this vapor is being trapped by the cold acetone, so the recoveries are slightly lower.

Recovery in increments of the distillate

It appears that acetophenone distills more slowly and is only about 90% recovered in the first 5 ml of distillate. An experiment was conducted where several collection receivers containing 1 ml of cold acetone were used to collect various fractions of the distillate as a distillation was performed. The increments collected were 0.5 ml each until 3 ml total was boiled over. Table VI shows recovery of most of the survey compounds is complete in the first 1.0-1.5 ml of distillate. However, acetophone requires a much larger distillate volume for complete recovery. An earlier experiment using sodium sulfate achieved a recovery near 100% for acetophenone.

Phenol Mixture

Simple Boiling

Because of their hydrophilic nature and their ability to form hydrogen bonds, many phenols are difficult to isolate from aqueous samples. One common method for the determination of phenols requires the distillation of 500 ml of water without any concentration (55-57).

Table VI. Relative recoveries of the survey mixture in 0.5 ml increments of the distillate

Component	Percent Recoveries						
	0.0-0.5 ml	0.5-1.0 ml	1.0-1.5 ml	1.5-2.0 ml	2.0-2.5 ml	2.5-3.0 ml	Total
Ethylbenzene	96.7	1.7	1.6	0	0	0	100
Anisole	97.1	2.9	0	0	0	0	100
Cumene	96.6	2.2	1.2	0	0	0	100
Bromobenzene	100.0	0	0	0	0	0	100
Benzaldehyde	85.5	9.7	4.8	0	0	0	100
2-Ethyl-1-hexanol	97.0	3.0	0	0	0	0	100
o-Dichlorobenzene	100.0	0	0	0	0	0	100
Acetophenone	64.5	14.7	7.0	5.2	5.2	3.4	100
Menthol	97.9	2.1	0	0	0	0	100
Butyrophenone	90.8	7.0	2.2	0	0	0	100

The standard mixture containing several phenols was added to 50 ml of water so that the concentration of each phenol was 1.0 ppm. As before, 5.0 ml of distillate was collected and a portion analyzed by gas chromatography. The recoveries of most phenols were quite low, as shown in Table VII.

Effect of adding a co-distiller

As with the survey mixture, the effect of a co-distiller was investigated by adding 3 ml of benzene to the distillation flask before boiling. The recoveries (column 2, Table VIII) are even lower than before. Obviously, the difficulty is in the boiling of phenols and not in the condensation. The lower recoveries are attributed to the fact that only 2.0 ml of aqueous distillate was collected, the other 3.0 ml being benzene. The phenols seem to distill slowly and their recoveries depend on the volume of water that is distilled.

Effect of a higher boiling temperature

An experiment was carried out where 10 ml of ethylene glycol was added to the boiling flask, before boiling, to increase the boiling temperature of the aqueous solution. Again, recoveries of the phenols were significantly lower than by simple steam distillation as can be seen in column 3 of Table VIII.

Effects of adding sodium sulfate

Table IX shows the recoveries of phenols when anhydrous sodium sulfate was added to the boiling flask before distillation. As the

Table VII. Recovery of the phenol mixture by simple boiling and collection of 5.0 ml of distillate. Boiling points are listed for reference

Component	Boiling Point (°C)	Percent Recovery
Phenol	182	24.2
o-Chlorophenol	176	80.2
p-Cresol	202	28.1
2,4-Dichlorophenol	210	85.4
p-Chlorophenol	220	19.8
p-Isopropylphenol	212	63.8
p-tert-Butylphenol	238	74.7

Table VIII. Recovery of the phenol mixture by adding a co-distiller and by adding ethylene glycol

Component	Percent Recoveries	
	3 ml Benzene added	10 ml of Ethylene Glycol added
Phenol	8.9	14.3
o-Chlorophenol	63.2	71.6
p-Cresol	14.2	19.8
2,4-Dichlorophenol	61.0	57.7
p-Chlorophenol	<5	<5
p-Isopropylphenol	33.2	28.7
p-tert-Butylphenol	38.5	36.8

Table IX. Recovery of the phenol mixture with increasing amounts of anhydrous sodium sulfate (Na_2SO_4) added to the boiling flask before distillation

Component	Percent Recoveries		
	7.1 grams Na_2SO_4 (1M)	14.2 grams Na_2SO_4 (2M)	21.3 grams Na_2SO_4 (Sat'd)
Phenol	37.9	68.6	88.3
o-Chlorophenol	79.7	101.1	101.1
p-Cresol	56.7	91.5	97.7
2,4-Dichlorophenol	87.2	92.0	92.3
p-Chlorophenol	31.4	50.0	65.4
p-Isopropylphenol	82.0	98.7	105.4
p-tert-Butylphenol	85.3	----	96.6

amount of sodium sulfate increased, the recoveries also increased. These results are compared to those with simple boiling in Table X. There is a drastic increase for 4 of the phenols which is vividly illustrated in Figure 2. It appears that addition of a salt reduces the affinity of the phenols for the aqueous liquid phase and makes them easier to distill. This is because the water is "tied up" in the solvation of the ionic salt. Since ionic interactions are stronger than the hydrogen bonding interactions between water and phenol, the phenols are freed to distill.

Addition of other salts

Several other salts were tried in a similar series of experiments. Here, enough of the salt was added to form a saturated solution. Table XI shows that both sodium chloride and magnesium sulfate work quite well, as does a saturated amount of sodium sulfate. The distillation of phenols is strongly inhibited by the addition of 49.1 grams of aluminum sulfate. Recoveries were <5% in every case. It is believed that the aluminum forms a salt with phenol which shifts the equilbrium away from molecular phenols.

The best results for the recovery of the phenols were obtained with the addition of magnesium sulfate. It has a highly negative enthalpy of solution and therefore heats the water as it dissolves. This reduced the time for distillation by approximately 5 minutes.

Table X. A comparison of the recovery of the phenol mixture with a simple boil and when a saturated amount of sodium sulfate is added to the flask before distillation

Component	Percent Recoveries: 21.3 grams Na_2SO_4 (Sat'd)	Percent Recoveries: Simple Boiling	Increase (Δ%)
Phenol	88.3	24.2	+64.1
o-Chlorophenol	101.1	80.2	+20.9
p-Cresol	97.7	28.1	+69.9
2,4-Dichlorophenol	92.3	85.4	+ 6.9
p-Chlorophenol	65.4	19.8	+45.6
p-Isopropylphenol	105.4	63.8	+41.6
p-tert-Butylphenol	96.6	74.7	+21.9

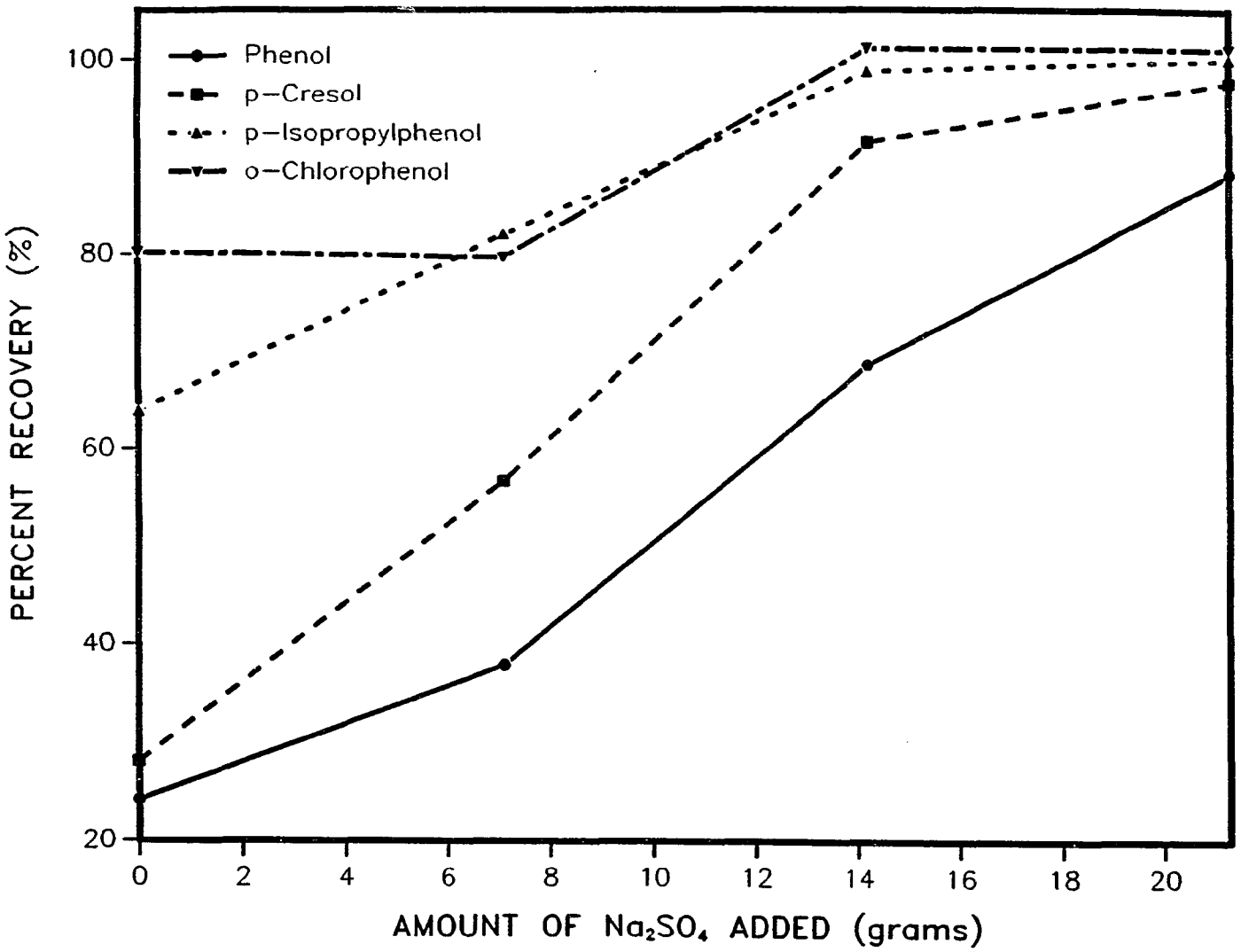

Figure 2. Recovery of 4 phenols when various amounts of Na_2SO_4 are added to the boiling flask before boiling

Table XI. The recovery of the phenol mixture when saturated amounts of various salts are are added to the boiling flask before distillation

Component	Percent Recoveries		
	19.5 grams NaCl (Sat'd)	36.9 grams $MgSO_4$ (Sat'd)	49.1 grams $Al_2(SO_4)_3$ (Sat'd)
Phenol	87.3	95.5	<5
o-Chlorophenol	100.8	95.6	<5
p-Cresol	97.0	91.2	<5
2,4-Dichlorophenol	101.0	96.0	<5
p-Chlorophenol	74.1	88.5	<5
p-Isopropylphenol	101.3	97.1	<5
p-tert-Butylphenol	99.8	95.7	<5

Volatile Mixture

A limited number of volatile polar organic compounds (VPO) have been determined in water and hospital waste water using steam distillation (58-60). Although such compounds are often quite volatile, their polar nature normally makes isolation difficult from aqueous samples.

A test mixture of several volatile polar organic compounds was added to water at the 1 ppm level. The solution was distilled and 5.0 ml of distillate collected in cold acetone. Recoveries in Table XII are all above 90%. Even butanone, 1-propanol and ethyl acetate are well recovered even though their boiling points are well below that of water. The volume of 5.0 ml of distillate collected is a conservative amount. As with the survey mixture, it is likely that these compounds can be collected in a smaller volume of distillate.

Table XII. Recovery of the volatile mixture by simple boiling and collection of 5.0 ml of distillate in cold acetone. Boiling points are listed for reference

Component	Boiling Point (°C)	Percent Recovery
1-Propanol	98	92.4
Butanone	80	99.6
Ethyl Acetate	77	100.0
1-Butanol	118	93.7
4-Heptanone	145	99.9

DISCUSSION

To this point, nothing has been mentioned about the reasons why compounds boil out of water. There has been a lot of material written about distillation from all aspects of science and engineering. It as outside the scope of this work to try to explain this very difficult topic from an empirical perspective. This would involve interpetation of three dimensional phase diagrams and a very high level of mathematics. Such a discussion could easily require several hundreds of pages and can be found in chemical engineering books dealing with this topic. Rather, a short, non-empirical discussion will be presented that includes general trends.

Organic compounds in water form two types of solutions. First, an ideal solution is considered. An ideal solution is one where the interactions of the solute with itself are similar to those interactions of water and itself. This is characterized by a large degree of hydrogen bonding or even partial ionization of the organic compound. Acetic acid, certain phenols, and glycol are examples of such compounds. When this is the case, distillation of the organic solutes occurs as the product of their vapor pressures and their mole fractions in the water. This product, termed the partial vapor pressure, is added to that of water's. Since the partial vapor pressure of the compound is likely to be very low compared to water's, distillation proceeds very slowly.

The second type of solution formed is a non-ideal solution. Here there are large differences in the interactions of solute and solute molecules. Hexane in water is an example of such a solution. Distillation depends only on the partial pressure of the solute and is

independent of its mole fraction. Therefore, even a solute present at a very low concentration contributes equally to the overall vapor pressure of the solution as does water. The result is that compounds with very high boiling points compared to water are boiled at a moderate rate.

When the boiling point of an organic compound forming a non-ideal solution with water is not too high, a negative azeotrope can form. An azeotrope is characterized by a constant vapor composition that is formed below the boiling points of either the organic compound or water. Therefore, the organic boils at a temperature well below its boiling point and is very efficiently removed from the water. Compounds with boiling points above 300°C rarely form azeotropes, yet still form non-ideal solutions. An example of this behavior is oil in water.

Certain phenols and water form solutions that are in between ideal and non-ideal. An azeotope forms, but its boiling point is just below that of water's. At this temperature large amounts of additional water vapor are generated because water is in a large excess. The result is that the phenols boil slowly with time and are not effeciently removed from water unless an inorganic salt is added. Many compounds form azeotropes with water. If two compounds that form azeotropes with water have almost the same boiling points but different polarities, the less polar compound boils at a lower temperature. For example, methyl lactate (b.p. 144.8°C) forms an azeotrope that boils at 99°C while 4-heptanone (b.p. 149.0°C) boils at 95°C in water.

To demonstrate the importance of azeotrope formation in the distillation of organic compounds from water, the survey solution was added to an organic solvent this new mixture was distilled. Since the

organic solvents chosen, acetonitrile and 1-propanol, have interactions similar to those of the survey compounds, azeotrope formation is unlikely and recoveries should reflect a simple partial vapor pressure relationship. In fact, 1-propanol was selected because its boiling point is very close to that of water and the partial pressure relationships should be similar to water. The recoveries of the test compounds were all below 5% except for ethylbenzene (20.5%) and anisole (6.8%) from 1-propanol.

These recoveries are low because an ideal solution is formed in the organic solvent.

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SECTION III. STEAM DISTILLATION WITH RESIN EXTRACTION FOR ISOLATION AND CONCENTRATION OF ORGANIC COMPOUNDS FROM AQUEOUS SAMPLES

INTRODUCTION

Steam distillation as a method of sample preparation is described in SECTION II of this thesis. A method was presented to isolate organic compounds by steam distillation that was effective for a wide variety of organic compounds with different boiling points. This method was effective at a concentration of a part-per-million when 5 ml of distillate was collected and a portion was injected into a gas chromatograph with flame ionization detection. It was shown that most compounds distill in less than 5 ml and a concentration factor of 10 was realized. Although collecting a smaller volume of distillate would yield a greater concentration factor, some coumpounds, e.g., acetophenone need more time to boil over so 5 ml was always collected. The detection limit is about 300 ppb for this method and is limited by the sensitivity of the FID.

Many times the organic compounds of interest are not present at the ppm or 300 ppb level so that additional concentrating is needed. Several papers were referenced in SECTION II that used liquid extraction to concentrate the organics after distillation. In many cases, the volume of the extract is reduced by evaporation to further concentrate analytes. The same problems remain with liquid-liquid extraction in these systems. The nonpolar extracting solvents fail to extract polar compounds. When evaporation is used to reduce the volume, impurities in the solvent are concentrated and analytes are vaporized by their partial pressures.

Solid phase resin extraction (SPE) is a method that has been gaining more and more attention as a method of concentrating organic compounds from water. Here, a large volume of water containing organic impurities (up to a liter or more) is passed through a small amount (typically 100 mg or less) of small, hydrophobic resin particles in a column. The impurities stick to the resin as the water is passed. Once the extraction is complete, the compounds are recovered by passing a small amount of organic solvent through the resin column and collecting the effluent. Since a much smaller volume of organic solvent is used compared to the volume of water, the impurities are concentrated.

SPE is limited by particulate matter in the sample. Solids and semi-solids can plug resin columns rendering them useless for dirty samples. Many times filtration can be used to clean up samples. This leads to errors because analytes can be adsorbed on the particulate matter. Also, samples that contain a large amount of solids, e.g., sludge, are very difficult to filter, especially by membranes.

Combining distillation with SPE seems to be a natural fit. Distillation provides an excellent means for isolating organic compounds from water or complex matrices with moderate concentration factors. SPE provides large concentration factors for samples that are clean. Combining both methods would yield a process that is good for both isolating and concentrating organics. Since distillation has been previously discussed, the remainder of this INTRODUCTION will be concerned with solid phase extraction.

Many different types of materials have been used for SPE of which the Rohm and Haas Amberlite XAD series and silica based resins will be

discussed. A 40-page review describing many of these materials, including XAD resins, is available (1). Of the XAD resin, XAD-2 and XAD-4 have been most widely used. Two articles review the uses and applications of these resins (2,3). XAD-2 and XAD-4 are copolymers of polystyrene and divinylbenzene and have the structure shown in Figure 1. Their properties and uses have been described in great depth (4). Generally, these resins are porous and have large surface areas. Because of their hydrophobic nature and large surface areas, XAD resins are ideal for adsorption of organic compounds from aqueous media.

Burnham et al. (5) used XAD-2 in 1972 for the isolation and estimation of neutral contaminants in potable water with subsequent analysis by gas chromatography-mass spectrometry. More compounds were identified in the same manner a year later (6) from several sources of water. Richard and Fritz (7) compared XAD-2 extraction to the more common ether extraction for chlorinated pesticides. Their results show that XAD-2 was superior and could be used for river water samples.

In a comprehensive study, Junk et al. (8) showed that XAD-2 and XAD-4 were useful for a wide range of compounds. Here 1.5-2.0 grams of 20-60 mesh size resin was used and an average recovery of 84 different compounds was 78%. A method for cleaning the resin was presented as was the development of an analytical procedure for routine analysis. This procedure was used to study pesticides in water from several Iowa sources (9) and contaminants in waters and fish (10).

In 1976, a scaled down version of the previous extraction apparatus was introduced (11). Here, only 80 mg of 80-100 mesh resin was used and was applied for the recovery of halocarbons in water. Also, only 30 ml

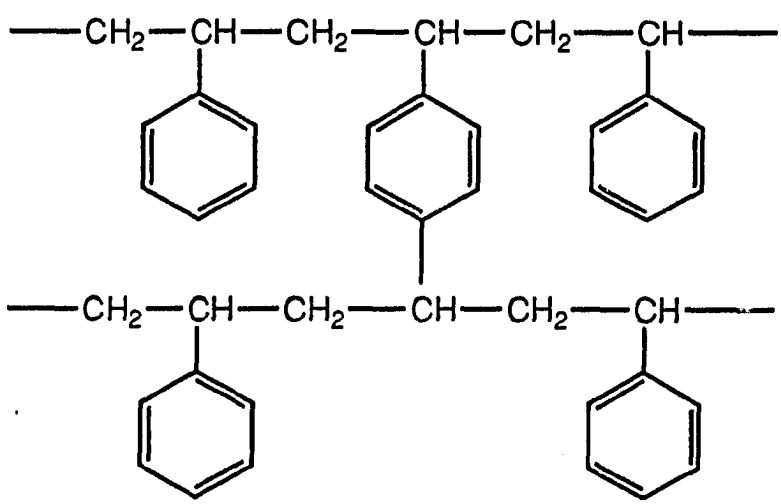

Figure 1. The structure of XAD-4 and XAD-2. The surface areas (m^2/g) the resins are 784 and 300 respectively. These are porous polymers that are used for solid phase extraction

was needed to recover the organics from the resin. A comparison to carbon absorption for several compounds was presented with an average recovery of 59% for XAD-2 and 22% for the carbon. A similar method using thermal desorption was later presented by Chang and Fritz (12). Since all of the organics removed from the water are used for chromatographic analysis, much smaller water sample sizes can be used. Unfortunately, this type of desorption suffers from interferences from impurities that are removed from heating the resin.

Chriswell et al. (13) compared the efficiency of several resins for the removal of organics from water. In this study and other unpublished results (14), XAD-4 was found to be superior to 15 other synthetic resins and activated carbons. More importantly, a study of flow rate versus the percent recovery was made. The results indicate that there is no dependence. This means that very little attention needs to be paid to the speed at which the contaminated water is passed through the resin column.

In 1978, Tateda and Fritz (15) introduced a mini-column procedure for concentrating organic contaminants. A small pipet tip was filled with a small amount of 150-200 mesh size XAD-4 resin and 50 to 100 ml of contaminated water was passed. Afterwards, only 50 to 100 µl of an organic solvent were used to elute the organics and no evaporation step was needed. Even though a detection limit of 2 ppb is claimed, only small sized water sampled can be analyzed.

Rossum and Webb (16) showed that several types of mixed beds containing XAD-2,-4,-7,-8 could be used and tailored to fit a particular application. The impurities in XAD resins were studied by two research

groups (17,18). It was originally assumed that impurities in the resin occurred in their manufacturing process. Later it was shown that most of these impurities occur when the resin fractures releasing more impurities over time. Even with these impurities, Ryan and Fritz (19) showed that XAD-4 could be used with thermal desorption with proper conditioning. Frei and Brinkman (20) discussed on-line and off-line sample preparation using SPE. Afterwards, the column is coupled to either a gas or a liquid chromatograph.

More recently, Richard and Junk (21) used XAD-4 extraction to determine munitions. It was shown that ethyl acetate is better for desorption of compounds from XAD-4. Also, XAD-4 was better than methylene chloride for the extraction of a munition. Several organosulfur compounds were concentrated on XAD and other porous polymer resins (22). Of the six different resins evaluated, XAD-2 proved to be the best for these compounds.

The drawback to using XAD resins has been the processing required before use. The resins need to be ground, sized and cleaned in order to obtain a usable product. Very recently, Rohm and Haas introduced small, spherical beads for SPE and these are now commercially available. These beads are similar in structure to XAD-4 and can be used as purchased. Since these resins are so new, they were not evaluated in this work.

In the past few years, the trend in SPE has been to use silica-based resins rather than polymers. This is because these resins are commercially available in small, spherical beads and are conveniently sold in pre-made extraction columns. Therefore the user needs to do little or no preparation of the resin and can purchase an extraction

cartridge ready to use. Materials are available with many types of functional groups bonded to the silica. Also, automated systems are now commercially available (23, 24). Unfortunately, there is very little information comparing these resins with polymer based ones. Any comparison made to the XAD work cited above is invalid because of the differences in particle sizes. The silica based resins are typically 400 mesh size particles (40 μm) while the XAD resin used was about 60-100 mesh size.

Silica based resins (most commonly octyldecyl) have been used as solid phase extracting resins for: azaarenes in water (25), phenoxy acid herbicides in riverwater (26), phenols in groundwater (27), phenols, guaiacols, and catechols in waste waters (28), tributyltin chloride in seawater (29), pesticides in sediment and fish (30) and endogenous biological compounds in different matrices (31).

A general study of several compounds was performed by Junk and Richard (32) using octadecyl bonded porous silica. Here, the average recovery of over 85% for polycyclic organic materials and pesticides shows the usefulness of these resins. Similarly, Wolfoff and Creed (33) evaluated this resin for environmental samples. Compounds in the ppb range were concentrated and determined successfully. Junk et al. (34) examined the impurities present in the resins. It was found that there were a wide degree of impurities present and these varied greatly depending on the manufacturer. Although these silica-based resins are gaining great popularity, recent results in our laboratories indicate they are not as good as the XAD-4 resin in the systems evaluated.

Results to be shown later confirm this in one system. Therefore, XAD-4 was used in almost all of the present work.

The goal of this work was to develop a method that combines SPE with distillation for the analysis of organic compounds at ppb levels. Again, most of the modelling has been done in a water matrix to evaluate the system.

EXPERIMENTAL SECTION

Glassware and Apparatus

The distillation glassware was illustrated in SECTION II of this thesis. Two types of resin collection apparatus were used. A slurry system shown in Figure 2 and a suction system, Figure 3, were both evaluated. Glass autosampler vials with a volume of 2 ml were used to collect the ethyl acetate and organics during the elution step.

Reagents and Chemicals

All chemicals used were reagent grade or better and were not further purified. All solvents were "blanked" before use. Ethyl acetate contained no interfering peaks and was used as is. Distilled water was further purified with the Barnstead Nanopure II water system before use. A mixture of 7 methyl esters was purchased form Alltech Associates, Inc. (Deerfield, IL).

The extacting resin, XAD-4, (Rohm and Haas, Philadelphia, PA) was ground and sized using mesh screens. The 200-325 mesh size was acid washed and cleaned according to a proceedure by Junk et al. (8). About 70 mg was used in all experiments.

Gas Chromatography

A Hewlett-Packard 7673A autosampler was used to perform automated, splitless injections with the Hewlett-Packard 5790A gas chromatograph. An injection temperature of 280^{o}C and a flame ionization detector at 325^{o}C were used. The oven temperature profile used for the survey

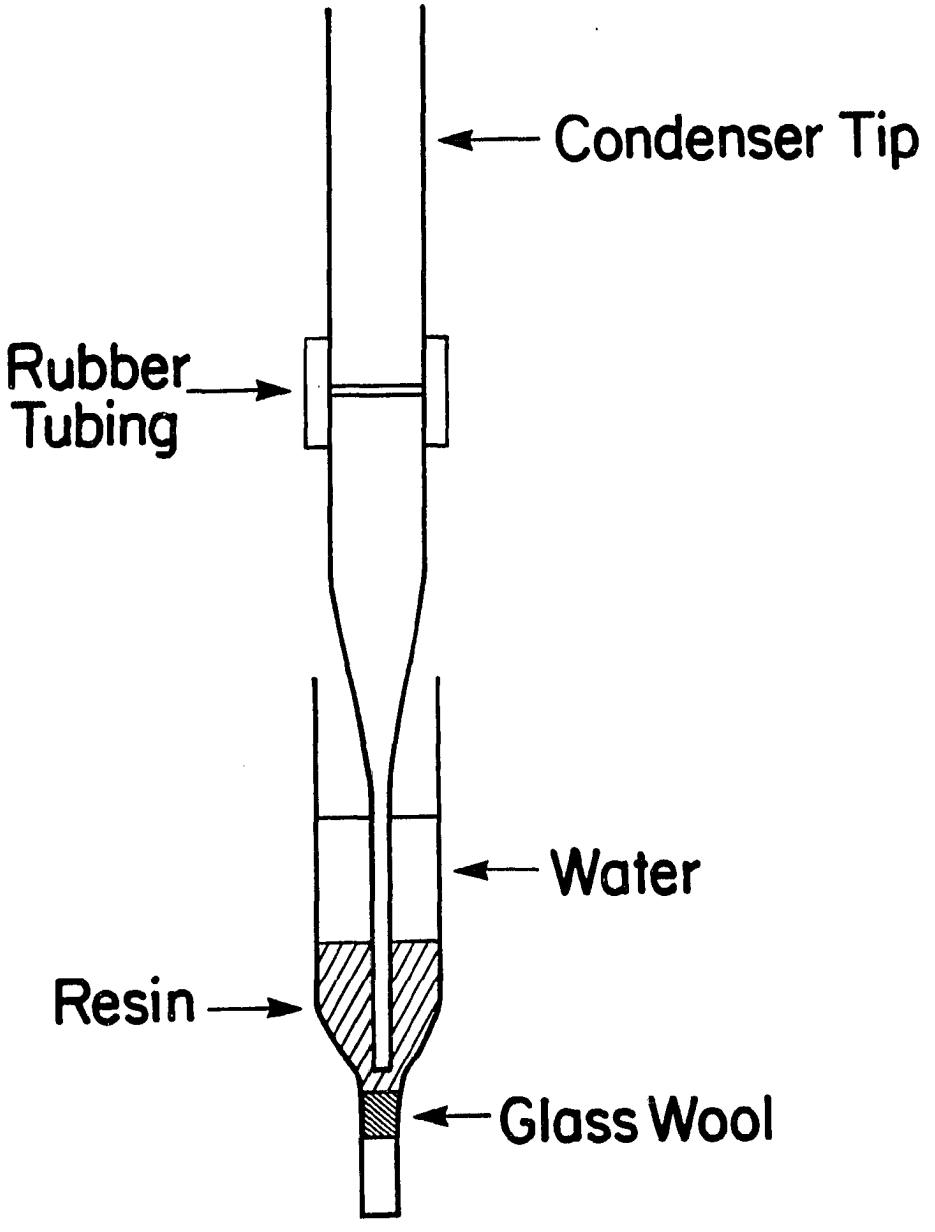

Figure 2. Illustration of the slurry system used for solid phase extraction of the distillate

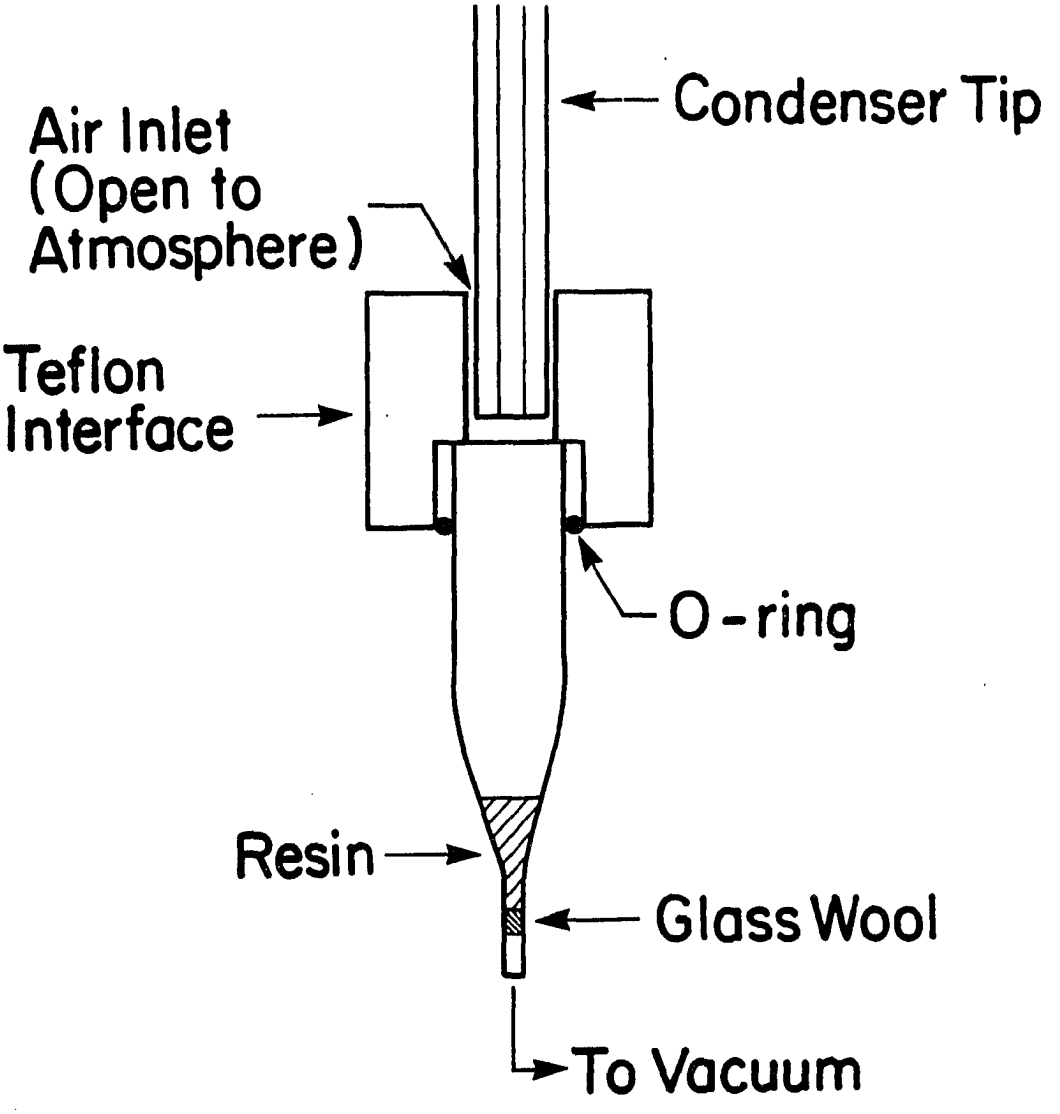

Figure 3. Illustration of the suction system used for solid phase extraction of the distillate

mixture was 2 minutes at 50°C, then 4°C/min to 135°C. For the essential oil mixture, the profile was 2 minutes at 50°C, then 7.5°C/min to 140°C. The profile for the methyl esters was 2 minutes at 80°C, then 15°C/min to 305°C. Finally, for the polynuclear aromatic hydrocarbon (PAH) mixture the profile was 2 minutes at 120°C, then 6°C/min to 260°C. The column used was a 30 m x 0.32 mm J&W DB-5 with a film thickness of 1.0 μm. The carrier gases were either zero grade He at 1.5 ml/min or zero grade H_2 at 2.4 ml/min measured with methane at 80°C.

Stock Solutions of Synthetic Mixtures

The following solutions were made for evaluation of the system:

(1) a. "Survey mixture": a mixture of 10 compounds with various functionalities and boiling points ranging from 136 to 232°C. These were dissolved in acetone at about 12.5 mg/25 ml.

b. "Survey mixture" internal standard: 5-nonanone was dissolved in acetone as above.

(2) a. "Essential oil mixture": 9 essential oils with boiling points ranging form 151 to 222°C were dissolved in acetone at about 12.5 mg/25 ml.

b. "Essential oil mixture" internal standard: a solution of mesitylene in acetone was prepared at about 12.5 mg/ 25 ml.

(3) a. "PAH mixture": 9 PAHs with boiling points ranging from 218 to 448°C were dissolved in acetone at about 12.5 mg/25 ml.

b. "PAH mixture" internal standard: triphenylmethane was dissolved in acetone at about 12.5 mg/25 ml.

(4) a. "Methyl ester mixture": The mixture of 7 methyl esters (C8-C20) obtained from Alltech was dissolved in acetone at about 14.3 mg/25 ml.

b. "Methyl ester mixture" internal standard: isopentyl benzoate was dissolved in acetone at about 12.5 mg/25 ml.

All of the above mixtures were used as described or diluted ten-fold in acetone for lower spiking concentrations.

Spiking and Distillation Procedure

A 50 ml volume of the purified water was added to a 100 ml round bottom flask containing a few boiling chips. A 10 µl micropipet was used to add the appropriate synthetic mixture to the water to make either a 10 or 100 ppb solution. The solution was boiled for a designated period of time. In some cases, it was advantageous to leave the water flow in the condenser off in order to allow steam to pass through the entire glass apparatus.

Collection Procedure

Initially a procedure was used in which a slurry of 70 mg of resin in 1 ml of water or organic solvent was placed into the glass column shown in Figure 2. After collecting 5 ml of distillate, the distillate was forced through the resin tube by applying pressure or suction. Air was passed through the tube, then the sorbed organics were eluted with ethyl acetate and determined by GC as described below.

In the suction method used in almost all of the work in this section, the resin tube was placed in the teflon interface shown in Figure 3 and held in position with an o-ring and an aluminum nut. A

rubber vacuum hose was placed at the narrow end of the column and this region was evacuated with a water aspirator. No special alterations need to be made to the aspirator and normal water flow is all that is needed for suction. The resin is first washed with about 5 ml of acetone followed by 5 ml of the purified water. Next, the interface is placed at the tip of the condenser. There is about a 1 mm gap between the tip and the interface to prevent high or low pressure to occur during boiling, since it is not a closed system. The flask is boiled and the condensate is drawn through the resin by suction. Once complete, the interface is removed and a small amount of air is drawn through the column to dry the resin. The vacuum line is disconnected and the organic analytes are removed by elution. Approximately 500 µl of ethyl acetate is used and is collected in a 2 ml autosampler vial. An internal standard is added and the mixture is ready for injection into the gas chromatograph.

Standardization

While the distillation was proceeding, a reference solution was injected into the GC. This solution contains the same amount of the synthetic mixture and internal standard in 500µl of ethyl acetate as the original sample. The peak areas of the components of both mixtures are compared to the peak areas of the internal standards and ratios are calculated. The percentage recovery is obtained by comparing the ratios of the reference solution with those of the distillation solution. This type of standardization takes into account the errors associated with

the complete procedure. All runs done in triplicate had a relative standard deviation of less than 6%.

RESULTS

Slurry System

Resin comparision

The slurry system was evaluated using three different types of resins; Tenax, octadecyl (C18) silica, and XAD-4. Approximately 70 mg of each resin was placed in 1 ml of water in the resin collecting tube. The tip of the condenser was placed near the bottom of the resin and the distillation started. After the collection of 5 ml of distillate, the distillate was passed through the resin column to sorb the organics. The survey mixture was used in these experiments. Table I lists the recoveries using the three resins. It is apparent that XAD-4 is far superior than either Tenax or C18 silica and was used in the remainder of experiments.

Tip placement

The survey mixture was used to determine the functionality of the tip placement on the percent recovery. Previously the tip of the condenser was placed at the bottom of the resin in the column. The resin acts as a solid organic trap and collects the compounds as they are boiled over. Table II lists the recovery when the tip is placed just above the resin, but still in the 1 ml of water and when the tip is placed just above the water. Significant differences are noted with small differences in the location of the tip. This type of behavior is very undesirable because of the difficulty in reproducing the exact location of the tip from run to run.

Table I. Recovery of the survey mixture using three different types of resin in the slurry interface

	Percent Recoveries		
Component	Tenax-GC	C-18 Silica	XAD-4
Ethylbenzene	55.7	9.1	72.6
Anisole	96.7	3.8	93.6
Cumene	45.7	24.4	72.7
Bromobenzene	84.4	9.2	88.8
Benzaldehyde	71.4	0.0	87.5
2-Ethyl-1-hexanol	90.0	62.6	90.6
Acetophenone	51.8	0.0	88.1
1,2,4-Trichlorobenzene	80.5	48.5	81.7
Butyrophenone	87.9	59.1	93.9
2-Undecanone	55.0	81.9	76.3

Table II. Recovery of the survey mixture at different locations of the tip of the condenser in the slurry interface

Component	Percent Recoveries	
	Tip 2 mm above water	Tip 2 mm above resin
Ethylbenzene	17.0	33.5
Anisole	52.1	77.5
Cumene	18.8	29.8
Bromobenzene	28.7	58.6
Benzaldehyde	64.1	85.2
2-Ethyl-1-hexanol	67.5	82.9
Acetophenone	64.7	83.4
1,2,4-Trichlorobenzene	22.8	63.9
Butyrophenone	69.5	87.1
2-Undecanone	30.3	65.8

Organic traps

Instead of using 1 ml of water mixed with the resin, several mixtures of water and organic solvents were used. Isopropanol, methanol, and acetone were either used or mixed with a portion of water. As was shown in SECTION II, organic liquids work well in trapping the organic distillates. Unfortunately, the results using these traps were inconclusive and not reproduceable. This is because any amount of organic solvent present in the collected distillate has the ability to elute the sorbed organic compounds from the resin. There was no direct correlation of the percent organic in the 1 ml and the percent recovery. While the organic solvents may act as a trap, they also act as a eluent.

System problems

Besides the problem with tip location discussed above, there were many other difficulties with this interface system. First, the geometry of the collector plays an important role in the percentage of recovery. Many different collector shapes were investigated with large differences in the recoveries. Second, the resin was drawn into the tip of the condenser causing plugging. Several experiments were ended when the plug finally blew out and all over. Also, many times the resin would get sucked into the distillation apparatus and end up in the boiling flask. Finally, the interface required constant attention and manipulation to assure none of the above occurred.

A major goal of this research was to employ SPE in an easy to use system with steam distillation. For this reason, the slurry method was scrapped and replaced with the suction method described below.

Suction System

Recovery of the survey mixture

The survey mixture containing 10 compounds with various functionalities was spiked into the boiling flask as previously described in the experimental section. The flask was heated for 18 minutes and the condensate was drawn through the XAD-4 resin column. The resin column was removed and the compounds were eluted with ethyl acetate. A 1 µl portion of this was introduced into a capillary gas chromatograph with splitless injection. The results in Table III show excellent recoveries for all compounds at the 100 and 10 ppb level except for 2-undecanone.

Recoveries for many compounds in the survey mixture can be increased by careful cleaning of the glassware. The recoveries in Table III were obtained by washing the distillation glassware with methanol between runs. When the glassware is washed with acetone then hexane, then acetone and water, the average recovery increases 3-5%. As shown in Table IV, all compounds are now recovered above 80%. It is believed that the components are sticking to oils or particles that accumulate at the head of the cold condenser and are not removed with methanol. Using a non-polar solvent such as hexane removes this build up and the recoveries are increased. With this mixture, longer distillation times do not increase the recovery.

Recovery of the essential oil mixture

Distillation is often used in the determination of essential oils by perfume and flavor industries. To evaluate this distillation method for

Table III. Recovery of the survey mixture at 10 and 100 ppb. Boiling points are listed for reference

Component	Boiling Point (°C)	Percent Recoveries	
		100 ppb	10 ppb
Ethylbenzene	136	90.8	86.8
Anisole	155	97.6	90.4
Cumene	153	89.0	82.3
Bromobenzene	156	95.1	88.0
Benzaldehyde	178	99.9	91.3
2-Ethyl-1-hexanol	184	98.7	88.7
Acetophenone	202	96.9	88.2
1,2,4-Trichlorobenzene	214	86.8	82.1
Butyrophenone	222	100.0	91.1
2-Undecanone	232	74.4	74.3

Table IV. Recovery of the survey mixture with "clean" glassware at 100 and 10 ppb

	Percent Recoveries	
Component	100 ppb	10 ppb
Ethylbenzene	97.8	89.5
Anisole	98.4	94.0
Cumene	97.8	92.9
Bromobenzene	97.0	96.1
Benzaldehyde	98.6	93.9
2-Ethyl-1-hexanol	100.0	94.9
Acetophenone	91.4	90.9
1,2,4-Trichlorobenzene	92.2	83.9
Butyrophenone	97.9	92.6
2-Undecanone	88.7	80.4

this purpose, a mixture of 9 various essential oils was prepared and spiked at the 10 and 100 ppb levels. The flask was heated for 18 minutes and the recoveries were tabulated as before. Again, excellent recoveries are obtained in a short period of time as seen in Table V. At the 10 ppb level, an impurity interferes with the determination of cyclohexanol.

Recovery of higher boiling mixtures

Most of the determinations using steam distillation have used compounds with boiling points under 240°C. It is of primary environmental importance to address compounds with higher boiling points such as polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls, or agrichemicals. To do this, a mixture of 9 PAH compounds was made and spiked and boiled as before. The recoveries as a function of boiling time are shown in Table VI. It is apparent that a problem exists because of the low recoveries obtained in the second ten minutes of boiling. For example, it would be expected that a recovery greater than 8.2% should be obtained for anthracene in the second ten minutes of boiling when 42.9% is recovered in the first ten.

Effect of turning off the condenser

Passing cold water through the condenser condenses most components except for lower boiling point ones. A drawback to this is compounds with high boiling points will condense and are not likely to be very water soluble. They remain concentrated on the cold walls of the condenser and will not be effectively swept into the resin column by the

Table V. The recovery of the essential oil mixture spiked at 10 and 100 ppb. Boiling points are listed for reference

Component	Boiling Point (°C)	Percent Recoveries 100 ppb	10 ppb
Cyclohexanol	161	96.0	-----
Ethoxyethyl Acetate	156	81.2	78.7
Methyl Hexanoate	151	95.9	92.8
α-Pinene	156	85.6	86.5
β-Pinene	166	90.9	92.3
Limonene	176	89.9	89.7
Cyclohexyl Acetate	173	96.7	93.3
Camphor	177	99.3	92.8
Methyl Salicylate	222	95.2	88.3

Table VI. Recovery of the PAH compound mixture at 10 minute additional boiling times

Component	Percent Recovery			
	First 10 min.	Second 10 min.	Third 10 min.	Fourth 10 min.
Naphthalene	89.3	0.0	0.0	0.0
Acenaphthene	78.2	5.5	2.0	0.0
Fluorene	51.2	10.2	4.9	3.7
Anthracene	42.9	8.2	6.8	6.6
Phenanthrene	26.7	5.0	3.6	2.0
Fluoranthrene	38.6	9.2	6.5	4.3
Pyrene	39.3	11.2	8.1	2.6
1,2-Benzanthracene	13.4	2.0	1.0	0.0
Chrysene	6.3	2.0	1.0	0.0

cold condensed water. The solution to this problem is to stop the flow of water in the condenser. The first 12 minutes of all distillations is a heating up period. Only non-condensed vapors are carried over. From 12 minutes to 18 minutes, about 5 ml of condensate is collected and passed through the resin. It takes another 6 minutes (24 minutes total for the entire run) for steam to reach the resin column when the condenser is left off. Since steam is passing through the whole system, there are no cold spots for the compounds to stick, except on the resin.

Table VII shows the recoveries of the PAH mixture when the condenser is left off and a 24 minute run time is used. A comparison of the usefullness of this is dramatically illustrated in Figure 4. A recovery of 87.8% is obtained for pyrene which has a boiling point over 400°C.

Recovery of the methyl ester mixture

A high boiling point mixture of 7 methyl esters was made. The methyl esters are different only by C2 in their alkyl chain. The mixture was spiked in the flask and boiled for 24 minutes with the condenser on and off. Figure 5 illustrates the vast difference in recoveries and the behavior is similar to that of the PAH compounds. Table VIII shows that all esters through methyl palmitate are well recovered.

To prove that the methyl esters were sticking to the glassware when the condenser was left on, a run was performed with cold water flowing through the condenser. After boiling, the glass apparatus was extracted with 5 ml of methylene chloride. The volume was reduced to 500 µl by

Table VII. Recovery of the PAH compounds with the condenser off. The total heating time was 24 minutes. Boiling points are listed for reference

Component	Boiling Point (°C)	Percent Recovery
Naphthalene	218	93.1
Acenaphthene	279	91.5
Fluorene	298	92.2
Anthracene	340	92.4
Phenanthrene	340	83.5
Fluoranthrene	384	86.7
Pyrene	404	87.8
1,2-Benzanthracene	438	25.4
Chrysene	448	14.7

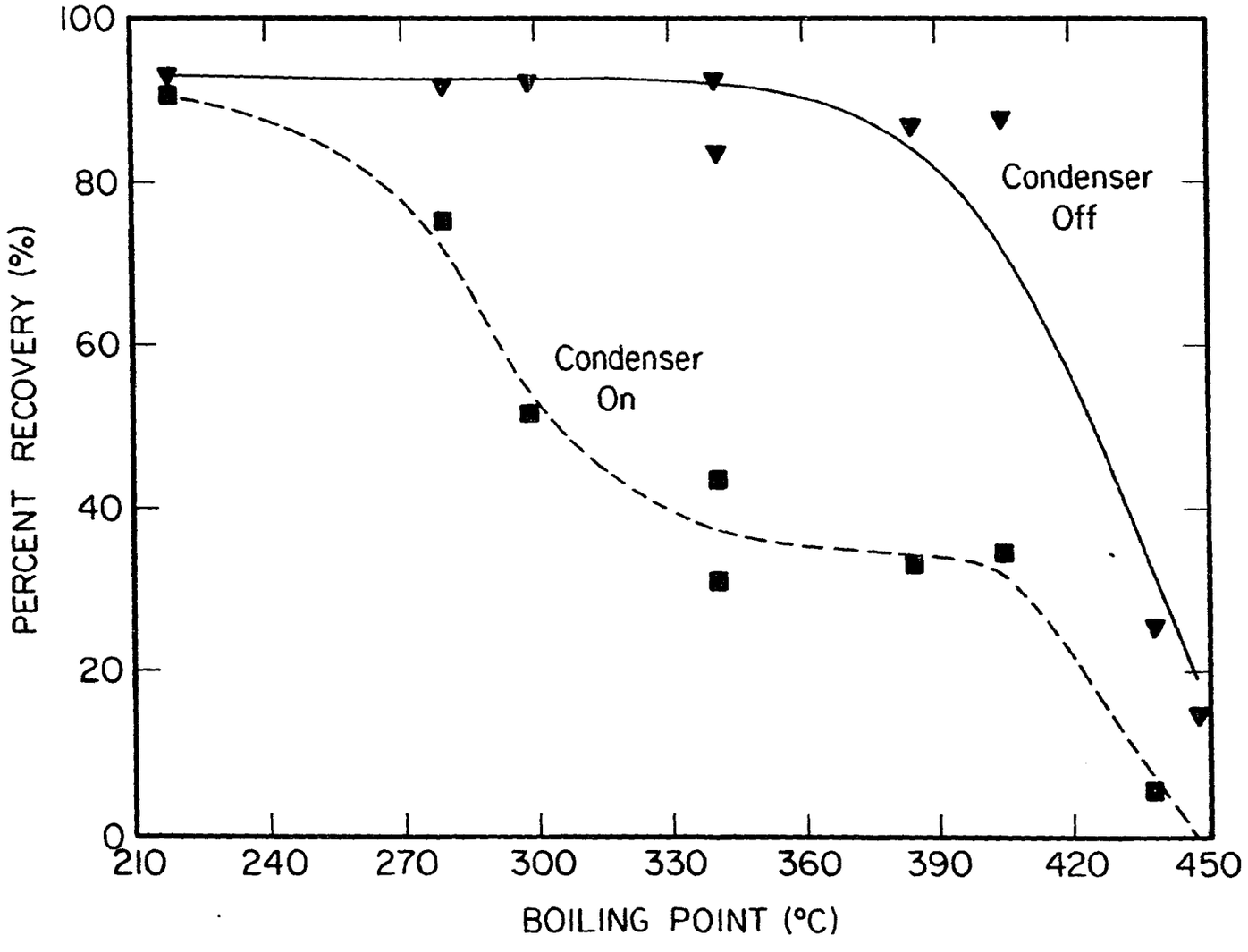

Figure 4. The recovery of the PAH compounds when the condenser is on and off vs. their boiling points

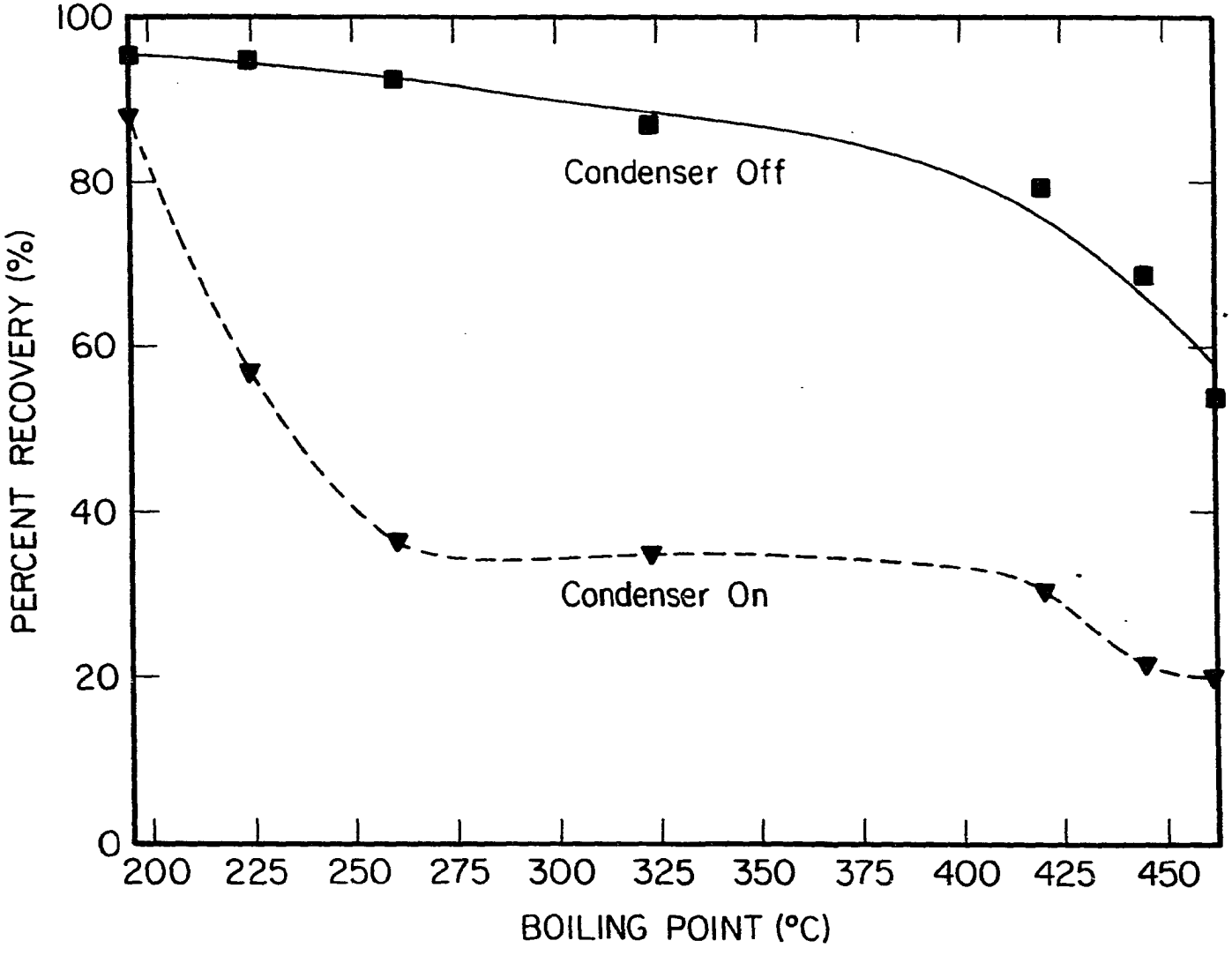

Figure 5. The recovery of the Methyl ester compounds when the condenser is on and off vs. their boiling points

Table VIII. Recovery of the methyl ester mixture with the condenser on and off. Boiling points are listed for reference

Component	Boiling Point (°C)	Percent Recoveries	
		Condenser On	Condenser Off
Methyl Caprylate (C-8)	195	87.9	95.3
Methyl Caprate (C-10)	224	56.9	94.8
Methyl Laurate (C-12)	260	36.4	92.6
Methyl Myristate (C-14)	323	35.0	87.0
Methyl Palmitate (C-16)	420	30.6	79.3
Methyl Stearate (C-18)	445	21.7	68.7
Methyl Arachidate (C-20)	462	20.2	54.0

evaporation and a portion was injected into the GC. The chromatogram shows peaks for all of the esters in the mixture.

Effect on the survey mixture

Steam is carried to the resin when the condenser is left off. This allows the recovery of higher boiling point compounds. It was questioned whether the analytes of the survey mixture would be stripped off the resin when either steam or hot water passed though the column. The survey mixture was boiled for 24 minutes with the condenser left off. This would allow steam in the system to pass into the resin column. There is an average loss of only 3% for the compounds (Table IX).

Table IX. Recovery of the survey mixture with the condenser on and off.

Component	Percent recoveries	
	Condenser On	Condenser Off
Ethylbenzene	97.8	91.7
Anisole	98.4	95.4
Cumene	97.8	92.7
Bromobenzene	97.0	93.3
Benzaldehyde	98.6	94.3
2-Ethyl-1-hexanol	100.0	92.9
Acetophenone	91.4	96.9
1,2,4-Trichlorobenzene	92.2	88.8
Butyrophenone	97.9	93.7
2-Undecanone	88.7	90.4

DISCUSSION

Recoveries of 80% or better are obtained for a wide variety of organic compounds with boiling points ranging form 136 to 404°C with a run time of under 25 minutes. A concentration factor of at least 100 allows for the determination of compounds at part-per-billion levels with a common flame ionization detector. A larger sample size or a more sensitive detector should allow the analysis at even lower concentrations.

The eluent, ethyl acetate, is efficient in the removal of all analytes tested. None of these compounds were further recovered when additional amounts of ethyl acetate was used to wash the column. Other research groups have shown that smaller volumes of ethyl acetate on the order of 150 µl effectively remove all sorbed species. A volume of 500 µl was used in these experiments to insure complete removal. Ethyl acetate is also more ammendable to splitless injection than some of the other commonly used eluents such as methanol, acetone, or ether. This allows for better reproducibility.

It is interesting to note that XAD-4 resin still performed well even though it was not kept "wetted" as almost all SPE procedures require. The resin, in fact, is dried during the distillations by the passing of lab air through the column. This is because the suction system pulls additional air from the atmosphere during a run. There were no additional peaks found from this impure air.

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SUMMARY

The amount of water in an organic sample can be determined indirectly by using the reaction of 2,2-dimethoxypropane with water and subsequent gas chromatographic determination of the product acetone. Nafion, a solid acid catalysis, is effective for catalyzing the reaction in a very short period of time and can be easily removed prior to injection onto fused silica capillary columns.

A simple analytical procedure is developed such that no special instrumentation or difficult manipulations are needed. A wide range of concentration of water can be determined by simply reducing the size of the sample, when needed. Several organic samples were analyzed for their concentration of water and excellent recoveries were obtained for additional water additions. The method compares closely with a Karl Fischer titration for some samples with a relative standard deviation of less than 3% for six successive runs. Samples that contain ascorbic acid, an interferrent in the Karl Fischer titration, are easily determined by this GC method.

Simple steam distillation can be used for the isolation of organic compounds from aqueous matrices. Here, the organics are spiked into water, boiled, and the percentage recovered in the distillate is determined by analyzing a portion using gas chromatography. Excellent recoveries are obtained for a wide variety of compounds in 18 minutes. Acetone is used to trap non-condensed species such as alkyl and halogenated benzenes. A concentration effect of 10 is realized, although other experimentation showed that many compounds are

quantitatively distilled in the first 0.5 ml of condensate, yielding a concentration effect of 100.

The method presented is simple, fast, and effective for the concentration and isolation of even polar compounds, such as phenols. Traditionally, phenols boil very slowly in water and large amounts of distillate needs to be collected. By adding large amounts of inorganic salts to the boiling flask before distillation, it was found that phenols can be recovered quickly and effectively in a short period of time. The addition of one salt, magnesium sulfate, worked best and reduced the distillation time by five minutes.to 12 minutes.

The direct analysis of the distillate was effective for organic compounds at the part-per-million level. By combining steam distillation with solid phase extraction (SPE), compounds in the part-per-billion level can be determined. Steam distillation combined with SPE provides both isolation and concentration of organic compounds. Concentration factors of 100 are easily obtained with very little sample manipulation.

Two different interfaces were evaluated for their overall performance. The suction interface worked best and required no adjustments during the course of a distillation. No special glassware or apparatus is needed which should allow this method to be used by virtually any laboratory. Distillation-SPE was shown to be effective for a wide variety of compounds. Most notably were compounds with very high boiling points. By simply turning off the flow of water in the condenser, compounds with boiling points in excess of 400^{o}C were recovered above 80% in less than 25 minutes. Steam is forced through

the entire system leaving no cold spots for the higher boiling point components to stick. Even though steam or hot water reaches the resin, only a slight reduction in the recovery of more volatile components occur.

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