

1984

Studies of cation exchange for the isolation and concentration of trace level components of complex aqueous mixtures

Joseph Robert Kaczvinsky Jr.
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STUDIES OF CATION EXCHANGE FOR THE ISOLATION AND
CONCENTRATION OF TRACE LEVEL COMPONENTS OF COMPLEX
AQUEOUS MIXTURES

Iowa State University

Ph.D. 1984

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Studies of cation exchange for the
isolation and concentration of trace level
components of complex aqueous mixtures

by

Joseph Robert Kaczvinsky, Jr.

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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DOCTOR OF PHILOSOPHY

Department: Chemistry
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1984

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PREFACE

Ion exchange is an extremely useful and versatile technique for chemical analysis. Coupled with dynamic elution and a suitable detection method, it can be used to separate and quantify the components of a complex mixture of ionic species. Applied in a simpler fashion, the ion exchange phenomena can be used to isolate groups of organic or inorganic compounds into broad classes, based on their ionic character and affinity for the particular resin. In addition, if elution conditions are avoided, trace level species of interest can be at once separated from the rest of the sample and concentrated on the resin. After removal from the resin, this would allow quantitative determination of the species of interest within the normal sensitivity range of the analytical method used. This combination of attributes makes ion exchange an excellent initial step in the analysis of trace level components of complex samples.

This dissertation will present and discuss two applications of cation-exchange resins to the concentration and isolation of low level components of complex mixtures. In Section I, a cation-exchange procedure is used to isolate basic organic compounds from aqueous solution. Section II describes the development of porous cation-exchange resins containing an added chelating group. These resins are then

used to selectively remove cesium-137 and strontium-90 radioisotopes from nuclear waste streams. Other approaches to the removal of these radioisotopes using various types of ion exchangers are also briefly examined.

Dr. Koichi Saitoh, a post-doctoral associate from Tohoku University, Japan, collaborated with the author on the work presented in Section I. The work in Section II was completed under a contract from E. I. Dupont's Savannah River Laboratory, with Dr. D. Douglas Walker as the principal collaborator.

SECTION I. CATION-EXCHANGE CONCENTRATION OF BASIC ORGANIC
COMPOUNDS FROM AQUEOUS SOLUTION

INTRODUCTION & LITERATURE REVIEW

The analysis of organic contaminants in natural or potable water is usually complicated by three factors:

- 1) The organic compounds are present in very low, often trace level, concentrations.
- 2) Complex mixtures containing a variety of compound types may be present.
- 3) Water is a poor solvent choice for many common instrumental analytical techniques, most notably gas chromatography.

In order to alleviate these problems, the analysis of organic compounds in such samples usually involves preliminary isolation and concentration steps (1-6). Any preliminary separation should be selective, while minimizing analyte loss. This separation may consist, entirely or in part, of a division of the compounds of interest into one of several general classes (3,4). Classification is usually based on a particular compound characteristic, such as hydrophobicity or acidity. Analysis of several less complex mixtures of compounds will be inherently less complicated. In addition, the compounds in each mixture are intrinsically similar in some way. This gives the analyst greater flexibility, perhaps

permitting the use of a technique that would prove futile when applied to a larger, less consistent mixture. A preconcentration step is often necessary to permit direct analysis by conventional methods within their usual sensitivity limits (5,6).

An excellent example of the need for preliminary fractionation and concentration in the analysis of trace aqueous organics is found in a recent paper by a group of workers at the Environmental Protection Agency (7). The overall goal was to analyze several 400 gallon samples of municipal drinking water for potentially harmful organic compounds. After preliminary concentration of the samples by reverse osmosis, each reduced sample was sequentially extracted with petroleum ether, diethyl ether, and acetone. The diethyl ether fraction, which contained most of the mutagenic activity, was further fractionated by extraction with 5% NaOH and re-extraction of the aqueous base layer with methylene chloride after readjustment of the pH to 2 (removal of acids). The remaining ether solution was dried and chromatographed on a silica gel microcolumn. Sequential elution with a variety of solvent mixtures further separated the base-neutral fraction into subgroups by polarity. After each elution, further concentration was achieved by solvent evaporation. A total of 460 compounds of various classifications were determined in the diethyl ether extract

by gas chromatography-mass spectrometry. Clearly, identification, much less quantification, of this many widely disparate compounds without an extensive group fractionation procedure would have been impossible.

In addition to preliminary fractionation and concentration, the transfer of the analytes from aqueous solution to an organic solvent would also facilitate the use of several common analytical techniques. For example, in gas chromatography, water can cause degradation of many stationary phases at the elevated temperatures commonly used. In addition, water is not volatile enough to be an effective gas chromatographic solvent for most organic compounds. Thus, in order to use gas chromatographic analysis, transfer of the species of interest into a volatile organic solvent is highly desirable. An ideal preparative method for organics in aqueous solution would combine the isolation, concentration, and transfer processes into a single step.

Many techniques have been developed to simultaneously fractionate and concentrate aqueous organics. The classic technique of solvent extraction has been used extensively for various types of organics (7-11). Typically, a solvent such as methylene chloride is used to extract neutral organics from aqueous solution. Methylene chloride is a good solvent for many types of organic compounds and can be used directly in gas chromatography. It has the added advantage of being

denser than water, which facilitates the removal of the organic layer. Extraction of organic acids and bases is subsequently accomplished by adjusting the pH of the aqueous sample. Acidic compounds will form salts at high pH and will not extract well into the organic phase, while the predominantly basic organics will be extracted. Similarly, bases will not be extracted at low pH, and acids can be removed. Thus, rough separation of aqueous organics into acidic, basic, and neutral fractions can be effectively achieved using solvent extraction.

However, extraction procedures can be tedious, especially if a large aqueous sample is to be extracted with a small volume of organic solvent. Additionally, the distribution coefficient of each analyte may not be favorable under the same conditions of pH and organic phase. Some compounds, especially those exhibiting a significant degree of hydrophilicity, may extract only poorly, if at all.

Several concentration methods have been developed that utilize the volatility of the organic analytes as the means of fractionation. In headspace analysis (11,12), the vapor above the aqueous sample is collected and analyzed. Gas-stripping (13-15) is a more dynamic version of the same technique. A large volume of gas is forced through the aqueous sample, and those organics that have an appreciable vapor pressure are "stripped" from solution by the circulating gas. The organics

are later concentrated from the gas phase, and analyzed. A solid sorbent, such as activated charcoal, is often used as a trapping agent (16). This technique is also referred to as the purge-and-trap method. Simple distillation has also been used to isolate and concentrate aqueous organics (17,18). However, these techniques suffer from severe restrictions in their usefulness. Generally, they can only be applied effectively to relatively insoluble, polar, low molecular weight analytes.

The technique of reverse osmosis has also been applied to the concentration of aqueous organics (7,19). Here the solvent (water) containing the trace level organics is forced through a semi-permeable membrane into a second volume of pure water, by the application of pressure above the contaminated solution. The membrane prevents the passage of the organic contaminants into the second volume, by either size exclusion or affinity effects. They are therefore concentrated in the now reduced volume of original sample.

The sorption of organics on a solid matrix is an effective concentration technique, and has become quite popular recently, primarily because of its simplicity. By far the most common solid sorbent is activated carbon. The value of this sorbent for the removal of organics from water is abundantly demonstrated by the extensive and supportive studies of its use by such organizations as the National

Academy of Sciences (20) and the Environmental Protection Agency (21). The references to the use of activated carbon sorbents for organics are too numerous to be covered completely here, but the reader is referred to a recently published two-volume monograph on the subject as a representative example (22). Unfortunately, removal of the sorbed organics from the carbon matrix is often difficult. Thus, while activated carbon is the sorbent of choice for the large-scale, total removal of organics from water, its use in analytical procedures is limited.

A number of other solids have been applied to the isolation and concentration of aqueous organics. Materials such as cellulose and Sephadex have been used with some success (23). The application of a wide variety of porous polymers, including poly(styrene-divinylbenzene)s, polyurethanes, and poly(phenylene-oxide)s (such as Tenax GC) to this problem has been reviewed by Dressler (24). In recent years, macroreticular poly(styrene-divinylbenzene) resins have been used extensively to sorb aqueous organic compounds (3,24-30). The term "macroreticular" refers to polymers whose physical structure consists of numerous microspheres that are bonded together, but have large channels (pores) between them. They are produced by performing the polymerization in a two-solvent system (31-33). The first solvent is water, which is the usual solvent for these polymerizations. The second

solvent is one in which the monomer will dissolve, but the resulting polymer will not. Macroreticular synthesis produces resins with rigid structures, which will not swell when placed in a solvent. These resins characteristically have high surface areas and relatively narrow ranges of pore size. Although not strictly correct, the terms "macroporous" and "macroreticular" are often used interchangeably. Macroreticular poly(styrene-divinylbenzene)s have proven useful as adsorbents for aqueous organics primarily because of these high surface areas, and the overall hydrophobicity of the resin matrix. Although their capacities are considerably lower, resins of this type have been shown to complement activated carbon for the adsorption of many types of compounds (20,34-36). Unlike activated carbon, however, flushing these resins with an appropriate organic solvent easily removes the sorbed organics, and allows the resin to be reused. This permits broader application of these resins in analytical methods. Unfortunately, while these resins are very effective for concentrating neutral organics, especially those exhibiting aromatic character, they have been less successful for acidic and basic compounds (25).

Anion-exchange resins have been widely used to remove acidic organic compounds from water and aqueous matrices (37-41). Richard and Fritz (42) developed an excellent method for the isolation and concentration of organic acids and acid

anions from aqueous samples. The organic acids are retained on a small column containing macroporous anion-exchange resin. After sorbed neutral organics are washed off the resin, the anions are converted to the molecular form and eluted from the column with HCl gas in ethyl ether. The procedure has since been applied to more specific samples (43-45).

Now, a similar scheme employing a cation-exchange resin is used to isolate basic organic compounds from aqueous samples. The sorption of organic bases by cation-exchange resins is well documented (46-50). A cation-exchange method has been used to isolate and concentrate pyridines from worts and beers (51). In the present work a macroporous cation exchanger in the hydrogen form is used to retain organic bases as cations from aqueous solution. Neutral organic compounds that might be sorbed by the resin are removed by washing with methanol and ethyl ether. Any unoccupied exchange sites are converted to the quaternary ammonium form by passing ammonia gas through the column. The protonated bases are then converted to their free base forms and eluted with either ammonia-saturated methanol or ammonia-saturated ethyl ether. After careful evaporation of most of the solvent, the individual bases are separated by gas chromatography.

EXPERIMENTAL

Cation-Exchange Resin

A cation-exchange resin was prepared from the macroreticular poly(styrene-divinylbenzene) copolymer XAD-4 (Rohm & Haas, Philadelphia, PA). The resin was ground and dry sieved. The -80/100+ fraction was retained and sequentially Soxhlet extracted with methanol, tetrahydrofuran, acetonitrile, acetone, and ethyl ether for 10 hrs each. The purified resin was then dried overnight at 50°C.

The XAD-4 resin was sulfonated by a procedure adapted from that of Morgner and Wilharm (52). A 10-g sample of resin was added to 200 mL of concentrated (96%) sulfuric acid and 100 mg of Ag_2SO_4 that had been heated to 110°C. Metal sulfates, most notably silver sulfate, act as catalysts in the sulfonation reaction (53). The silver salt was included here to ensure a high yield of sulfonate cation-exchange groups on the resin. The reaction mixture was stirred for 2.5 hrs and then allowed to cool to room temperature. When cool, the reaction was quenched by pouring the reaction mixture into 2 L of distilled water with ice. After quenching, the resin was filtered off and placed in a 15 cm X 8 mm i.d. Pyrex column with a stopcock at the bottom. The resin was flushed with 2 N H_2SO_4 until the effluent was free of Ag^+ ions (this was tested by

precipitation with 1 M NaCl). The sulfonated resin was removed from the column and Soxhlet extracted for 10 hrs each with methanol, acetonitrile, and ethyl ether. The resin was then returned to the column and alternately changed from the H^+ form to the Na^+ form several times with 2 N NaOH and 2 N HCl. Finally, the resin, in the H^+ form, was washed with 100 mL each of distilled water, methanol, and acetone, and dried overnight at 50°C.

The average capacity for three batches of sulfonated XAD-4, as determined by indirect titration with 0.1 N HCl (using a phenolphthalein indicator) was 2.58 ± 0.30 meq/g. Most of the recovery study work was completed using a batch of resin with a capacity of 2.86 meq/g.

Concentration Apparatus

The columns, reservoirs, and three-plate Snyder distillation columns used are similar to those described elsewhere (3,26). The column dimensions were 15 cm X 8 mm i.d., and the reservoirs were of 250-mL and 1-L capacity. Concentration flasks used were those described by Junk et al. (26), and were of 100-mL capacity. The inner surfaces of all reservoirs were deactivated to minimize adsorption of analyte compounds on the glass. This was accomplished by treatment with a 5% (v/v) solution of dimethyldichlorosilane in toluene.

Deactivation of the columns or concentration flasks was not performed, to prevent possible contamination of the reduced volume samples.

Gas Chromatography

The recovery studies were performed with a Tracor 550 gas chromatograph, with both packed and capillary columns, using an FID detector. The packed columns used for most of the recovery studies were 2 m X 4 mm i.d. glass columns packed with 10% Carbowax 20M/2% KOH on -80/100+ mesh Chromosorb W AW. Several high-boiling basic compounds and most of the neutral compounds were separated by using the same columns packed with 3% OV-17 on -100/200+ mesh Supelcoport. Capillary columns were fused silica, 30 m X 0.25 mm i.d., coated with SE-54. Analysis of the natural samples was performed on a Hewlett-Packard 5794A gas chromatograph using a 27 m X 0.25 mm fused silica capillary column with a thick film (1.0 μ m) of the bonded phase DB-5.

Reagents and Chemicals

All solvents except methanol were reagent grade. Methanol was "distilled-in-glass" grade from Burdick & Jackson (Muskegon, MI). All solvents except ethyl ether were used as

received. The ethyl ether used in the elution procedure was specially purified by sequential extraction with one-tenth volume each of 1 M NaHSO₃, saturated NaCl solution, NaCl saturated 1 N NaOH, NaCl saturated 1 N H₂SO₄, and finally twice with saturated NaCl solution. The purity of the solvent was checked periodically by blank analysis.

Anhydrous ammonia gas had a purity of 99.99% and was purchased in lecture bottles from Matheson (Joliet, IL). All other chemicals were reagent grade or better, and were obtained from various commercial sources. Model compounds and other reagents were used without further purification.

Water used in the recovery studies was purified by passage through a multibed purification system manufactured by Barnstead (Boston, MA).

Cation-Exchange Procedure

A 2.45-g resin sample (total capacity of 7 meq) was allowed to stand in pure water for 2 hrs and was then added, as a slurry, to a column plugged with silanized glass wool. The aqueous sample was added to the column from a reservoir attached to the top of the column using gravity flow. The flow rate was approximately 3 mL/min. After the passage of the sample was complete, the reservoir was rinsed twice with 20 mL of water. Each washing was allowed to enter the column

and drain. The column was then blown out briefly with a gentle stream of air. The reservoir was reattached, the walls rinsed with 10 mL of methanol, and this washing was then allowed to completely fill the column. The column was capped and shaken to remove entrapped air. After allowing the methanol level to drain to the top of the resin bed, the column was eluted with a second 10-mL portion of methanol. Excess methanol was blown out of the column with a gentle stream of air. Without reattaching the reservoir, the washing procedure was repeated with a 10-mL portion of ethyl ether, followed by a 15-mL portion.

A concentration flask was then placed beneath the column and any residual ether was blown out with a stream of ammonia gas. Ammonia gas was further passed through the column until about the top 90% of the resin bed became lighter in color, indicating conversion of the resin sites from the H^+ to the NH_4^+ form. At this point the flow of ammonia gas was stopped, and 10 mL of ammonia-saturated eluent was added to the column. This eluent was prepared by bubbling ammonia through the cooled solvent for about 10 minutes. When the liquid level reached the top of the resin bed, a second 10-mL portion of eluent was added, the column was capped, and then shaken gently to remove entrapped air. The remaining solution, plus a final 20-mL portion of NH_3 eluent were passed through the resin column, and allowed to drain into the concentration

flask. The 40 mL of eluent were concentrated to approximately 1 mL according to the evaporation procedure of Junk et al. (26). If the final volume was below 1 mL, enough solvent was added to adjust the volume to 1 mL. A portion of this 1-mL final concentrate was used for gas chromatographic analysis of the individual sample bases.

The column was regenerated immediately after elution by sequential washing with 30 mL of NH_3 eluent, 50 mL of pure water, 50 mL of 3 M hydrochloric acid, and 150 mL of 1 M sulfuric acid. Finally, the column was flushed with pure water until the effluent was neutral.

Procedure for Recovery and Column Studies

To prepare samples of known solute concentration for recovery studies and column procedure tests, a certain volume of water was added to the reservoir, and a calculated amount of standard solution was then added from a syringe to produce a water sample of the desired final concentration. The solution was mixed by swirling. The spiked sample was carried through the cation-exchange concentration, evaporation, and gas chromatographic steps as outlined above. The percentage recoveries were calculated by comparing the peak heights (or peak areas) in the spiked water sample with those obtained by adding the same volume of standard solution to 1 mL of the

eluting solvent and chromatographing directly. All chromatographic peaks were normalized to an internal standard.

Analysis of Eluent Fractions

The usual sample addition and washing steps were performed for a standard sample of known concentration. During the conversion of the resin column with ammonia gas, the small amount of residual solvent that was blown out by the gas stream was collected. The total volume of this fraction was adjusted to 1 mL. The two 10-mL and one 20-mL portions of eluent were collected separately. Each was evaporated to 1-mL volume using the standard procedure, and the amount of each standard base determined by the gas chromatographic procedure outlined above.

Solvent Extraction Procedure

An aqueous sample, spiked with known concentrations of model organic compounds, was extracted with four 10-mL aliquots of purified ethyl ether. The aqueous layer was discarded and the last traces of water were removed from the combined extracts by selective freezing in a bath of liquid nitrogen. The 40-mL extract was then transferred to a concentration flask, concentrated as in the resin procedure,

and the percentage recoveries calculated after separation by gas chromatography.

Natural Samples

To prepare the river water samples, 2-L aliquots were filtered through a medium grade glass frit to remove particulates. To avoid possible adsorption on the glass collection vessels, the samples were analyzed as soon as possible after collection. Columns were loaded with 5 g of resin, and the samples were allowed to pass by gravity feed. Each column was washed with 50 mL each (2 X 25 mL) of methanol and ethyl ether to ensure complete removal of neutrals. The remainder of the procedure was identical to that used for the recovery study. After GC/MS analysis of the 1-mL concentrated sample, the sample volume was further reduced to 0.1 mL with a stream of dry helium, and rechromatographed to enhance peaks of minor components.

The same procedure was used for the disposal pit sample, except that a 300-mL aliquot was filtered through a Celite cake (0.5 cm in depth) and a fine grade glass frit. The 300-mL sample was then diluted with 700 mL of purified water for a total sample volume of 1 L. This sample was also reduced to 0.1 mL after GC/MS analysis and rechromatographed.

The shale process water sample was run without filtration,

since no particulates were present. A 50-mL sample was diluted with 50 mL of purified water and run through the same procedure as for the previous natural samples.

RESULTS AND DISCUSSION

Development of the Method

The general scheme for the selective concentration and determination of basic organic compounds in aqueous samples is as follows. A measured volume of the aqueous sample is passed through a small column filled with a special cation-exchange resin in the hydrogen form. Basic compounds take up a proton and are retained by the ion exchanger as protonated amine cations. Many neutral organic compounds are also taken up by the ion exchanger through adsorptive effects, but these are removed by washing the resin column with methanol and then ethyl ether. Next, the interstitial volume is blown out and ammonia gas is passed through the column to neutralize the hydrogen ions of the ion exchanger and partially convert the organic amine cations to the free, molecular bases. The organic bases are then eluted from the column with an organic solvent saturated with ammonia gas. The effluent is carefully evaporated almost to dryness and a portion is injected into a packed- or capillary-column gas chromatograph in order to separate the individual sample components.

In previous work in which an anion-exchange resin was used to selectively retain anions of organic acids, quaternized XAD-4 was found to work much better than the other resins

tried (42). Gel-type resins and commercial macroporous resins were found to partially disintegrate after repeated swelling and shrinking in the columns used. In addition, XAD-4 has the highest surface area of the polystyrene-based XAD resins (54). This should produce the most favorable exchange kinetics, promoting rapid exchange between the sulfonic acid sites and the analyte species. Because of this combination of factors, the cation-exchange resin in this work is prepared by sulfonating XAD-4.

Relatively strong sulfonation conditions are used, and the resin produced is dark brown in color. When the reaction period is complete, a thorough washing of the sulfonated resin is necessary to remove residual reagent and some degradation products. Nonetheless, because of these strong conditions, the capacities produced are high, averaging 2.58 meq/g.

The reproducibility of the capacities is quite respectable, with an 11.6% relative error in capacity for three separate batches of resin. In addition, the resin maintains its integrity very well despite prolonged use. The capacity of a column of resin changes by only 18.5% (from 2.86 to 2.33 meq/g) after approximately 30 cycles of adsorption, washing, elution, and regeneration. With prior washing, the blank from the resin is negligible. Overall, the sulfonation is easy to perform and the resulting ion-exchange resin performs well in all respects.

In the washing step, methanol removes the residual water from the column and elutes (at least in part) neutral compounds sorbed on the resin. The subsequent wash with ethyl ether completes the elution of neutral organics and washes out any residual methanol.

Initially, only solvent (ethyl ether or methanol) saturated with ammonia gas was used to convert the sample cations to neutral species and elute them from the column. However, it quickly became apparent that this procedure was not sufficiently reproducible. It is difficult to prepare reproducible solutions of ammonia in either solvent. Therefore, the elution of sample components varied considerably from one run to another unless a large volume of eluent was used. However, a large eluent volume necessitates a longer time for evaporation and the blank is also increased. The prior addition of ammonia gas to the column, followed by elution of sample compounds with a rather small volume of ammonia in solvent, avoids the difficulties mentioned above. Conversion of the excess exchange sites from the hydrogen form to the ammonium form artificially concentrates the eluent. Instead of these sites taking up ammonia from the eluent, no net exchange occurs (i.e. ammonium ion is exchanged for ammonium ion). Thus, all the ammonia present in the eluent is now available for exchange with the amine cations. The extremely large excess of ammonia in this situation, when

compared to the amine cations, eliminates the need for reproducibly prepared eluents. In addition, the total amount of eluent required is reduced. Neutralization of the hydrogen ion function of the exchanger with ammonia gas is followed easily by a change in color of the resin column, from dark brown to light brown.

The rather extensive purification procedure for the ethyl ether eluent was found to be necessary. The final evaporation step concentrated any impurities in the solvent as well as the compounds of interest. It was found that an untreated ether "blank" contained some interference peaks, most notably butylated hydroxytoluene, which served as an antioxidant in the solvent. After trying several less involved cleanup methods, the previously described procedure (which is based on a literature procedure (55)) was found to produce the cleanest blank.

When this research was begun, only packed chromatographic columns or coated glass capillaries were available for the gas chromatographic separation of various sample bases. This severely limited the chromatographic resolution that could be attained. However, recently developed fused silica capillary columns with a chemically bonded stationary phase provided easy separation and excellent resolution of most base mixtures.

Recovery and Column Studies

Recoveries for a wide variety of model organic bases by the cation-exchange procedure are presented in Table 1 (56). The recovery for each compound has been determined at the 1 ppm and 50 ppb concentration levels from 100-mL and 1-L samples, respectively. The following conclusions seem justified:

Virtually all of the basic compounds tested give good to excellent recoveries with at least one of the eluents. Indole and carbazole do contain nitrogen but are hardly basic at all, as indicated by their pK_b 's (57). The low basicity of these compounds is responsible for their nearly zero percentage recoveries. Diphenylamine is also a weak base and might be expected to give a low recovery. While no direct relationship between K_b and percent recovery was found, it is reasonable to assume that the procedure will work better for stronger bases than weaker ones. Stronger bases form cations more easily, because of their higher affinities for protons. Considering the wide range of compound basicities covered by this survey study, the fact that the majority of the compounds tested exhibited a high recovery with at least one eluent attests to the potential usefulness of the technique.

Several basic compounds give significantly higher recoveries when ammonia-saturated methanol is used as the

Table 1. Recovery of basic compounds from aqueous samples by the cation-exchange method^a

Compound	Recovery, %			
	<u>NH₃-ether</u>		<u>NH₃-CH₃OH</u>	
	50 ppb ^b	1 ppm ^c	50 ppb ^b	1 ppm ^c
<u>Aliphatic Amines</u>				
n-hexylamine	34	46	80	85
cyclohexylamine	35	47	79	84
n-octylamine	38	45	80	91
2-ethylhexylamine	34	48	72	98
diallylamine	84	86	88	86
dipropylamine	33	--	83	87
dibutylamine	89	93	99	99
dihexylamine	90	86	84	95
N-methylcyclohexylamine	91	91	99	97
dicyclohexylamine	84	88	86	95
triallylamine	88	88	89	91
tributylamine	89	93	91	96
<u>Aromatic Amines</u>				
aniline	88	90	95	95
o-toluidine	88	87	88	96

^a Column is 90 X 8 mm filled with sulfonated XAD-4; total capacity is 7 milliequivalents. All recoveries are an average of four runs.

^b 1 L sample.

^c 100 mL sample.

Table 1. Continued

Compound	<u>Recovery, %</u>			
	<u>NH₃-ether</u>		<u>NH₃-CH₃OH</u>	
	50 ppb ^b	1 ppm ^c	50 ppb ^b	1 ppm ^c
m-toluidine	87	99	89	99
o-chloroaniline	83	85	82	97
p-chloroaniline	84	92	83	97
2,5-dichloroaniline	65	92	79	92
N-methylaniline	90	90	98	98
N,N-dimethylaniline	86	88	99	99
N,N-diethylaniline	91	89	96	97
diphenylamine	10	15	46	48
1-naphthylamine	80	74	80	81
o-phenylenediamine	35	69	39	71
<u>Heterocyclic Compounds</u>				
pyrrolidine	<3	6	65	71
piperidine	6	17	93	93
morpholine	46	67	99	98
N-methylmorpholine	93	99	92	99
piperazine	<3	4	86	92
imidazole	<3	10	91	100
3-methylpyrazole	44	78	87	97
3,5-dimethylpyrazole	45	78	91	97
indole	0	0	0	0
carbazole	<3	4	<3	4
pyridine	76	87	95	95

Table 1. Continued

Compound	Recovery, %			
	<u>NH₃-ether</u>		<u>NH₃-CH₃OH</u>	
	50 ppb ^b	1 ppm ^c	50 ppb ^b	1 ppm ^c
2-picoline	87	89	94	98
4-picoline	96	90	95	99
4-isopropylpyridine	88	88	92	96
2,4-lutidine	90	91	91	94
2,6-lutidine	98	98	98	97
2,4,6-trimethylpyridine	90	88	100	100
2-aminopyridine	40	60	89	99
2,2'-bipyridyl	86	100	90	100
quinoline	90	97	99	99
isoquinoline	87	100	99	100
quinaldine	88	87	97	97
2,6-dimethylquinoline	90	90	97	98
acridine	90	90	88	89
benzo[h]quinoline	90	91	95	96
benzo[f]quinoline	92	93	98	98
2-methylpyrazine	83	88	93	96
quinoxaline	77	76	99	94
2,3-dimethylquinoxaline	84	85	90	95

eluent. This is a consequence of the higher solubility of ammonia in methanol, and perhaps of the better solvating properties of methanol, compared with ethyl ether. Distilled-in-glass methanol is available, which requires no further purification, while ether must be purified before use. However, the greater volatility of ethyl ether and its superior properties as a gas chromatographic solvent make it the eluent of choice for those compounds where the recovery is satisfactory.

The lower recoveries of some aliphatic amines and o-phenylenediamine were due at least partly to losses during the concentration and evaporation steps. This is illustrated by the data in Table 2. A series of aliphatic primary amines of varying chain length were added to a 40-mL aliquot of purified ether, and were then taken through the evaporation procedure. Several of the poorly recovered model bases were also included in the experiment. After reduction of the solvent volume to 1 mL, the recoveries of the model compounds were compared to a spiked 1-mL standard according to the usual gas chromatographic procedure. Losses of at least 35% were seen for all of the aliphatic primary amines through tetradecylamine. This probably resulted from a combination of volatility losses for the low molecular weight homologs and adsorption of the long chain amines on the glass walls of the concentration flasks. Adsorption of straight chain primary

Table 2. Recovery of organic bases after evaporation step^a

Compound	Recovery, % ^b
n-butylamine	33
n-pentylamine	65
n-hexylamine	60
n-heptylamine	59
n-octylamine	50
n-decylamine	52
n-dodecylamine	45
n-tetradecylamine	35
o-phenylenediamine	60
diphenylamine	101
carbazole	105

^a Ammonia-saturated ether eluent. All compounds at a concentration of 625 ppb.

^b Average of two trials.

amines on glass had been previously reported (58). The loss of the strong base o-phenylenediamine during the concentration step was also large. The surface of the concentration flasks was not deactivated, in order to keep any possible contamination of the reduced volume samples to a minimum. Considering these results, this decision may have to be reevaluated when analyzing samples suspected of containing strong bases or aliphatic primary amines. The weak bases, carbazole and diphenylamine, were completely recovered during the concentration procedure. This further indicated that loss of these compounds was primarily due to their poor affinity for the cation-exchange resin. The losses of n-hexylamine and n-octylamine in the evaporation step were nearly equal to the losses that occurred in the entire procedure (compare the recoveries listed in Tables 1 and 2). This would indicate that the cation-exchange part of the procedure works well for compounds of this type. Use of ammoniacal methanol as the eluent would probably increase any evaporative losses because of the higher temperatures and longer evaporation times required. However, adsorptive losses could be lessened somewhat by the use of methanol because of its higher polarity compared to ethyl ether. Apparently, the reduction in adsorption was a more important factor, because the recoveries of aliphatic bases with the methanol eluent were much higher than those with the ether eluent. Methanol should therefore

be considered the eluent of choice when analyzing samples containing (or suspected of containing) aliphatic bases.

A series of experiments were run to test various aspects of the column recovery procedure. Most of the survey recovery data was determined using packed column gas chromatography. However, capillary columns have been much better suited to the analysis of real samples. The vast improvement in resolution obtainable with capillary gas chromatography was desirable, since the actual complexity of the sample would be unknown. Table 3 shows that the recoveries of a series of representative model compounds were generally consistent whether the final gas chromatographic step was performed using packed or fused silica capillary columns (Columns 1 and 2). Significant differences in recovery were only seen for poorly recovered compounds. These discrepancies could be better attributed to variability in the exchange and concentration steps than to the gas chromatography. Table 3 also shows that the recoveries of most compound types were somewhat improved by deactivation of the reservoirs used for sample addition (Columns 2 and 3). Improved recoveries on deactivated glassware were seen for 9 of 11 compounds. Generally, recoveries for well-retained bases were reproducible to within 5% or less for multiple runs. Accounting for this reproducibility, improved recoveries were seen in four instances, with several others being borderline cases.

Table 3. Recoveries of selected organic bases using packed and capillary GC^a columns with normal and deactivated glass reservoirs^a

Compound	Pckd/Datvd ^c	Recovery, % ^b	
		Cply/Datvd	Cply/Active
n-octylamine	45 ± 4	11 ± 3	6 ± 5
diphenylamine	15 ± 3	22 ± 7	21 ± 12
triallylamine	88 ± 2	98 ± 1	83 ± 1
m-toluidine	99 ± 3	101 ± 4	94 ± 3
2,5-dichloroaniline	92 ± 5	93 ± 3	95 ± 2
1-naphthylamine	74 ± 3	96 ± 6	92 ± 6
4-picoline	90 ± 2	91 ± 2	85 ± 1
4-isopropylpyridine	88 ± 3	94 ± 3	89 ± 1
2,4,6-trimethylpyridine	88 ± 1	98 ± 5	85 ± 3
2-methylpyrazine	88 ± 3	91 ± 2	82 ± 1
o-phenylenediamine	69 ± 5	16 ± 4	20 ± 5

^a Ammonia-saturated ether eluent.

^b All are averages of 3 or more runs. Analyte samples were 100 mL of 1 ppm solution.

^c Data from Table 1 and reference 56.

Considering that the glass surface contact area of the reservoirs was large and the concentrations of the compounds of interest in the sample low, it was decided that any adsorption problems at this stage in the procedure would outweigh possible contamination resulting from deactivation reagents. In addition, most contaminants from the surface of the reservoirs would either pass through the resin column to waste, or would be removed during the washing steps. Coupling the results of this study with those of the study on losses during evaporation, it was concluded that deactivation of the reservoirs, while perhaps not essential, was probably a prudent measure.

In the usual experimental procedure, care was taken to convert only about 90% of the resin column to the ammonium form. The purpose of this was to prevent losses of volatile bases that might undergo gas-phase exchange with the ammonia. The few milliliters of interstitial ether that were blown out of the column by the ammonia gas were collected for the same reason. Two experiments, using ammoniacal ether as the eluent, were run to determine whether or not any losses actually occurred under these circumstances. In each experiment, a mixture of model compounds was concentrated in the usual fashion. However, in one experiment, elution was preceded by complete conversion of the resin column with ammonia gas. In the second experiment, two columns were run,

and eluent fractions (the 1 mL of residual ether, two 10-mL portions, and one 20-mL portion of eluent) from each column were collected separately, concentrated, and the amount of the model compounds present in each fraction determined chromatographically. Residual ether was removed from one column in the second experiment by passage of the ammonia gas. A stream of air was used to remove the ether in the second column, prior to the treatment with ammonia gas.

Table 4 compares the recoveries of the model compounds on the completely converted columns with recoveries obtained under standard conditions. The recoveries for all of the model compounds tested were the same within experimental error. Complete conversion of the column appeared to have a negligible effect on recoveries, at least for compounds that were strongly retained. None of the compounds in the survey study was particularly volatile compared to ethyl ether. For those that had some degree of volatility, one would expect higher losses in the final evaporation step than in the ammonia gas treatment. Therefore, the most appropriate conclusion seemed to be that great care need not be taken to prevent complete conversion of the resin column. While the 90% conversion procedure was maintained for consistency, any data obtained from columns that may have been completely converted unintentionally were considered valid.

Table 4. Comparison of recoveries for completely converted and 90% converted columns^a

Compound	Recovery, %	
	Total Conv.	90 % Conv.
triallylamine	87	88
m-toluidine	93	99
4-picoline	87	90
4-isopropylpyridine	93	88
2,4,6-trimethylpyridine	87	88

^a Samples of analyte mixtures are 100 mL of 1 ppm solution. Ammonia-saturated ether eluent was used.

The data in Table 5 represent the fractional recoveries obtained during each step in the elution procedure. Several conclusions can be drawn from this data. Elution of the model bases was 80-90% complete (i.e. 80-90% of the final recovery value was obtained) after passage of the first two 10-mL portions of eluent. The percentage of elution was approximately equal between the two aliquots. The final 20-mL elution removed a considerably smaller percentage of the total. Therefore, it was inferred that further reductions in the elution volume might be possible without a large loss in recovery efficiency.

With the exception of a very small amount of 2,4,6-trimethylpyridine, none of the test compounds was found in the residual solvent initially blown out of the column. In fact, even the peaks identified as trimethylpyridine were so small that they could conceivably have been spurious peaks, rather than the test compound. Nonetheless, it appeared that a negligible amount of elution occurred during this process. Therefore, small losses of eluent in this step should affect the final recovery very little.

The combined fractional recoveries were consistent with, although slightly lower than, those obtained by the usual procedure. This was most probably a result of the study requiring three collection and concentration steps instead of one. Any small losses that occur each time would have been

Table 5. Fractional recoveries of organic bases on air-dried and ammonia-dried columns

Compound	Recovery, % ^a									
	<u>Interstitial</u>		<u>1st 10 mL</u>		<u>2nd 10 mL</u>		<u>Final 20 mL</u>		<u>Total</u>	
	Air	NH ₃	Air	NH ₃	Air	NH ₃	Air	NH ₃	Air	NH ₃
Triallylamine	0	0	43	52	41	32	10	2	94	86
m-Toluidine	0	0	28	46	41	50	11	10	80	106
4-Picoline	0	0	30	31	34	35	17	7	81	73
4-Isopropylpyridine	0	0	36	42	32	30	13	7	81	79
2,4,6-Trimethylpyridine	3	2	40	42	32	30	10	5	85	79

^a Ammonia-saturated ether eluent. Samples are 100 mL of 1 ppm solution.

additive. Additionally, the recoveries of the model compounds on the air-dried column were generally lower than those on the ammonia-dried column. This was an unanticipated result and cannot be readily rationalized. Since negligible elution occurred during the drying step, one would expect the gas used to have little bearing on the overall recovery. This was borne out by the fact that the amount of each model compound in the interstitial solvent fraction was the same in each case. The only potentially significant change in the general elution pattern seen was an increase in the amount of each base eluted by the final 20-mL portion on the ammonia dried column. Any effect of the choice of drying gas would be expected to manifest itself in the early elution pattern, when unoccupied sites might still be available, so it is doubtful that this could be caused by the choice of column drying gas. Therefore, larger than normal experimental error seems to be the most probable explanation, and no real difference in the procedures can be assumed. Combining the residual solvent removal with the conversion step through the use of ammonia gas was the most convenient procedure, and therefore was the method of choice.

The selectivity of the cation-exchange concentration process for basic compounds was checked by running several neutral organic compounds through the procedure. With either eluent, the recoveries of ethylbenzene, o-dichlorobenzene,

indene, naphthalene, methyl benzoate, and diethylphthalate were essentially zero at 1 ppm initial concentration. In addition, acetal, hexanal, bromoform, n-decane, mesitylene, and 2-ethyl-1-hexanol gave zero percent recoveries at 1 ppm using the NH_3 -ether eluent. This selectivity was undoubtedly a consequence of the washing steps because at least some neutral organic compounds were known to be taken up on the ion-exchange resin. Dichlorobenzene was detected in the concentrated methanol wash during the analysis of dichlorobenzene and several organic bases. Indeed, most of the neutral organics seemed to have been removed with the methanol wash, because no compounds in significant concentration were detected in a concentrated ether wash during the analysis of a mixture of bases and neutrals.

Solvent Extraction Study

For several model compounds, a spiked aqueous sample was extracted four times with 10 mL of ethyl ether. The combined extracts were evaporated and the solutes present separated by gas chromatography. Ammonia-saturated ether was not used because extraction of basic material would be reduced with a basic extractant. The recoveries of these model compounds were compared with recoveries obtained by the ion-exchange procedure in Table 6. The model compounds were chosen so as

Table 6. Comparison of recoveries with solvent extraction and cation-exchange^a

Compound	Recovery, %	
	Solvent Extraction	Resin Procedure
dihexylamine	64 ± 5	86 ± 1
tributylamine	73 ± 4	93 ± 4
o-toluidine	81 ± 7	87 ± 2
N-methylaniline	78 ± 7	90 ± 4
N,N-diethylaniline	65 ± 8	89 ± 3
2,5-dichloroaniline	78 ± 8	92 ± 5
2,4,6-trimethylpyridine	72 ± 6	88 ± 1
2-aminopyridine	12 ± 2	60 ± 2
quinoline	83 ± 6	97 ± 3
isoquinoline	79 ± 9	100 ± 3
imidazole	2 ± 3	10 ± 4
indole	75 ± 12	0 ± 0

^a Samples are 100 mL of 1 ppm solution.

to represent a wide variety of classes of organic bases. A higher recovery (and better precision) was obtained in every case by the ion-exchange method except for indole, which is really not basic and should give a low recovery in the ion-exchange procedure. The low recovery of imidazole by each method could be due to its high polarity (in the solvent extraction procedure) and to losses during evaporation. These data indicate that the ion-exchange method should be superior to simple solvent extraction for the concentration of most types of organic bases.

Analysis of Natural Samples

No analytical procedure is really useful unless it can be readily applied to the analysis of natural samples. Several different naturally occurring complex mixtures of aqueous organics were used to test the utility of the cation-exchange procedure. These samples varied in complexity, as well as in the concentrations and classes of organics present. Generally, the amount and variety of basic compounds found in natural water samples are much less than for acids and neutrals (59). Basic material may be adsorbed on particulate matter in the water or associated with the humic and fulvic acids usually present. In addition, there are fewer natural sources of basic materials, so the presence of organic bases

in a natural water system can usually be attributed to an outside source. As an example, the discovery of aromatic amines in the Buffalo River was attributed to the effluent from a nearby dye manufacturing plant (60).

Analyses of water samples from the Skunk River (IA) and the Delaware River (PA) by the cation-exchange procedure also showed little basic material. The chromatogram of the Delaware River extract showed three small peaks, two of which were tentatively identified as pyrazole and a methylethylpyridine isomer by GC/MS analysis (with the best match for the latter being the 5-ethyl-2-methyl isomer). The third peak was unidentified. Possible sources of these compounds were not readily known. However, 5-ethyl-2-methylpyridine had been previously reported as one of 11 malodorous pollutants identified in the Kanawha River (WV) (61). Nicotine was the only compound identified by GC/MS in the Skunk River sample. A second 2-L aliquot of the same sample again showed the presence of nicotine, but also some benzo(h)quinoline. A third aliquot was analyzed to check for these two compounds, but only nicotine was found. Nicotine has been found previously in natural bodies of water and drinking water (59,62). Several other very small peaks remained unidentified. While a quantitative analysis was not performed, a rough estimate of the nicotine concentration would be below 50 ppb.

Identification of compounds present in the river water samples, and in the rest of the natural water samples analyzed, was based on combined gas chromatography-mass spectrometry. The mass spectrum of each peak in the chromatogram was matched to the standard reference library of the National Bureau of Standards. Direct retention time matching was not possible because the columns and gas chromatographic conditions used in the initial work and the GC/MS work were not identical. The best library match for a particular unknown compound (if found) was determined by comparing the number of mass peaks in the unknown that corresponded to a peak of the same mass in a reference spectrum, and the relative intensities of all such peaks. Initial runs on river water concentrates produced "matches" that were highly suspect. Further tests of the system by running standard nitrogen-containing compounds also gave poor matches to the library file, especially for aliphatic amines. Investigation of this problem discovered a flaw in the comparison procedure. Rather than compare an unknown spectrum to each spectrum in the reference file, a subfile of the 50 most likely candidate compounds was created by checking two criteria:

- 1) The presence of a peak in the unknown spectrum (especially an intense one) corresponding to the molecular mass peak of the reference compound.

- 2) Matching the eight largest peaks in the unknown spectrum above $m/e=45$ with peaks in the reference. At least 7 of the 8 had to be present, or the reference spectrum was rejected.

As a rule, amines, especially aliphatic amines, do not exhibit a large M^+ peak, and they tend to fragment very easily. Therefore, the preponderance of peaks in their mass spectra appear below $m/e=45$. Thus, the subroutine was actually rejecting out of hand the best fitting reference spectra because the initial matching criteria were not being (and in many cases, could not be) met. This situation was rectified by adding the spectra of many of the standard compounds to the reference file and expanding the m/e range over which the matching was performed. In retrospect, the tentative identifications originally proposed by the system, typically long-chain hydrocarbons, are reasonable once the initial matching criteria are taken into account.

This problem did not reappear in the later work that was performed on a different GC/MS system. A general absence of low molecular weight bases and aliphatic amines in the disposal pit and shale oil supernatant samples examined could also be a mitigating factor here.

The gas chromatogram of compounds isolated from a sample of supernatant water from an agricultural chemical disposal

pit after concentration by the ion-exchange procedure is shown in Figure 1. Many of the compounds present were identified, at least tentatively by GC/MS analysis. The compounds identified were the following: 1-naphthylamine, Simazine, Atrazine, Dichlobenil, Diphenamid, N,N-dimethylcyclohexylamine, and Trietazine. All but the last two have been confirmed by matching retention times with those of authentic samples (standards were not available for the remaining two compounds). In addition, acetophenone was identified, which of course contained no nitrogen. The herbicide Dichlobenil (2,6-dichlorocyanobenzene) contains only cyano nitrogen. The herbicide Diphenamid (N,N-dimethyl-2,2-diphenylacetamide) contains only the very weakly basic amide group. In this particular case, the resin did not discriminate cleanly against neutral and weakly basic compounds, as had been observed in the previous studies of the column procedure. The reasons for this were not entirely clear. Perhaps there were strong interactions of these compounds with the resin matrix or sulfonate groups. Another possibility is that if any of these compounds was present in very high concentrations, the amounts of solvent used in the washing steps may have been insufficient to remove them completely. Following elution, this column was washed with another 20 mL of ethyl ether, and the wash solution was concentrated and chromatographed. Acetophenone, Diphenamid,

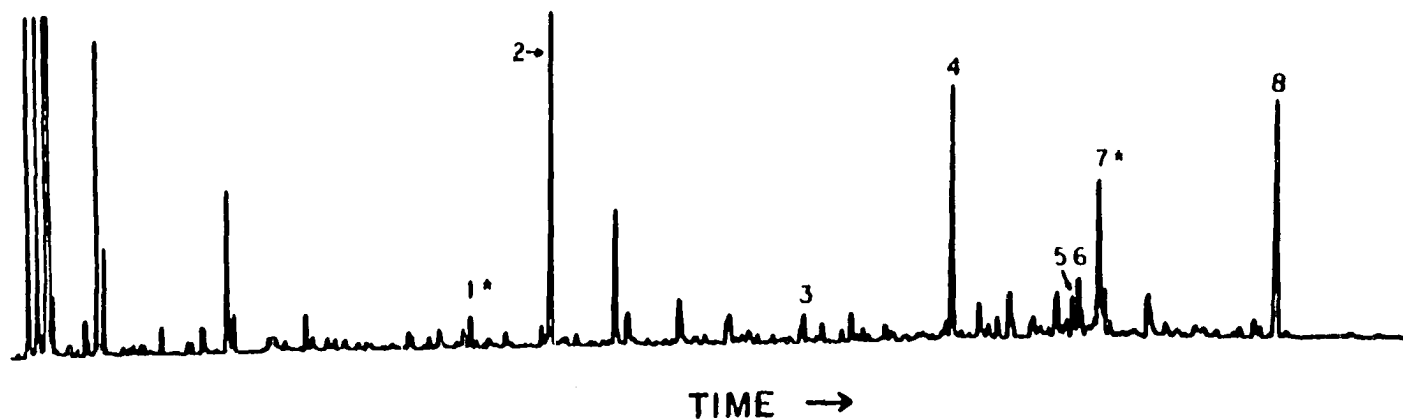


Fig. 1. FID chromatogram of compounds isolated by the resin procedure from 300 mL of water from an agricultural chemical disposal pit. Sample concentrated to 0.1 mL. Column is 27 m x 0.25 mm thick film (1 micron) DB-5. Column held at 50°C for 4 min, then programmed at 5°C/min to 250°C and held for 10 min. Injection volume was 2 μ L split 100:1; with helium carrier gas. Compounds identified by GC/MS: 1 = N,N-dimethylcyclohexylamine; 2 = acetophenone; 3 = Dichlobenil; 4 = 1-naphthylamine; 5 = Simazine; 6 = Atrazine; 7 = Trietazine; 8 = Diphenamid. *Indicates compounds not confirmed by retention time matching.

and very small amounts of the triazine herbicides were found in the wash solution. None of these compounds are particularly strong bases, but all of them do have a significant degree of aromatic character. It is likely then that the predominant mode of retention for these compounds was adsorption, rather than exchange. Washing the column with larger volumes of organic solvent probably would have removed them completely. The amount of Dichlobenil in the eluted sample was very small, so it is not surprising that it is not seen in the succeeding ether wash concentrate. The triazine herbicides, which contain amino functionalities, do have some basic character, so they may be at least partially taken up by exchange.

A sample of shale oil process water was carried through the ion-exchange concentration scheme with subsequent gas chromatographic analysis. The chromatogram, shown in Figure 2, contained over 60 peaks. Combined GC/MS analysis indicated that most of the peaks were substituted pyridines, anilines, and quinoline isomers. The identification of several compounds was confirmed by retention time matching with known compounds. Those compounds identified include pyridine, 2-picoline (2-methyl-pyridine), 4-picoline, 2,6-lutidine (2,6-dimethylpyridine), 2,4-lutidine, aniline, 2,4,6-trimethylpyridine, and isoquinoline. Quantitative analysis was performed for these compounds. The

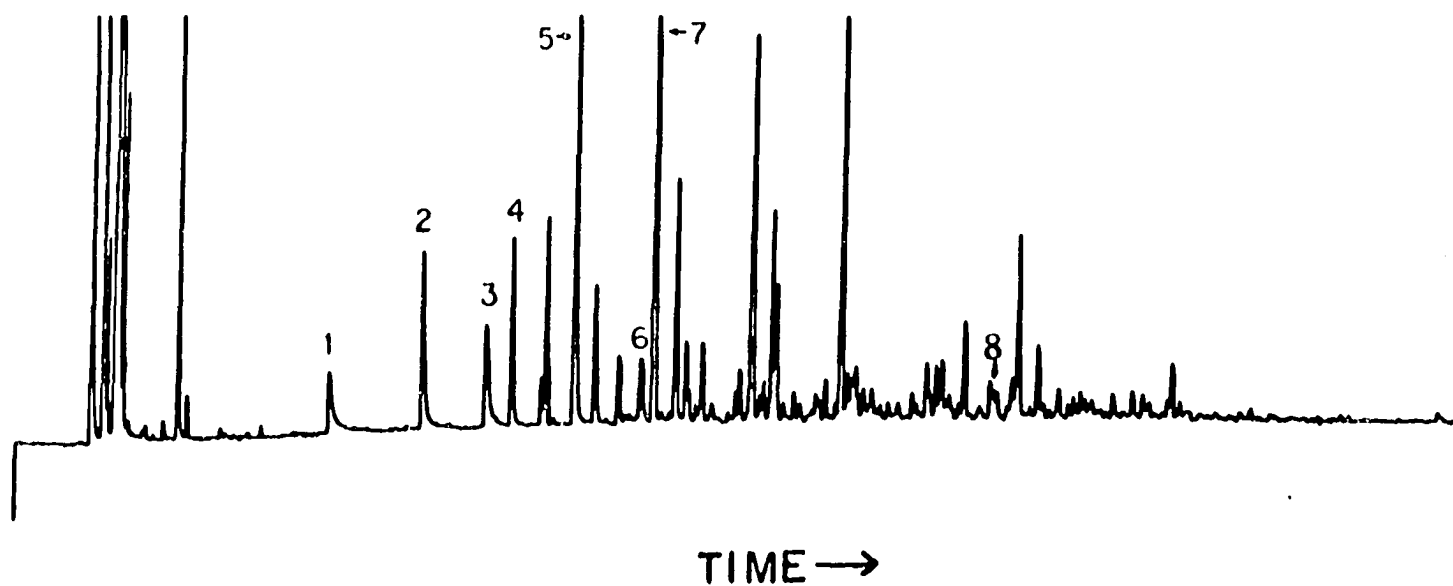


Fig. 2. FID chromatogram of basic material isolated from shale oil process water. GC conditions same as in Fig. 1. Compounds identified by GC/MS and confirmed by retention time matching: 1 = pyridine; 2 = 2-picoline; 3 = 4-picoline; 4 = 2,6-lutidine; 5 = 2,4-lutidine; 6 = aniline; 7 = 2,4,6-trimethylpyridine; 8 = isoquinoline.

concentrations were estimated by comparison to external standards, followed by correction for the percent recovery attained at 1 ppm concentration in the eluting solvent, ethyl ether (refer to Table 1). This recovery figure was used because comparison to standards and previous analytical results placed most of the concentrations in the 1-10 ppm range from 100 mL of solution (63). It was felt that recoveries at 1 ppm concentrations would most closely resemble those for concentrations larger than 1 ppm. In addition, the recoveries at this concentration level were generally higher than those at 50 ppb, so that any estimation of concentrations using these recovery figures would be maximum estimates. Triallylamine was used as internal standard to account for any discrepancies in the gas chromatography. Two 50-mL samples of shale oil water, each of which was diluted to 100 mL total volume with distilled water, were analyzed. The combined results for the eight test compounds are shown in Table 7. These results were compared with those from other analyses of the same sample, using methylene chloride extraction and steam distillation. These analyses were performed by workers both at the Ames Laboratory and at other laboratories across the country (64). The concentrations estimated by the cation-exchange method were in excellent agreement with the other results for 7 of the 8 compounds tested as seen in Table 8. Only the results for pyridine deviated markedly from the

Table 7. Compounds found in shale oil process water

Compound	Concentration (ppm) ^a
pyridine	22.0
2-picoline	5.8
4-picoline	5.2
2,4-lutidine	17.0
2,6-lutidine	2.9
2,4,6-trimethylpyridine	17.6
aniline	1.6
isoquinoline	1.3

^a Average of two runs.

Table 8. Concentration of bases present in shale oil process water by different analytical methods

Compound	Concentration (ppm)		
	Steam Distr ^a	Solvent Extn ^a	Resin Extn
pyridine	5.4	--- ^b	22.0
2-picoline	5.0	3.4	5.8
4-picoline	4.7	5.3	5.2
2,4-lutidine	15.0	18.0	17.0
2,6-lutidine	3.2	2.1	2.9
2,4,6-trimethylpyridine	19.0	21.0	17.6
aniline	1.9	1.8	1.6
isoquinoline	1.4	2.1	1.3

^a Data from Reference 64.

^b Not determined.

results of the other analyses. Concentration values for pyridine of >20 ppm were determined in the two runs described, but analysis of a third, smaller sample for pyridine gave a value of 1 ppm. There appears to be a serious source of error somewhere in the analysis of this compound, and the concentration results obtained for it are extremely questionable. The pyridine peak in the gas chromatogram was somewhat tailed, and its relatively poor chromatography under the conditions used may account for some of the error. However, when the overall concurrence of the values for the remaining compounds was taken into consideration, the resin technique seems to have performed quite well.

CONCLUSIONS

A cation-exchange resin can be used to selectively remove basic material from complex mixtures of organic compounds in aqueous solution. Bases are retained as cations at the exchange sites of the resin. Adsorbed neutrals are removed by washing the resin column with organic solvents. Unoccupied H^+ -form sites on the resin are converted to the NH_4^+ form by passage of ammonia gas. The concentrated bases are then eluted with an ammonia-saturated organic solvent, the eluent further concentrated by evaporation, and the bases separated by gas chromatography.

The cation-exchange resin used was synthesized by sulfonation of the macroreticular resin, XAD-4. The rigid structure of this poly(styrene-divinylbenzene) prevents swelling of the resin column upon changing from aqueous to organic solvents. The high surface area of XAD-4 and the use of a silver-salt catalyzed sulfonation procedure produces a high capacity cation exchanger.

A survey study of over 50 different organic bases was performed to test the ability of the column to retain bases of various types from aqueous solution. The majority of the compounds tested show recoveries of greater than 85% at the 1 ppm and 50 ppb levels with either ammonia-saturated ethyl ether or ammonia-saturated methanol. While no direct

relationship between basicity and retention was discovered, the procedure works better for stronger bases, because of their enhanced proton affinities. In particular, aromatic amines and pyridines are recovered well. To test the selectivity of the method for basic material, the procedure was applied to a variety of neutral compounds. The recoveries of all of the neutral compounds examined were zero.

Significant losses of long-chain primary amines and o-phenylenediamine occurred during the evaporation step, probably through volatility losses or adsorption on the glass vessels. Either packed column or capillary column gas chromatography can be used as the final separation technique. Insignificant losses of well-retained compounds were observed if the column was completely converted with ammonia gas, rather than 90% converted. In addition, insignificant amounts of most bases were present in the interstitial solvent blown out during the resin conversion step. Deactivation of the reservoirs used for sample addition marginally improved recoveries. Although 40 mL of eluent was usually used, recovery was 80-90% complete after addition of first 20 mL (as two 10-mL portions).

The cation-exchange procedure was shown to be superior to a simple solvent extraction procedure for the isolation and concentration of organic bases. Ethyl ether was used as the extracting solvent. Percent recoveries were higher for 11 of

the 12 compounds tested. Run-to-run reproducibility was also improved.

The procedure generally performed well when applied to a number of natural samples. Pyrazole and 5-ethyl-2-methylpyridine were tentatively identified in a sample of Delaware River (PA) water. Nicotine was found in a sample of water from the Skunk River (IA). Analysis of supernatant water from an agricultural chemical disposal pit produced a variety of basic herbicides, plus some neutral compounds. Insufficient removal of these neutral compounds by the preliminary washing steps was evident. The compounds were probably retained by adsorption on the resin matrix. A sample of shale oil process water produced a basic fraction containing over 60 components. Most of the compounds present were pyridines, substituted anilines, and quinoline isomers. Eight of the compounds present were identified by GC/MS and retention time matching. Quantitative analysis of these 8 compounds gave excellent agreement with data collected from other workers in 7 of the 8 cases.

Cation exchange appears to have great potential as an analytical technique for the concentration and isolation of basic organic material from aqueous solution. Resin synthesis is simple to perform. The method is easy to use and relatively rapid. The possible concentration factors that can be achieved are virtually unlimited. Major interferences from

other components of a complex mixture are almost always eliminated. The aqueous matrix is replaced by an organic solvent, so gas chromatography can be applied easily. The future of this technique appears to be limited only by the variety of samples that it can handle.

FUTURE WORK

With the exception of some possible streamlining of the procedure, all of the future work on this method should deal with its application to various specific sample types. Interesting uses might possibly include the isolation of drugs and drug metabolites from physiological fluids, and the concentration of basic herbicides from natural water. Testing the procedure in nonaqueous solvents might produce a technique useful for the separation and analysis of the basic fraction of crude oils, coal tars and other petroleum products. Crude fractionation of coal tar and similar products has shown that all of the carcinogenic activity is found in the basic fraction. Adaptation of this technique to gas-phase exchange may produce a means of isolating the organic bases found in cigarette smoke and other gaseous emissions. Finally, combining this cation-exchange method with the analogous anion-exchange procedure already developed for acids may result in a simple total fractionation scheme for aqueous acids, bases, and neutrals that would take only a few steps to complete.

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SECTION II. POROUS, BIFUNCTIONAL CHELATING RESINS AND OTHER
ION EXCHANGERS FOR THE DECONTAMINATION OF NUCLEAR
WASTE

INTRODUCTION

Nuclear Waste Decontamination

The decontamination and storage of nuclear waste are among the most significant problems facing today's nuclear industry. A safe and effective means of waste cleanup will be essential if fission is to become a popular and lasting energy alternative.

Radioactive waste, both from defense-related processing and industrial reactors, occurs in several different forms. Perhaps the most voluminous is "high level" (≥ 1 Ci/L) liquid waste. In most industrial reactors, the nuclear fuel used is uranium-238 that has been isotopically enriched with uranium-235. When bombarded by a flux of thermal neutrons, the uranium-235 fissions into heavy and light daughter isotopes. The energy released during fissioning is harnessed, usually as heat, to do useful work. In other instances, unenriched uranium-238 is used as a fuel. Here the flux of neutrons transmutes the uranium-238 to useful isotopes, such as plutonium-239. However, all uranium-238 contains small amounts of uranium-235, and some fissioning of this material occurs along with the transmutation of uranium-238. In either situation, removal of troublesome residual radionuclides would facilitate both waste disposal and fuel reprocessing.

A wide variety of extraneous isotopes are associated with the fission process, including transuranics, transition metal isotopes, and smaller nuclei. Of those contained in high-level waste, the most common are the cesium-137 and strontium-90 daughter isotopes produced from the fission of uranium-235. Cesium-137 is a high-energy gamma emitter with a 30 year half-life. Strontium-90 is a beta emitter with a 29 year half-life. Generally, only gamma emitters pose a serious radiation danger, because alpha and beta particles will not penetrate the skin. However, strontium-90 can be incorporated into the body, as a replacement for calcium (1,2). Once ingested, beta emitters can be a significant health risk. The hazards from these radionuclides require, therefore, that high-level waste be isolated from the biosphere until the activity decays to safe levels. In the cases of cesium-137 and strontium-90, this would be a period of several hundred years. Various waste management procedures have been instituted to ensure that radioactive waste material produced from fission reactors is safely isolated from the environment. The three general approaches to waste management are "delay and decay", "dilute and disperse", and "concentrate and contain" (2). The third option, concentrate and contain, is the only viable approach to the management of wastes containing cesium-137 and strontium-90, because of the long half-lives and relatively large degree of radioactivity

involved. Whereas the work in this section of the dissertation deals exclusively with ion exchange for the selective removal and concentration of cesium-137 and strontium-90, any further discussion of decontamination methods will be restricted to methods for radioisotopes of these two elements.

The waste processing performed at the Savannah River Laboratory (USDOE) typifies most waste management procedures (3). After irradiation of the fuel rods is complete, they are dismantled and dissolved in nitric acid. Any useful product isotopes and unburnt uranium fuel are removed from this acidic solution during reprocessing, usually by selective solvent extraction. The most common procedure, called the Purex process, uses tributylphosphate as the extracting agent. The remaining waste solution, designated high-level waste, is made alkaline with sodium hydroxide to inhibit corrosion of pipes and storage tanks, and stored temporarily in settling tanks. In these tanks, particulates are allowed to settle out and heavy metal ions precipitate as their hydroxides. Most of the radioactive strontium present (primarily strontium-90) is carried down during the precipitation, as well. The sedimentation of these materials gradually forms a sludge layer in the tanks. This sludge, containing most of the total radioactivity of the waste, will be permanently immobilized in one of a variety of forms. Among the materials under

consideration as permanent waste forms are borosilicate glass (currently the most popular) (4,5), cement (6), ceramics (7,8), thermosetting resins (9), and asphalt or bitumen (10,11). After immobilization, the waste will be permanently stored, either in a geological repository or by a process such as shale hydrofracture (12,13). The supernatant solution that remains after sedimentation of the sludge is an alkaline aqueous brine containing about 10% of the original radioactivity of the waste, mostly as cesium-137. The approximate composition of this supernatant solution is given in Table 1. This supernatant salt solution is concentrated by evaporation and is stored onsite in subterranean tanks. Approximately 70 million gallons of waste is currently being stored in this fashion at three different sites (13).

Isolation Methods for Cesium-137 and Strontium-90

Tank storage of waste supernatant is precluded as an effective isolation procedure for cesium-137 and strontium-90, because the tanks' integrity cannot be guaranteed for a sufficiently long time. In recent years, much research has been conducted on methods for the selective removal of these isotopes during processing. If these radionuclides can be separated from the bulk supernatant and concentrated into a small volume, this could be added to the radioactive sludge

Table 1. Composition of solids in soluble nuclear defense waste

Compound	Weight Percent	Molarity
NaNO ₃	48.8	2.33
NaOH	13.3	1.34
NaNO ₂	12.2	0.71
NaAl(OH) ₄	11.1	0.38
Na ₂ CO ₃	5.21	0.20
Na ₂ SO ₄	5.99	0.17
NaCl	0.368	0.025
NaF	0.183	0.0175
Na ₂ SiO ₃	0.139	0.0046
Na ₂ CrO ₄	0.160	0.00395
NaHgO(OH)	0.0101	--- ^a
Na ₂ MoO ₄	0.0263	---
NaAg(OH) ₂	2.28 x 10 ⁻⁴	---
KNO ₃	0.599	---
CaSO ₄	7.69 x 10 ⁻⁴	---
Na ₂ C ₂ O ₄	0.319	---
Na ₃ PO ₄	0.419	---
NH ₄ NO ₃	0.0240	---
Other Salts	0.633	---
Cs-137	---	7.00 x 10 ⁻⁵
Total Cs	---	1.80 x 10 ⁻⁴
Sr-90	---	2.00 x 10 ⁻⁸
Total Sr	---	6.00 x 10 ⁻⁸

^a Three dashes indicates an amount of insignificant magnitude or importance.

for permanent immobilization. The remaining decontaminated supernatant could then be desalinated and recycled. Should disposal of the remainder of the supernatant eventually be preferred, it could be done with minimal precaution in a nonrestricted repository or landfill. In addition, cesium-137 and strontium-90 have both been found to have beneficial applications, for example, in thermoelectric devices and sterilization procedures. Recovery from high-level waste would provide an abundant source of these isotopes to industry.

Any suitable method for the removal of cesium-137 and strontium-90 from waste supernatant should meet certain criteria. Among these desirable characteristics would be the following:

- 1) Selectivity for the ions of interest.
- 2) High capacity for both analyte species.
- 3) The ability to concentrate the hazardous isotopes into a small volume.
- 4) The possibility of converting the liquid waste to a solid form prior to immobilization.
- 5) Ease of use on an automated, remote-control basis.
- 6) Cost effectiveness.

A number of different analytical techniques fulfill these

requirements to varying degrees, and their potential for waste decontamination has been examined. A bibliography of articles on the recovery of fission products published through 1966 has been compiled by Vojtech (14). An excellent review on the separation of fission products from liquid wastes, covering the literature up to 1972, is that by Kourim and Vojtech (15).

Among the earliest methods used for the removal of cesium-137 and strontium-90 from liquid wastes were the related techniques of precipitation, co-precipitation, and co-crystallization. Cesium-137 can be removed from slightly acidic waste by co-crystallization with aluminum sulfate (16). Heteropoly acids, such as phosphomolybdic and phosphotungstic, have also been used to remove cesium-137 from acidic waste, either by direct precipitation or, for low levels of cesium-137, by co-precipitation with another alkali metal carrier (15,17). Transition metal ferrocyanides will precipitate cesium-137 from moderately alkaline solution (18, 19). For example, nickel ferrocyanide has been tested for the removal of cesium-137 from waste at pH=10 (20). The cesium salt of dipicrylamine is insoluble in water, and this reagent has been used to precipitate cesium-137 from basic aqueous solution (21). Recent work has focused on the precipitating agent sodium tetraphenylboron (22,23). This compound is very effective for the removal of cesium-137 from strongly alkaline solution.

There are fewer precipitation techniques available for the removal of strontium-90 from liquid wastes. Perhaps the most successful and widely used procedure is coprecipitation of strontium-90 sulfate from acidic waste with lead sulfate (24). Barium sulfate has also been used as a carrier (25). Application of this procedure to stored waste would require a substantial pH adjustment. The coprecipitation of strontium-90 with calcium oxalate has also been reported (26).

While precipitation is an extremely effective means of removing these ions, with decontamination factors of 10^3 in many cases, where decontamination factor is the ratio of initial activity to final activity, it suffers from several shortcomings. Precipitation is not easily applied in a continuous, dynamic flow system. The addition of the reagent, mixing, and settling of the precipitate would require static conditions at some point. Centrifugation and flocculents have been used in attempts to speed the settling process. Some sort of final filtration procedure is also required, which adds to the complexity of the overall method. The volume of liquid waste that could be remotely handled easily and efficiently is also somewhat limited, without necessarily obtaining a substantial reduction in the volume of solids compared to the salt cake produced by merely evaporating off the solvent.

Despite the overall selectivity of precipitation methods,

problems with unwanted coprecipitants do exist. Ruthenium-106, the alkali metals and aluminum can be carried along with cesium during the aluminum sulfate precipitation. Similarly, precipitation with dipicrylamine cannot separate cesium from the any of the other alkali metals except sodium. A number of metal ions will adsorb to ferrocyanide precipitates. The problem of selectivity is especially severe in the precipitation of strontium-90 with lead sulfate. Rare earth elements, such as promethium-147 and cerium-144, are ubiquitous and useful fission byproducts. These elements are also precipitated as sulfates under acid conditions. Further separation steps, usually dissolution and reprecipitation with a different reagent, must be employed to separate these nuclides from the strontium-90 before storage.

Finally, the stability of many of the precipitates can be affected by radiation, pH changes, or the ionic environment present. Any instability of a precipitate under variable conditions could lead to leaching problems during storage or within particular immobilization forms. The fate of tetraphenylboron precipitating agents during immobilization is currently under study.

Solvent extraction has been used as an alternative to precipitation for the removal of both cesium-137 and strontium-90 from radiochemical wastes. Phenols such as 4-sec-butyl-2-(α -methyl-benzyl)-phenol (BAMBP) are perhaps the

most common agents used by the nuclear industry to extract cesium from highly alkaline solution (27,28). A hydrocarbon solvent is usually used as a diluent. Dipicrylamine is an extremely stable and selective reagent for the extraction of cesium-137 from alkaline waste solutions (29). A solvent with a high dielectric constant, such as nitrobenzene, is usually used as the organic phase. The extraction of cesium-137 as a polyiodide complex has been accomplished using iodine in nitrobenzene. Cesium is extracted effectively at pH's >2, and the addition of a small amount of NaI to the aqueous waste improves the extraction (30). Other less successful extracting agents have included long-chain sulfonic or monoalkylphosphoric acids (27,31), sodium tetraphenylboron (32) and triphenylcyanoborane (33). Poor selectivity, reagent instability, pH restrictions and stripping problems have been the major drawbacks in the use of these compounds. The recent development of crown-ether complexing agents for the alkali metals has led to their application in the removal of cesium-137 from waste solution with some success (34,35). Another relatively new series of extracting agents are the carbolides. These carborane pi-complexes of cobalt are large, hydrophobic anions. With nitrobenzene as the solvent, they will separate cesium-137 from a mixture of radionuclides in alkaline aqueous solution (36).

The primary extracting agent for strontium-90 is

di(2-ethylhexyl)phosphoric acid (D2HEPA) (27). A hydrocarbon diluent is also used with this agent, and some tributylphosphate may be added to improve miscibility if the sodium salt of D2HEPA is used. Strontium-90 is most effectively extracted with this reagent at pH 4.5-6.0, so some pH adjustment of tank waste is necessary if strontium is not removed early in the processing. The crown-ethers will remove strontium-90 from acidic solution (most efficiently at pH 3-6) (34,37) and carbolides have extracted strontium-85 from simple aqueous solutions (38).

Despite the large amount of work being done on the subject, solvent extraction for the isolation of Purex waste radionuclides has several significant disadvantages. First, the separated isotopes remain in a liquid phase. The reduction in liquid volume is usually minimal, and direct immobilization of the waste isotopes remains difficult. Therefore, both stripping and solidification steps are usually required after extraction. Precipitation with one of aforementioned reagents is a common choice. At the very least, an additional step to separate the solvent layers is necessary. Although extraction might remove the nuclides of interest more completely and more cleanly, the added complications to the overall processing procedure often outweigh these gains.

Secondly, introducing a second solvent into the system

increases the possibility of cross-contamination. The organic solvent often has to go through a separate cleanup procedure to remove final traces of radioactivity. In addition, small amounts of the solvent may remain in the decontaminated brine solution, which might pose a disposal problem. Related concerns include the final disposal of the organic solvent itself and the effect of traces of the solvent on the various immobilization procedures and forms.

Solvent extraction is also ill-suited to a large-scale dynamic processing system. The mixing, re-separation, and removal of the solvent layers can be awkward in a flow system. As with precipitation, only a limited volume of waste could be effectively processed during a single cycle.

Finally, the stability of many of the extracting agents currently being used, and their selectivity for the ions of interest, is sometimes suspect. For example, strontium-90 coextracts with the rare earths when D2EHPA is used, and they must be further separated by a stripping procedure utilizing either pH control or the addition of competing complexing agents. Dipicrylamine is only an effective extracting agent for cesium-137 in the absence of potassium. Radiolysis of D2EHPA with gamma radiation is documented (39), and the decomposition of tetraphenylboron after extended exposure to radiation has been cited (29). Recycling of such reagents is desirable, and is severely curtailed by any instability.

Some of the more exotic separation techniques that have been applied to the removal of cesium-137 and strontium-90 from nuclear waste include separations using foams (40), reverse osmosis (41,42), and electrodialysis, a technique that is closely related to both reverse osmosis and ion exchange (43).

Ion exchange itself is perhaps the technique that is best suited to nuclear waste processing. Readily applicable to flow systems, it can be installed and operated relatively easily on a remotely controlled basis. The volume of waste that can be decontaminated is limited only by the size of the column, the capacity of the resin, and any prudent flow rate or pressure considerations. The resin can usually be regenerated and reused. This provides the alternatives of removal of the nuclides from the resin with a small volume of concentrated eluent solution, or disposal of the resin after it is fully loaded with radioactive material. Disposal or elution of a resin produces fewer potential process design problems than the filtration of a precipitate or the separation of solvent layers, and a resin column is easily cleaned. The solidification of some types of ion-exchange resins has been examined, with satisfactory results for most waste immobilization forms (44). The decontamination factors possible with ion-exchange resins can be high and selective resins can be designed for the ions of interest, if necessary.

When all this is considered, it is not surprising, then, that a great deal of work has been done world-wide on the use of ion-exchange resins for nuclear decontamination. Similar arguments regarding the advantages of ion exchange for waste decontamination have been presented by workers at Battelle-Northwest Laboratory (45).

The majority of ion exchangers used in waste processing are inorganic materials. This is primarily due to the high capacities obtainable with these materials, and their greater radiation stability. In many cases the ion exchanger is an insoluble salt of one of the precipitating reagents previously mentioned for cesium-137 or strontium-90. For example, ammonium molybdophosphate has been used to sorb both cesium-137 and strontium-90 (46,47). This compound is often attached to a solid support material because of its poor mechanical properties. Salts of other heteropolyacids have been used in a similar manner (48,49). A number of transition metal ferrocyanide salts have been utilized as exchangers for cesium-137 in simulated waste supernatant. The synthesis of these materials and their application in waste processing has been reviewed by Loewenschuss (50). Ferricyanide salts of some transition metals have been similarly studied (51). The physical properties of these salts are such that they generally require a support material as well. Almost all of the metal complexes show a high affinity for univalent metal

ions, particularly cesium. Titanate salts will sorb strontium-90 from Purex waste (52) and titanium dioxide has been used as an exchanger for cesium in strongly alkaline solution (53). Zirconium phosphate can be used for both ions (54,55). An interesting study by Kenna and Murphy (56) describes the selective separation of cesium-137 from nuclear waste using sodium zirconate as the ion exchanger. Sodium zirconate has a high affinity for cations with high valences and low ionic radii. Thus, this exchanger sorbs most of the ions usually present in Purex waste, with the exception of the alkali metals, and cesium-137 can be effectively isolated at strongly acidic pH.

The inorganic ion exchangers that have been applied most successfully to waste decontamination are the aluminosilicates, in particular natural and synthetic zeolites (48,57,58). These materials exhibit a number of properties that make them useful in nuclear waste processing. They are generally selective for univalent ions and the alkaline earths, with large equivalent capacities. Zeolites sorb ions by a combination of exchange and sieving mechanisms. The relative contributions of these two mechanisms vary with the aluminosilicate structure. Thus, the selectivity of zeolites can, to some extent, be synthetically altered to fit a particular application. In addition, zeolites are stable to radiation (57,59) and have the necessary mechanical stability

for use in columns. They are unstable in strongly acidic or basic solution, however, and this limits their applicability to some extent.

Less use has been made of organic ion exchangers for the isolation of radionuclides, for two basic reasons. A number of studies have determined that organic ion-exchange resins tend to degrade after prolonged exposure to radiation (59,60). Radiolytic attack on the functional groups of sulfonated poly(styrene-divinylbenzene) type cation exchangers produces acidic by-products (60). Such products could serve as a potential source of corrosion within steel waste-form canisters. The production of CO_2 gas from attack on the organic polymer, and hydrogen gas from the radiolysis of occluded water have also been observed. A radioactive environment would require an organic polymer to be highly cross-linked in order to maintain its structural integrity. This, in turn, limits the capacities that can be reasonably obtained. However, a claim of increased cross-linking occurring within a irradiated organic polymer (Dowex HGR) because of a radiolytic loss of water content has been proposed (59). A second limitation is that although organic resins, especially chelating resins, can be highly selective, they are generally less selective for alkali and alkaline earth metals than inorganic exchangers. However, the selectivities of organic resins can often be chemically

altered more easily than those of their inorganic counterparts. The variety of ion-exchange and chelating resins that are commercially available, coupled with their stability over a wide pH range and the potential for chemical modification through the addition of selected functional groups, makes them a desirable alternative to inorganic exchangers.

Although it is not an ion exchanger, the simplest organic polymer, activated carbon, has been utilized to sorb cesium-137, along with a variety of other radionuclides from aqueous solution (61). No selectivity for cesium-137 over the other isotopes tested was indicated, however. Other organic polymers can be used for the selective removal of cesium-137 and strontium-90 from fission wastes either alone (62-71) or in combination with inorganic exchangers (52,64,72). In most cases, a different exchanger is used for each of the ions of interest. Typically, the cation-exchange resins used are poly(styrene-divinylbenzene)s with sulfonic acid exchange groups such as the macroreticular resin Amberlite 200 (63,72). However, phenolic-type exchangers, because of their high affinity for alkali metals in basic solution, have been used extensively to sorb both cesium (73) and cesium-137 (23,52,62,66,68,71,74). The affinity of iminodiacetic acid (IDA) moieties for alkaline earths is well known (75). Organic chelating resins containing this functional group are

used for the selective uptake of stable strontium (76) and the radioisotope strontium-90 (23,66,68). Utilizing phenolic ion exchangers and iminodiacetic acid chelating resins, decontamination factors as high as 4×10^5 for cesium-137 and 5×10^3 for strontium-90 have been reported (66).

Recent efforts by workers at the Savannah River Laboratory have produced a resin that selectively removes both cesium-137 and strontium-90 from simulated waste supernatant (77). A base-catalyzed condensation polymer of resorcinol and formaldehyde is synthesized that contains IDA moieties. These functional groups are added during the polymerization procedure by a base-catalyzed Mannich condensation with formaldehyde. The phenolic groups take up cesium-137 from alkaline solution by ion exchange, and strontium-90 is removed by chelation with the IDA groups. Similar resins have been synthesized by Japanese workers and used to sorb alkaline earths and heavy metals from aqueous solution (78-80). The resins produced at Savannah River show greater selectivity and improved capacity for the ions of interest compared to commercially available resins. However, the useful capacity of these polymers for cesium-137, and especially strontium-90 under column operation represent only a fraction of the exchange sites present in the polymers. This could be at least partially attributed to the low surface areas of these glassy resins.

Current Approach to the Problem

The simplest way to increase the surface area (and so the intrinsic capacity) of these resins would be to introduce porosity into the resin mass. Early attempts by others to produce porous phenol-formaldehyde-iminodiacetic acid (P:F:IDA) resins were made by adding an insoluble solid into the prepolymer mixture, and then dispersing it in a solvent. The polymer thus formed around the solid particles. The added solid was later removed, leaving a macroporous structure. Resins produced in this manner showed much improved equilibrium adsorption times for transition metal ions than their nonporous counterparts. However, the total capacities of these porous resins were slightly less than those of nonporous resins synthesized in a similar manner. Typical solid additives have included sucrose, ammonium acetate, and sodium sulfate (81,82).

In this section of the dissertation I will describe porous bifunctional chelating resins produced by the introduction of an insoluble solid powder (which shall be loosely referred to as a "template") during the polymerization of various phenols with formaldehyde and iminodiacetic acid. The resins produced will be evaluated according to their ability to remove cesium-137 and strontium-90 from simulated waste supernatant. A number of different solids that are insoluble in base are

tried as templates. In addition, experimental parameters for the polymerization reaction are varied and any effect on the affinities of the resulting resins for cesium-137 and strontium-90 examined. Various attempts at elucidating the structure of the polymers are also described. After evaluation of these resins in the decontamination of nuclear waste, their affinities for certain other transition metal ions are tested to examine the scope of their potential application.

Finally, preliminary results concerning several other approaches to the removal of cesium-137 and strontium-90 from nuclear waste by ion exchange will be presented. These will include studies on coated resin exchangers, functionalization of poly(styrene divinylbenzene)s (PS-DVBs), and liquid ion exchangers. Inert solid supports coated with dipicrylamine (83,84) and tetraphenylboron (85) have been used previously to sorb and separate fission products, including cesium-137 and strontium-90. Here, several different supports are coated with either the P:F:IDA prepolymer mixture or a long-chain alkylphenol, and the affinities for cesium-137 and strontium-90 are determined.

In an effort to produce suitable ion-exchange resins with reproducible affinities, attempts are made to functionalize macroreticular PS-DVBs with phenol and IDA moieties, and use them to sorb the waste isotopes.

Lastly, long-chain aliphatic carboxylic acids and substituted phenols are tried as "liquid ion exchangers" to remove cesium-137 and strontium-90 by solvent extraction. All of the polymers and reagents studied in this section are primarily evaluated for their usefulness in the processing of high activity liquid nuclear waste.

OVERVIEWS OF THE PERTINENT CHEMISTRY

Phenol-Formaldehyde Polymerizations

The polymerization of phenols with formaldehyde has been known since the turn of the twentieth century. Among the earliest reports of the formation of resinous material from the reaction of phenol with formaldehyde was that of von Bayer in 1872 (86). In subsequent years, numerous other workers reported the production of resins of a similar nature. However, little economic advantage was taken of these polymeric materials until 1899, when the first patent covering materials of this type was granted to A. Smith (87). Henschke in 1903, and Lebach in 1907 described the formation of phenol-formaldehyde condensation polymers utilizing basic salts as catalysts (88,89).

The pioneering work of Baekeland in the early 1900s (90-92) literally gave birth to the synthetic polymers industry, with phenol-formaldehyde "Bakelite" polymers occupying a central role. The number and variety of applications for these versatile polymers has continued to expand since that time, as is indicated by the voluminous amount of patent literature on the subject. The reactions involved in the formation of these polymers have also come

under extensive scrutiny, with a number of books and monographs having been published on the subject (93-97).

In general, a phenol will react with formaldehyde in aqueous solution by electrophilic substitution to form a hydroxymethylated (methylol) adduct. This reaction is catalyzed by either acid or base. The hydroxymethylated adduct will then condense either with another phenol molecule to form a methylene-bridged dimer (and subsequent oligomers), or with another hydroxymethylated phenol to form oligomers containing ether linkages. The ether-bridged form can be converted to the methylene-bridged polymer by the application of heat (curing). This reaction sequence is shown in Figure 1. For convenience, phenol will be used as the example in all of the reactions that follow. However, each mechanism can be applied equally well to substituted phenols, with their reactivity, in terms of activating and directing groups, following the usual pattern.

Formaldehyde in aqueous solution exists as polyoxymethylene glycol, but depolymerizes to methylene glycol under acidic or basic conditions (97). The electrophilic reactive species that is formed in acidic solution is a carbonium ion, while under basic conditions, a partially charged species is formed, as seen in Figures 2a and 2b. It should be noted that the structure of the reactive intermediate in basic solution presented here is only

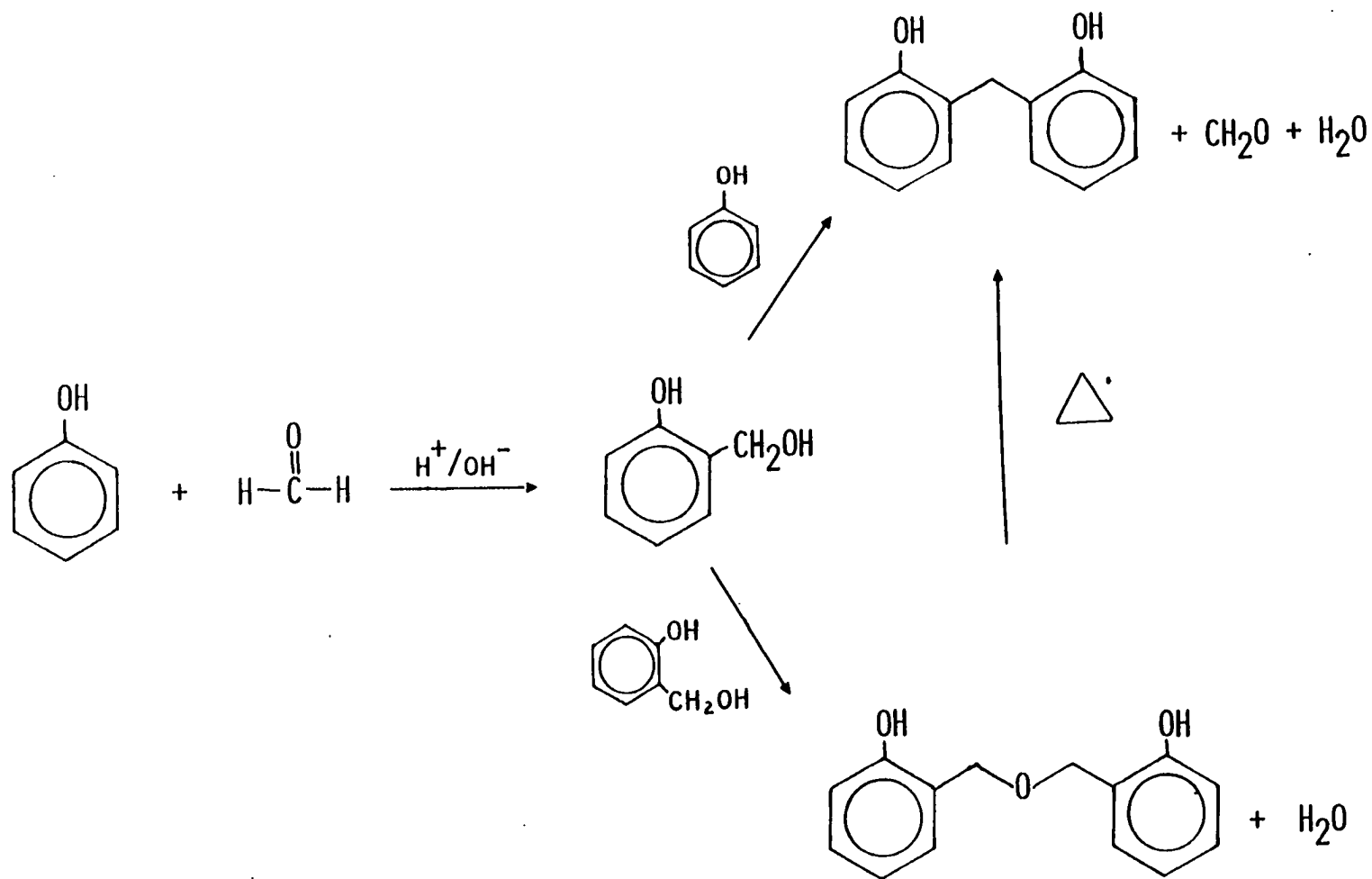
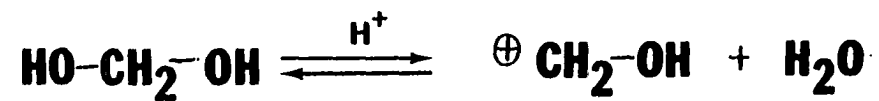
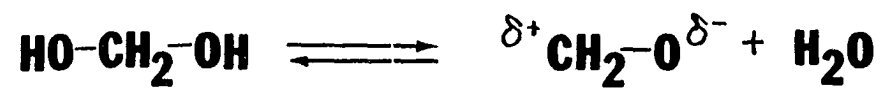


Figure 1. Polymerization of phenol with formaldehyde.



A



B

Figure 2. Forms of formaldehyde electrophiles. A) acidic medium
B) alkaline medium

representative of the consensus (see reference 97) and its actual nature has not yet been clearly established.

In acid, the carbonium ion species adds to the aromatic ring in the position ortho to or para to the hydroxyl group of the phenol. The substitution is aided by the activating effect of the hydroxyl group, and substitution is almost exclusively in the para position. The hydroxymethyl group, being unstable in acid, quickly forms the benzyl carbonium ion (95,96). This carbonium ion species then adds to another phenol molecule to form the methylene-bridged compound, as shown in Figure 3.

Such phenol-formaldehyde polymers formed under acid conditions are called "novolaks". A slight excess of phenol to formaldehyde is usually used. Since the formation of the hydroxymethylated intermediate is the slow step in the reaction mechanism, novolaks are generally low molecular weight linear polymers. They tend to be thermoplastic, and can only be cured to infusible materials after the initial polymerization by the addition of a hardener, typically more formaldehyde, and further heating.

The reaction sequence under basic conditions is somewhat different. This reaction was first reported separately by Lederer (98) and Manasse (99) in 1894 and often bears their name. A phenol forms the resonance-stabilized phenolate ion under basic conditions. The reactive species adds to the

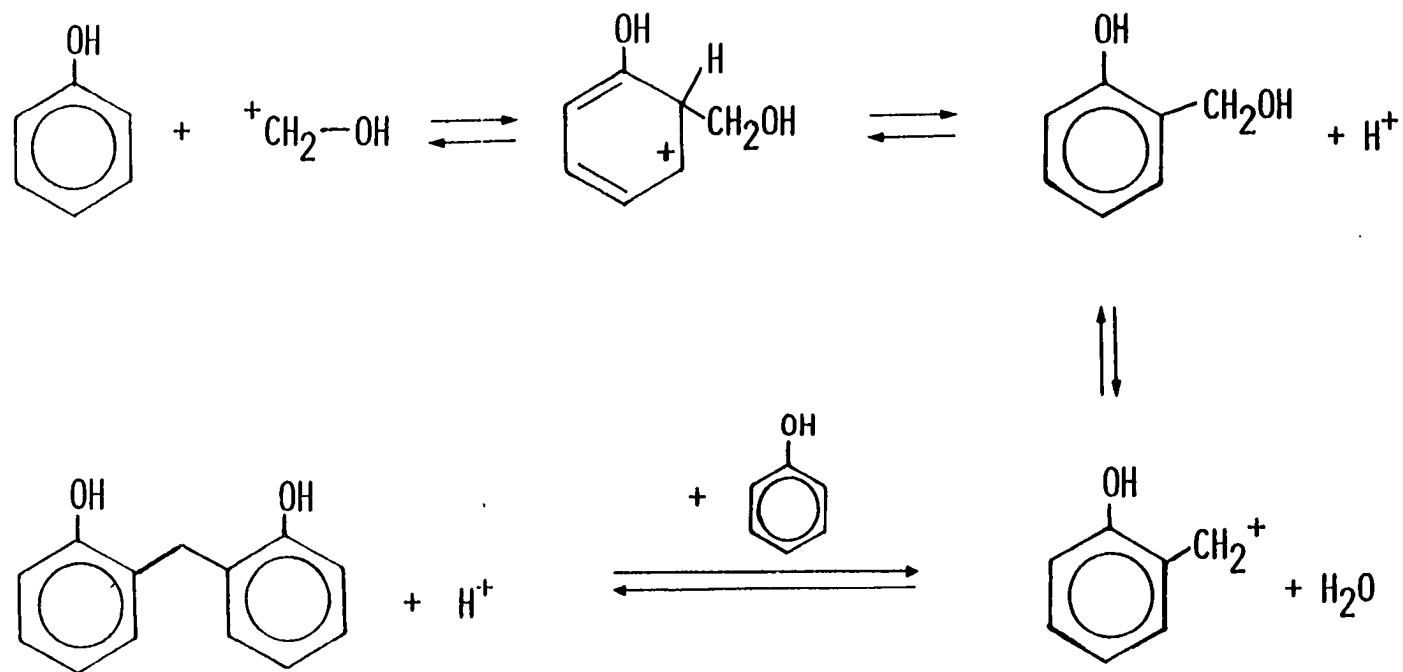


Figure 3. Phenol-formaldehyde polymerization mechanism under acidic conditions.

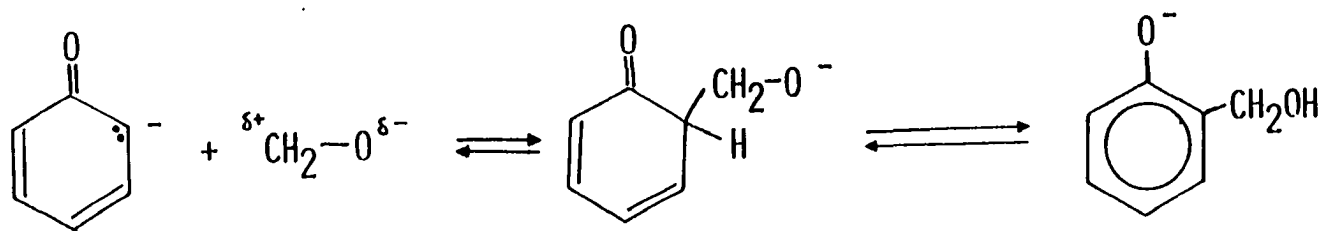
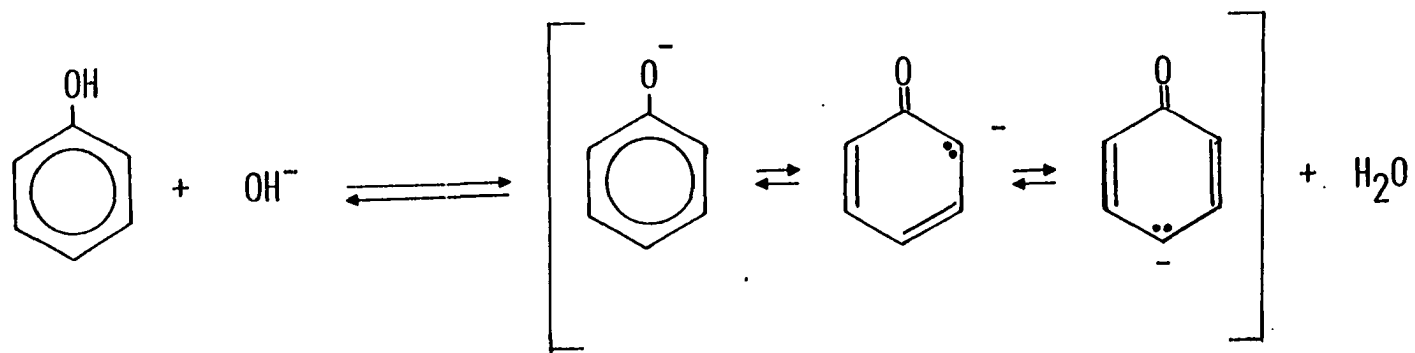


Figure 4. Hydroxymethylation of phenol under alkaline conditions.

phenolate ion electrophilically, going through a quinoid transition state to the hydroxymethylated product (97), as seen in Figure 4. The hydroxymethylated phenol condenses to form one of the two oligomeric structures shown in Figure 1. The methylene-bridged structure predominates under strongly alkaline conditions (100). Studies by Freeman and Lewis (101) established that condensation occurs primarily between two methylol molecules, with attack occurring through the hydroxymethyl group, splitting out water and formaldehyde to give a methylene bridge. Attack of a hydroxymethylated species on the unsubstituted phenol is not seen.

Although the para position in most phenols is more reactive, hydroxymethylation in the ortho position is often favored over that in the para position because of the duplicity of ortho sites. This trend increases with increasing pH (102-104), and ortho substitution is favored over para in strongly alkaline solution (pH > 10.5) even when a single site is available. Initial substitution ortho to the phenolic hydroxyl group was found to further activate the second ortho position in phenol as well as substituted phenols (by a proposed hydrogen-bonding mechanism), and subsequently, activate the remaining para position. This produces substantial di- and trisubstitution when possible (95,104,105). The facile formation of polymethylol species permits three-dimensional, as opposed to linear,

cross-linking. The choice of catalyst is also known to affect the ortho/para substitution ratio. Hydroxide salts of the alkaline earth and transition metals enhance ortho substitution compared to alkali metal hydroxide catalysts (97,104,106). Organic base catalysts vary in their effect on the substitution ratio. Heat curing at high temperature converts any ether linkages formed to methylene bridges by a mechanism that is not yet fully understood (94).

Phenol-formaldehyde prepolymers formed under basic conditions are termed "resols" (or resoles). Here the slow step is the condensation reaction to form oligomers. Hence, polymethylol precursors are often formed, and the resins tend to cross-link in a more three-dimensional fashion. An excess of formaldehyde is typically used in the synthesis, to obtain the final infusible products, or "resits". Any intermediate polymeric products are called "resitols".

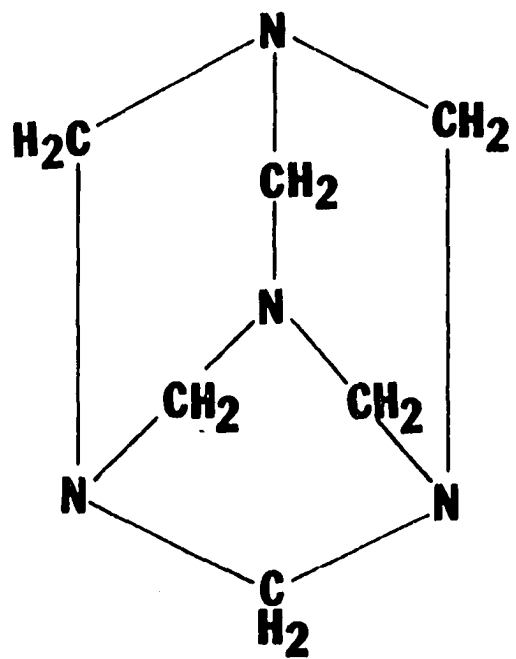
Two further points concerning phenol-formaldehyde polymerizations need to be made. First, aside from pH, reaction temperature is the most important synthetic variable. In the case of both novolaks and resols, prepolymer formation and chain growth tend to occur at temperatures below 100°C, with self-condensation occurring to varying degrees between 60-100°C. Extensive cross-linking occurs at higher temperatures (97). Novolaks, of course, require the addition of a hardener to form infusible resins, whereas resols

typically do not. Second, besides formaldehyde, other aldehydes have been used as cross-linking agents. Among the more common alternates are acetaldehyde, furfural, and hexamethylenetetramine (HMTA) (Figure 5a). Both resols and novolaks formed with HMTA contain methylamine cross-links, rather than methylene bridges, as seen in Figure 5b. The aminoalkylation sequence that produces these polymers is called the Mannich reaction; it will be discussed in the next section.

Mannich Reaction Chemistry

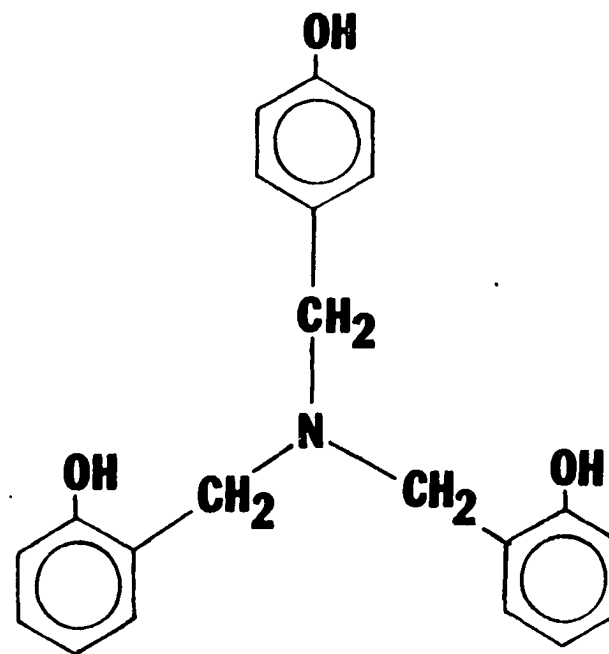
The Mannich reaction, named for its principal developer, is the condensation of a substrate having an active hydrogen (in this case a phenol) with formaldehyde and a primary or secondary amine (107,108). The resulting condensation product has the active hydrogen replaced by an aminomethyl group, and is referred to as a "Mannich base". The overall reaction sequence is presented in Figure 6.

The reaction is catalyzed by either acid or base, and proceeds by a two-step mechanism. In the first step, formaldehyde reacts with the amine to give the hydroxymethylamine, as seen in Figure 7. Under acidic conditions, this intermediate forms the methylene-bis-amine, followed by formation of the imonium ion, which



A

Figure 5A. Hexamethylenetetramine (HMTA).



B

Figure 5B. Methylamine cross-links.

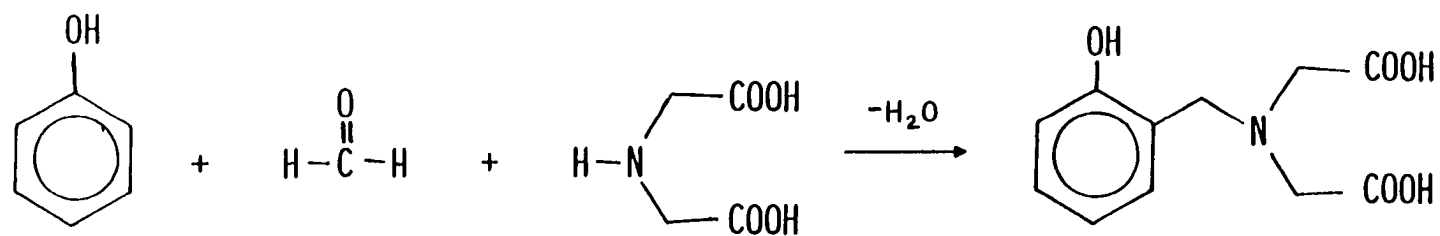


Figure 6. Mannich condensation of phenol and iminodiacetic acid.

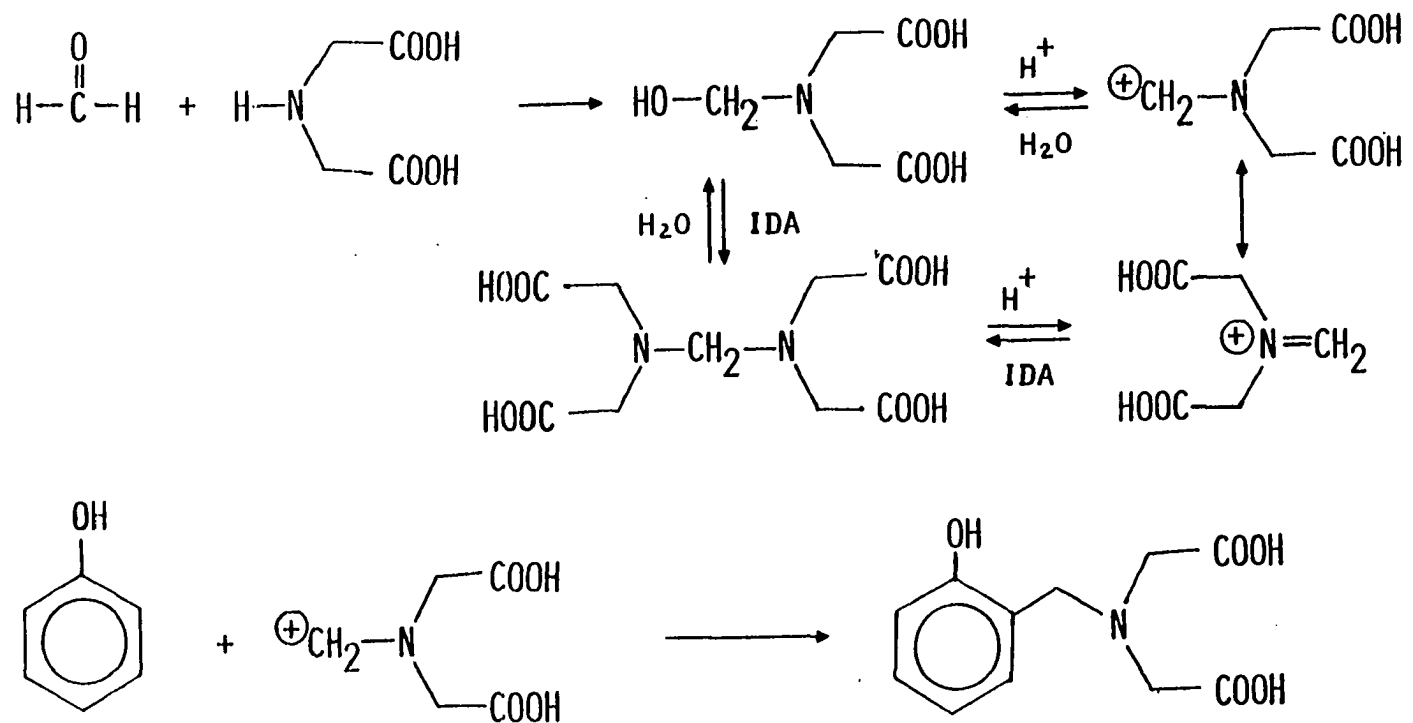


Figure 7. Mannich reaction mechanism under acidic conditions.

electrophilically attacks the substrate. In basic medium, the hydroxymethylamine (or possibly, the methylene-bis-amine) undergoes S_N2 displacement of the hydroxide ion by the carbanion form of the substrate. This reaction scheme is shown in Figure 8. With a phenolic substrate, the substitution is exclusively ortho, even if the para position is unoccupied. A proposed mechanism to explain this result involves a hydrogen-bonded intermediate (109,110), seen in Figure 9. Secondary amines generally form the methylene-bridged adduct. Primary amines will often cyclize with the phenol hydroxyl group, especially in basic solution, eventually yielding a bis-(2-hydroxybenzyl) amine.

Water and alcohols are typical Mannich reaction solvents, although others have been used. Basic catalysis is generally favored with phenolic substrates, and heat is usually used to speed the equilibria involved with the formation of the reactive amine species. However, too high a reaction temperature can sometimes lead to reversible elimination of the amine from the Mannich base product (111).

In the work presented in this dissertation, these two reactions are combined to form phenol-formaldehyde polymers containing iminodiacetic acid moieties. The Mannich condensation of iminodiacetic acid with phenols has been accomplished by several workers (112-114). Phenolic polymers containing a variety of substituted iminodiacetic acid adducts

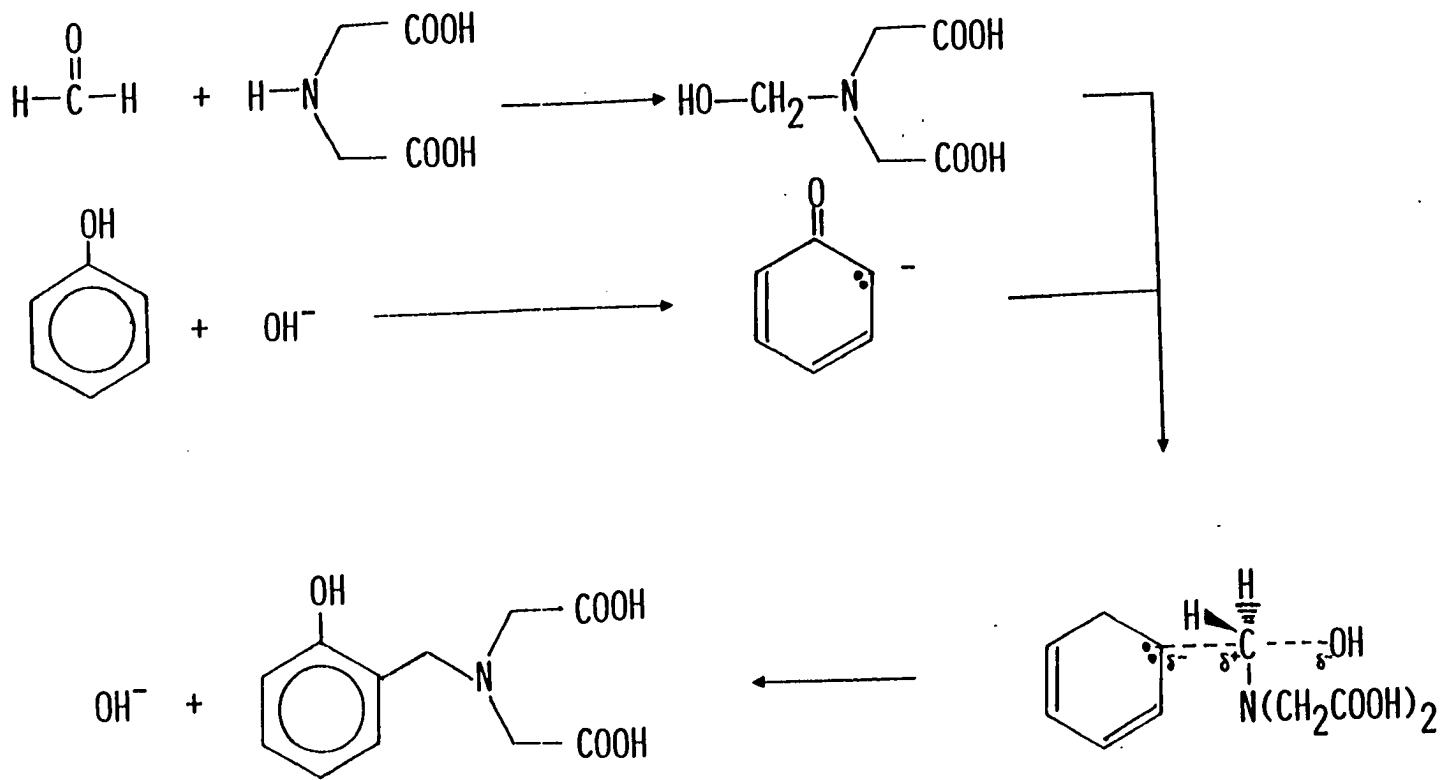
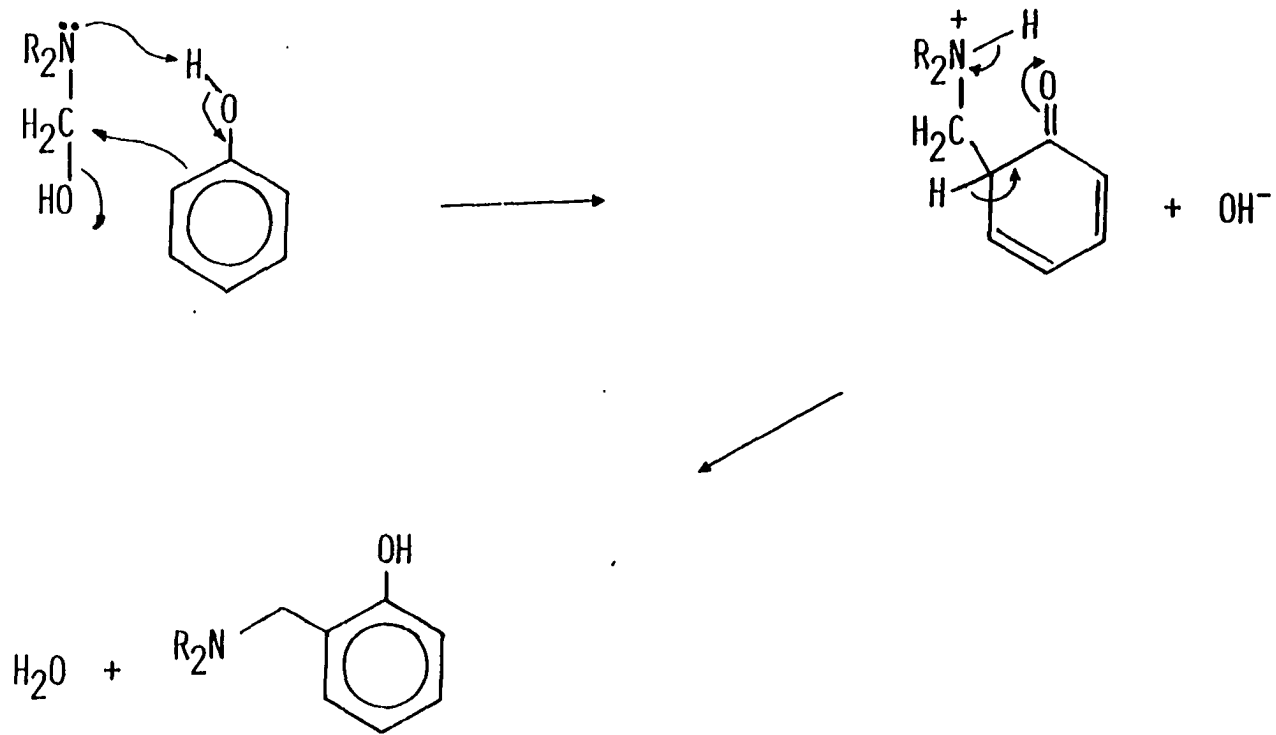


Figure 8. Mannich reaction mechanism under alkaline conditions.



R = COOH

Figure 9. Proposed hydrogen-bonding mechanism for Mannich condensations involving phenols.

have been synthesized by workers at the Savannah River Laboratory in the United States (77), a group of Japanese workers (78-82), and others (115-117).

Friedel-Crafts Alkylation

The Friedel-Crafts alkylation reactions being considered here are the electrophilic addition of an alkyl halide (most often an alkylchloride) to an aromatic center (118,119). A Lewis acid is used as a catalyst, the most common being aluminum chloride. The products are alkylaromatics and the appropriate haloacid. This reaction has been applied to phenols (119,120) to generate alkylphenols. The general reaction sequence is shown in Figure 10. The catalyst strips the halogen from the alkylhalide to form a carbonium ion reactive species. This electrophile then attacks the ring. The displaced H^+ attacks the Lewis acid complex, forming the haloacid, and regenerating the catalyst.

The most important variables in a Friedel-Crafts alkylation are the choice of solvent and catalyst. The most common solvent for these reactions is carbon disulfide, but nitromethane and other solvents have also been used successfully. A wide variety of Lewis acids have been used as catalysts. The most typical catalysts are metal halides; others include mineral acids and organic acids. These

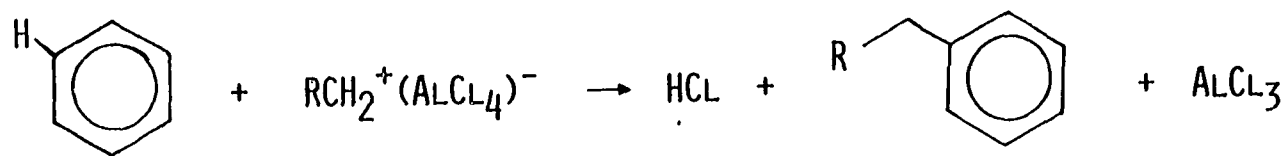


Figure 10. Friedel-Crafts alkylation reaction.

catalysts exhibit a wide range of activity. For example, aluminum chloride is a strong catalyst, giving the desired products in good yield under almost any conditions. Tin (IV) chloride is a more moderate one, and zinc chloride is a weak catalyst, producing the desired results with only certain electrophiles and substrates. This variability in catalytic properties can be used to advantage in the selective alkylation of specific reactive sites or species. The terms "strong" and "weak" are relative terms meant to be used as a guide to the general reactivity of a particular catalyst. However, this reaction tends to be "system specific", that is, the effectiveness of a particular solvent-catalyst pair does not vary systematically or predictably. Therefore, the proper choices of solvent and catalyst are almost always dictated by trial-and-error. One general property of every Lewis acid catalyst used, however, is high susceptibility to hydrolysis. Hence the reaction should always be carried out under dry conditions, and with thoroughly dried solvents. Typically, the reaction is facile, and heat is not necessary. Friedel-Crafts alkylations are therefore generally run at room temperature or below to permit the greatest amount of control possible.

The Friedel-Crafts alkylation of phenols is a well known reaction. Surprisingly, the presence of the activating hydroxyl group on the aromatic ring does not seem to enhance

the extent of the reaction compared to benzene (118). The presence of deactivating substituents, however, does impede the reaction. The hydroxyl group does impart its usual ortho, para directing influence. A molar excess of catalyst is generally required for the alkylation of phenols, because the Lewis acid (particularly metal halides) tends to complex with the hydroxyl groups present.

The Friedel-Crafts reaction of a phenol with a chloromethylated resin is presented in Figure 11. In this situation, the alkyl halide adduct is the resin. This approach has been used before to add hydroquinone to a chloromethylated PS-DVB, to produce a resin that was sensitive to oxidation-reduction couples (121). Attempts were made by the author to add resorcinol to a chloromethylated, macroreticular PS-DVB resin in a similar manner. This was followed by Mannich addition of iminodiacetic acid. In this way, a reproducible synthesis of a resin containing the desired sequestering groups for cesium-137 and strontium-90 might be achieved.

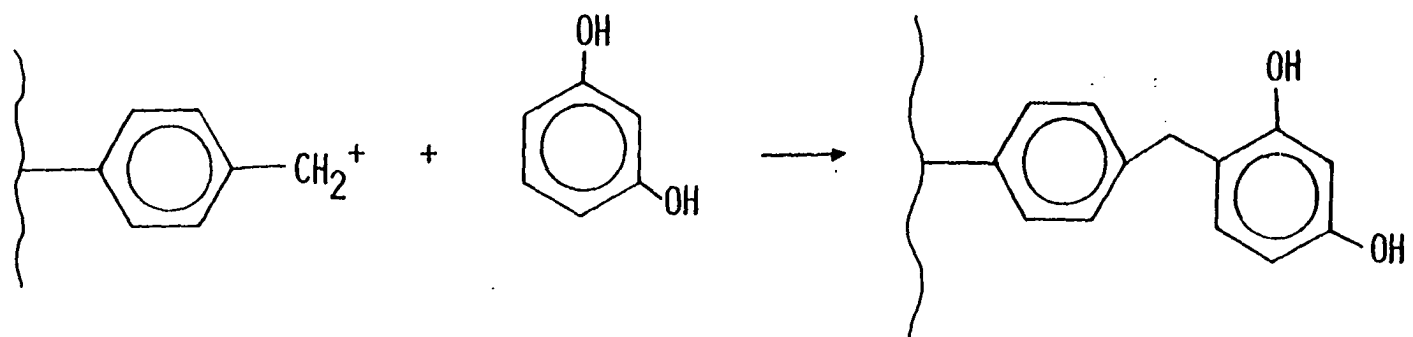
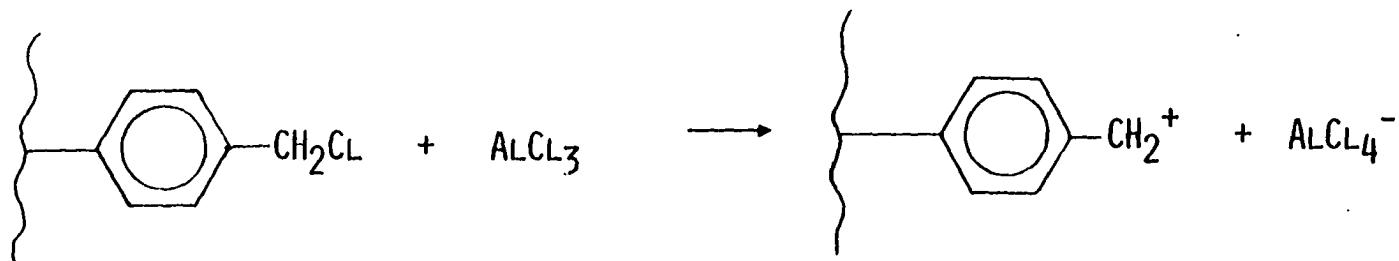


Figure 11. Friedel-Crafts reaction of resorcinol with a chloromethylated poly(styrene-divinylbenzene).

EXPERIMENTAL

Reagents and Chemicals

Reagents and solids used were obtained from a variety of sources. All were analytical reagent grade, except p-cresol, which was practical grade obtained from Eastman Kodak (Rochester, NY). Formaldehyde was generally used as a 37% (w/w) aqueous solution (Formalin) obtained from Fisher (Fair Lawn, NJ). Porasil A was obtained from Waters Associates (Framingham, MA). Porous glass beads and Chromosorb G were both obtained from Applied Science Laboratories (State College, PA). Cesium-137 (carrier free) and strontium-90 were obtained at 99% radionuclidic purity from New England Nuclear (Boston, MA).

Instrumentation

Gamma counting of tracer levels of cesium-137 and strontium-85 was done with a lithium drifted germanium detector (Princeton Gamma Tech, Princeton, NJ) and a Series 80 Model 8605 multichannel analyzer with a Model 8623 pulse height analyzer (Canberra Industries, Meriden, CT). Particle sizes of the template solids were measured with a Model 1 photomicroscope (Karl Zeiss, Oberkoken, DDR). Atomic

absorption measurements were taken with either a Model 2380 or Model 303 atomic absorption spectrophotometer (Perkin-Elmer Corp., Norwalk, CT). Uranyl ion distribution coefficients were determined using a Model 552 ultraviolet-visible spectrophotometer (Perkin-Elmer Corp., Norwalk, CT). Surface area measurements were taken with a Model 2100D Orr Surface-Area Pore-Volume analyzer (Micromeritics Instrument Corp., Norcross, GA).

Synthesis of P:F:IDA Polymers

The resins in this study were synthesized by polymerization of a particular phenol with an aldehyde in the presence of iminodiacetic acid. The following general procedure was used for most of the polymers synthesized. Approximately 0.01 moles of the desired phenol was dissolved in a minimal amount of deionized water and the desired amount of iminodiacetic acid (typically an amount equimolar with the phenol) was added. The pH of the solution was adjusted to 9 (± 0.05) with the required base, usually 6 N NaOH. The reaction was heated in a jacketed flask connected to a constant temperature circulating water bath, or, by a heating mantle or oil bath in the case of reflux-temperature reactions. The reflux temperature used was typically 115° to 120° C. As the reaction mixture was brought to temperature,

the template solid was added to the solution. Suspension of the template was maintained throughout the reaction period by simple mixing with a magnetic stirring bar. A seven-fold excess of the desired aldehyde (usually formaldehyde as a 37% aqueous solution) was then added to the solution, and it was allowed to stir overnight.

After this reaction period, the reaction mixture, either liquid or gel (depending upon the reaction temperature), was cooled to room temperature. If necessary, any residual solvent was removed by rotary evaporation. The resulting gels were then dried overnight (typically at 60°C) in a vacuum oven, to complete the curing process. During this curing step, the physical form of the resins changed, in general, to brittle solids.

After cooling, the resins were treated with a reagent to remove the template. For most of the templates, the resin was soaked in approximately 200 mL of 2 N HCl until dissolution was complete (typically 12 hrs). With Fe_2O_3 as the template, concentrated HCl was used. With silica as the template, either HF or caustic was used according to the procedures which follow. With HF, a 0.5-g portion of resin was wetted with concentrated H_2SO_4 in a platinum crucible. Enough HF was added to cover the resin sample, and this mixture was heated on a hot plate until it ceased fuming. With caustic, the same amount of resin was soaked twice in approximately 100-mL

portions of 6 N NaOH.

After dissolution of the template was complete, the resins were washed thoroughly with deionized water and dried under vacuum at 60°C. For each template except silica gel, the volume equivalent of 2 g of CaCO_3 was used (see Table 2). Four grams of silica gel powder were necessary to produce a reasonably thick slurry.

The Porasil polymerizations were similar to the method of Knox and Gilbert for the production of porous carbon (122). In this procedure, enough Porasil A was added to the resorcinol-formaldehyde-IDA (R:F:IDA) prepolymer mixture to produce a damp sludge. This sludge was then heated in a vacuum oven overnight at the prescribed temperature. The polymerization was thus completed within the pores of the silica. After cooling to room temperature, the conglomerate produced was either treated with $\text{HF}/\text{H}_2\text{SO}_4$ or soaked twice with 6 N NaOH to dissolve the silica from around the P:F:IDA polymer.

The densities of many of the resins produced were determined by adding a known mass of dry H^+ -form resin to exactly 10 mL of 1 N NaOH. After soaking for several hours, the volume displaced by the resin was determined, and the density calculated. The density in 1 N NaOH was preferred because this typified the solution used for the other determinations, as well as the waste supernatant solution.

Table 2. Volume equivalents of various templates to 2 g of calcium carbonate^a

Template	Density (g/cc)	Mass Required (g)
CaCO_3	2.71	2.00
Na_2CO_3	2.53	1.87
Cs_2CO_3	--- ^b	6.50 ^b
$\text{Ca}_2\text{P}_2\text{O}_7$	3.09	2.28
$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$	3.14	2.37
$\text{Mg}(\text{OH})_2$	2.36	1.74
Fe_2O_3	5.24	3.87

^a Total volume required = 0.7377 cc.

^b Density information not available from standard sources, so mass containing the same number of moles as 2 g of CaCO_3 was used.

Variations in Synthetic Conditions

To examine the influence of various reaction conditions on these resins, some changes in the overall synthetic procedure were introduced. In most cases, the appropriate alteration of the procedure described in the first section is obvious. Therefore, only those experimental details that are in some way unusual or significant will be presented in this section. Resorcinol-based resins with CaCO_3 templates were used in most of the work, which studied the following reaction parameters:

- 1) reaction temperature
- 2) ratio of reactants
- 3) basic catalyst used
- 4) amount of template added
- 5) cross-linking agent

In addition to the RE:F:IDA polymerizations performed at different temperatures, three special resins were synthesized to examine the effect of reaction temperature on the reaction mechanism. In one case, 1 molar equivalent of formaldehyde (as formalin) was added to the phenol-IDA mixture at 60°C on a heating mantle. This was allowed to stir for 4 hours. The temperature was then raised to reflux temperature, the

template (CaCO_3) added, and the remaining 6 molar equivalents of formalin added as a single aliquot. This mixture was allowed to reflux overnight. In a related reaction, equimolar amounts of formalin and IDA (0.01 moles) were combined in aqueous solution and the pH adjusted to 9 with NaOH. This mixture was stirred at 60°C for 1.5 hours. An aqueous solution containing 0.01 moles of resorcinol at pH 9 was added dropwise to the reaction mixture (Note: this aqueous solution of resorcinol turns yellow and then light brown after standing for a short while in air; it should be used quickly). The CaCO_3 template was added at this point and the mixture stirred for 3 hours. The remaining 6 equivalents of formalin were added and the temperature raised to 96°C . The reaction mixture was stirred overnight and then carried through the remaining procedure described in the general section. Finally, a resin was synthesized at reflux temperature with the aqueous formaldehyde solution being added dropwise over the course of several hours.

Although the basic catalyst used for the majority of the syntheses was sodium hydroxide, other bases were also tried as catalysts. Aqueous 6 N solutions of several alkali metal hydroxides and ammonium hydroxide were used to adjust the reaction pH to 9. Barium hydroxide was added as a solid until the pH was at the proper level. The organic bases diethylamine and triethylamine were added to the solution as

neat liquids in sufficient amounts to produce a pH of 9. Finally, in the reactions where zinc acetate is used as a catalyst, a 1:50 molar ratio of zinc acetate (as the solid salt) to resorcinol was used, with 6 N NaOH added to obtain the proper pH.

The use of different cross-linking agents required a few minor changes in the reaction procedure. Paraformaldehyde was simply added as the solid material. Polymers with different cross-linking groups in the polymer backbone, but containing methylene-bridged Mannich adducts, were produced with a two step reaction procedure. The desired amount of IDA was dissolved in a minimum of deionized water and the pH was adjusted to 9 with 6 N NaOH. One molar equivalent of formalin was added and the mixture was stirred for several hours at 60°C. A solution of resorcinol in aqueous base (1:1 RE:IDA; pH=9) was then added dropwise over the course of approximately 1 hour. The desired cross-linking agent (6-fold excess to resorcinol) was then added as a single aliquot and the reaction was heated to the desired temperature. An overnight reaction period was again used.

The addition of IDA groups to the surface of a resorcinol resin was attempted. A resorcinol-formaldehyde porous polymer without IDA was synthesized in the usual manner. A 0.5 g portion of this resin (-100/200+ fraction) was then added to a aqueous solution of 0.5 g IDA at pH 9. Excess formalin was

added, and the reaction was stirred overnight at 60°C. The resulting resin was filtered by suction, rinsed thoroughly with deionized water, and dried overnight at 60°C, and the distribution coefficients for cesium-137 and strontium-85 determined.

Distribution Coefficient Measurements (Cs-137 and Sr-85)

Dry, hydrogen-form resin (0.1 g) and simulated salt solution (15 mL) were shaken for 20 hours. The salt solution (Table 3), which simulates soluble defense nuclear waste, was spiked with tracer levels of cesium-137 and strontium-85. The equilibrium cesium and strontium concentrations were calculated from the measured residual activity in the salt solution after contact with the resin. Distribution coefficients (K_d) were calculated by the equation:

$$K_d = V/m [(C_0/C) - 1]$$

where V = volume of salt solution (mL)
 m = mass of resin (g)
 C₀ = initial Cs-137 or Sr-85 activity (counts)
 C = final Cs-137 or Sr-85 activity (counts)

It was assumed in all of the studies that there would be a negligible difference between the effectiveness of a resin for strontium-85 and that for strontium-90. Thus, results will be discussed in terms of uptake of strontium-90,

Table 3. Composition of simulated salt supernatant solution

Component	Concentration (molar)
NaNO_3	2.3
NaOH	1.3
NaNO_2	0.70
NaAl(OH)_4	0.38
Na_2CO_3	0.20
Na_2SO_4	0.17
NaCl	0.025
NaF	0.017
Na_2SiO_3	0.0045
Na_2CrO_4	0.0039
Na_2MoO_4	0.00051
KNO_3	0.024
$\text{Na}_2\text{C}_2\text{O}_4$	0.029
Na_3PO_4	0.012
CsNO_3	0.00025
$\text{Sr(NO}_3)_2$	0.0000005

even though strontium-85 was used for making measurements.

Column Studies (Cs-137 and Sr-85)

Column performance was measured using 2.0 mL of resin (wet volume in 1 N NaOH) in a cylindrical column 0.9 cm in diameter. Feed solutions for the column runs were the same as those used in the K_d determinations. The column effluent was collected in test tubes and the cesium and strontium concentrations determined by gamma counting methods. Liquid flowrates through the column were 40 mL/hr, obtained using a peristaltic pump.

Surface Area Determinations

The surface area of several of the porous P:IDA:F resins was measured using the Braunauer-Emmett-Teller (BET) method (123). The volume of an inert gas adsorbed to the surface of the resin is measured at various pressures and liquid nitrogen temperature. Applying the BET equation to the adsorption isotherm produced, the volume and surface area of a monolayer of the inert gas can be calculated, and so the surface area of the resin. Although nitrogen is typically used as the inert gas, krypton was used for these measurements because of the small surface areas involved. Surface area determinations

using krypton are more accurate than nitrogen for surface areas below $5 \text{ m}^2/\text{g}$. Complete theoretical and experimental details are given elsewhere (124).

Distribution Coefficient Measurements (Other Metals)

Standard solutions of seven different metal ions at a concentration $1 \times 10^{-3} \text{ M}$ were used to determine distribution coefficients for 60°C resorcinol and 2,4-dihydroxybenzoic acid resins. To determine the effect of solution pH on K_d for each metal ion, standard solutions were adjusted to the desired pH with either HCl or NaOH. Iron (II) was stabilized at high pH by the addition of ascorbic acid to the solution. In order to test the selectivity of these resins for each metal over calcium and magnesium, a simulated hard water solution was produced by addition of 200 ppm each of Mg^{2+} and Ca^{2+} to a standard solution of each metal ion at pH 5.

A 0.1-g sample of dry, hydrogen-form resin was shaken in 15 mL of a standard solution of the metal ion for 18 hours. After equilibration, 5 mL of supernatant were removed, diluted to 25 mL and the concentration of metal ion present in the supernatant determined by atomic absorption spectroscopy. The amount of uranyl ion present in the supernatant was determined by the spectrophotometric method of Fritz and Johnson-Richard (125). The uranyl ion was complexed with Arsenazo I and the

amount of complex present measured at 595 nanometers. Each supernatant sample was compared to a set of standards prepared by dilution of the appropriate amounts of standard solution. The distribution coefficients for each metal ion were then calculated using the following equation:

$$K_d = [(\text{moles}_r / \text{moles}_s) (V/m)]$$

where moles_r = moles of metal ion on the resin
 moles_r^r = moles of metal ion in solution
 V^s = total volume of solution (mL)
 m = mass of resin (g)

Functionalization of PS-DVB Resins

The overall synthetic approach was Friedel-Crafts alkylation of chloromethylated PS-DVB resins. The alkylating agent was resorcinol, in the presence of a Lewis acid catalyst. Subsequent addition of IDA would occur by Mannich condensation with formaldehyde, as in the polymerizations. A 0.5-g portion of -80/100+ mesh chloromethylated XAD-4 or XAD-1 (approximately 2-3 meq/g; Rohm & Haas, Philadelphia, PA) was added to 15 mL of organic solvent (either dioxane or nitromethane). Approximately 0.005 moles of resorcinol were added and the mixture stirred. The Lewis acid catalyst (1.5-3.0 mmoles AlCl₃, TiCl₄, or ZnCl₂) was added, and the reaction was stirred for various periods of time at temperatures ranging from room temperature to reflux. After

the reaction period was complete, the cooled resin product was suction-filtered through a sintered glass disc, then rinsed twice with solvent and twice with acetone. This product was Soxhlet extracted for 12 hrs with methanol to remove any remaining impurities, and dried thoroughly at 60°C. The amount of resorcinol added to the polymer was estimated by oxygen analysis (Galbraith Laboratories, Knoxville, TN) and the distribution coefficients for cesium-137 and strontium-85 measured.

Several 0.1-g samples of functionalized resin were mixed with a two-fold excess of iminodiacetic acid in 5-10 mL of 1 N NaOH. Approximately 1 mL of formalin was then added and the reaction mixture stirred overnight at 60°C. After cooling, the resins were filtered in a fritted glass funnel, rinsed copiously with deionized water and air dried. The dry resins were Soxhlet extracted for 12 hrs with methanol and dried at 60°C overnight in a vacuum oven. Distribution coefficients were determined as above.

Development of Coated Resins

Four separate coated ion-exchange resins were manufactured and tested. The following resins were produced:

- 1) RE:IDA:F prepolymer coated on spherical glass beads.

- 2) RE:IDA:F prepolymer coated on diatomaceous earth.
- 3) Octyl-3,5-dihydroxybenzoate on XAD-4.
- 4) Sodium tetraphenylboron coated on XAD-4.

To produce the first two resins, a RE:IDA:F polymer was synthesized at 60°C using the procedure outlined in the first experimental section, except that the template was omitted. Approximately 50 mL of the prepolymer liquid was added to enough porous glass beads (-80/120+ mesh) or Chromosorb G (-100/120+ mesh) to make a slurry. This slurry was rotovapped to dryness, rinsed thoroughly with deionized water, and air dried with suction. When dry, the solid material was gently ground with a mortar and pestle to remove any clumps, and cured in a vacuum oven overnight at 60°C.

Octyl-3,5-dihydroxybenzoate was synthesized by dissolving 1.5 g of 3,5-dihydroxybenzoic acid in 18 mL of n-octanol. A few drops of concentrated HCl were added and the reaction mixture heated to 85-90°C. The reaction was followed by TLC until a single spot was produced which took approximately 14 hours.

The resulting dark brown solution was taken up in 50 mL of methylene chloride, and extracted with 10 mL of saturated Na_2CO_3 . After separation (which produced three layers), the aqueous layer (top) was discarded and the organic phase washed twice with distilled water. The methylene chloride solvent

was stripped by rotary evaporation and vacuum drying. The remaining liquid, which was dark brown in color and somewhat viscous, was vacuum distilled to remove the remaining octanol. A dark brown semi-solid product resulted (^1H NMR data = broad signal δ 8.5, 2 protons; shouldered singlet δ 7.1, 2 protons; small singlet δ 6.7, 1 proton; triplet δ 4.3, 2 protons; broad unsymmetrical multiplet δ 0.8-2.0; 14 protons).

The brown product was taken up in approximately 6 mL of acetone. This solution was divided in half and 1 g of -150/200+ mesh XAD-4 was added to each aliquot. Enough extra acetone was added to wet the entire resin sample. The samples were then agitated in an ultrasonic bath for 1 hour. The first sample was poured into a 100-mL portion of distilled water, to drive the organic reagent onto the hydrophobic resin. The resin was filtered after settling, washed several times with distilled water, and air dried. In the second sample, the acetone solvent was removed by simple evaporation. This resin was also washed several times with distilled water and air-dried. In each case, a light brown resin was produced. Cesium-137 and strontium-85 distribution coefficients were determined for these resins by the aforementioned procedure.

The sodium tetraphenylboron coated resin was produced in a similar manner. A 0.5-g portion of -80/100+ mesh XAD-4 was added to 30 mL of 50 mM sodium tetraphenylboron in

acetonitrile. The mixture was agitated in an ultrasonic bath for 30 minutes, and then 250 mL of distilled water was added to the resin mixture to drive the tetraphenylborate reagent onto the surface of the resin. This solution was further sonicated for 30 minutes. The coated resin was then filtered, rinsed with several times with distilled water, and dried.

Extraction with Liquid Ion Exchangers

Several long-chain alkylcarboxylic acids and long-chain alkylphenols were tested as liquid ion exchangers for cesium-137 and strontium-85. Hexanoic acid and 2-ethylhexanoic acid were tested both as the neat liquids and as 0.5 M solutions in toluene. The acids were converted to the sodium salt form by preliminary washing with NaOH, or Allamine 336 (trioctylamine) was used as a co-ion for the extractions. The extraction of copper or nickel from a brine solution by these reagents was checked qualitatively (i.e. formation of a colored organic phase) as a preliminary step.

In the extraction procedure, a 50-mL brine sample containing 5×10^{-3} M Cs^+ or Sr^{2+} was extracted with 10 mL of reagent. After extraction, a 10-mL aliquot of the brine solution was taken, diluted to 50 mL with deionized water, and the amount of cesium or strontium determined by atomic absorption spectroscopy. The absorption of the sample was

measured versus standards made by diluting the proper amount of stock solution with deionized water.

The same procedure was used to test the uptake of cesium and strontium by p-nonylphenol and 4-hexylresorcinol. p-Nonylphenol was tested both as the neat liquid and as a 0.5 M solution in toluene. 4-Hexylresorcinol is a solid and was only used as a toluene solution. The brine matrices used included 5 M NaCl, 2.5 M NaCl/2.5 M NaClO₄, 4.5 M NaCl/0.2 M NaClO₄, and 4 M NaCl/1 M NaOH.

RESULTS AND DISCUSSION

Synthesis of P:F:IDA Polymers

The physical characteristics of the various polymers synthesized during the course of this study and their precursors are listed in Table 4. A number of condition dependent differences, as well as several general similarities can be noted.

In most cases, the polymers were colored, with the most common hues being shades of red, orange, or brown. The prepolymer mixtures typically turned yellow or brown upon addition of the aldehyde, and gradually darkened after several hours of reaction time. Further darkening of the resins often occurred during heat curing, but acid treatment for dissolution of the template caused them to lighten to the final color.

The physical forms of the cured resins were generally one of two types, and seemed to be dependent primarily on the phenols and aldehydes used. The phenols chosen for polymerization were considered to be representative of a variety of substitution patterns. Resins based on catechol and pyrogallol were found in an earlier study to be inferior to resorcinol resins (77), and so these phenols were disregarded in the present work.

Table 4. Physical properties of various phenol-aldehyde-iminodiacetic acid polymers

Phenol	Aldehyde	60°C		100°C	
		Prepolymer ^a	Resin ^a	Prepolymer ^a	Resin ^a
Resorcinol	Formaldehyde	R/L	RB/S	R/G	RB/S
Resorcinol	Glutaraldehyde	O/L	O/S	R/L	T/P
Resorcinol	2-Furaldehyde	RB/L	B/S	B/L	B/S
2,4-DHBA ^b	Formaldehyde	R/L	RB/S	R/G	RB/S
3,5-DHBA	Formaldehyde	R/L	Y/P	Y/L	OY/P
p-Cresol	Formaldehyde	Y/L ^c	T/P	Y/L ^c	W/P
m-Cresol	Formaldehyde	B/L ^c	YB/S	W/G	YB/S
Phloroglucinol	Formaldehyde	---	---	R/L	R/P
1:1 2,4-DHBA/RE ^b	Formaldehyde	R/L	RB/S	R/L	RB/S
1:1 p-Cresol/RE	Formaldehyde	R/L	O/P	R/G	RB/S

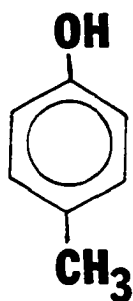
^a Color/form. R = red; B = brown; O = orange; Y = yellow; W = white; T = tan.
L = liquid; G = soft gel; P = powder; S = brittle solid.

^b DHBA = dihydroxybenzoic acid; RE = resorcinol.

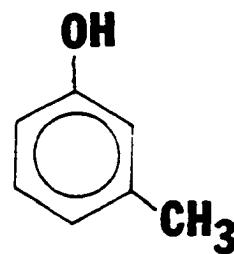
^c Rotovapped poorly; had to be thickened by further heating.

A resorcinol-formaldehyde-IDA (RE:F:IDA) polymer synthesis at 60°C reaction temperature under acidic conditions produced a powdery resin. This is probably representative of the low molecular weight novolak structure, which would require further hardening. Under basic catalysis, resins made with IDA, formaldehyde, and either p-cresol, phloroglucinol, or 3,5-dihydroxybenzoic acid (3,5-DHBA) had a similar structure. Resorcinol-glutaraldehyde-IDA resins synthesized at reflux temperature, and the mixed p-cresol-resorcinol resin produced at 60°C were also powders. The remaining polymers, generally those produced from resorcinol, 2,4-dihydroxybenzoic acid (2,4-DHBA), and m-cresol formed brittle solids after dehydration and heat curing.

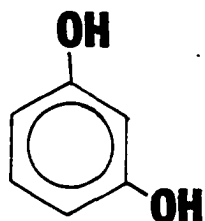
The structures of most of the resins can be explained by examining the number of sites available for electrophilic substitution on each phenol, taking into account the activating and orientating effects of each of the substituents present. For clarity, the phenols being considered are shown in Figure 12. Hydroxyl groups are strongly activating ortho, para directors, alkyl groups are weakly activating ortho, para directors, and carboxylic acids are deactivating meta directors. Therefore, p-cresol has four reactive sites, two strongly activated towards electrophilic substitution and two weakly so. Resorcinol, m-cresol, and phloroglucinol have three sites each. 2,4-Dihydroxybenzoic acid has two active



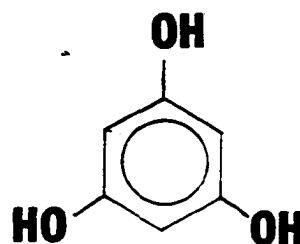
P-CRESOL



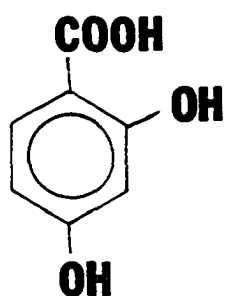
M-CRESOL



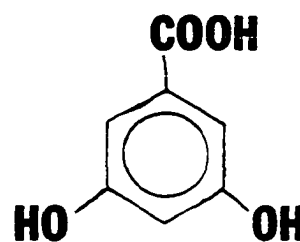
RESORCINOL



PHLOROGLUCINOL



2,4-DIHYDROXYBENZOIC ACID



3,5-DIHYDROXYBENZOIC ACID

Figure 12. Phenols used for polymerizations.

sites, and 3,5-DHBA has but one, if the meta-directing and strongly deactivating influence of the carboxylic acid group is considered to counterbalance the effects of the hydroxyl groups. However, since only one carboxylic acid group and two hydroxyl groups are present, it is possible for this molecule to have a second reactive site, although the susceptibility to electrophilic substitution should be drastically reduced when compared to resorcinol.

Studies of the polymerization of resorcinol and formaldehyde by Sebenik et al. (126) and de Breet et al. (127) have provided evidence that very little ring substitution occurs at the site between the hydroxyl groups, because of steric hindrance. This effect should also be produced by any methyl or carboxylic acid groups present. Therefore, the number of reactive sites is reduced to essentially zero for phloroglucinol and 3,5-DHBA, while resorcinol, m-cresol and 2,4-DHBA retain two each. The four sites in p-cresol are unaffected. Obviously, at least two cross-linking sites are necessary for polymerization to occur. Thus, phloroglucinol and 3,5-DHBA form soft, powdery polymers of poor mechanical stability. On the other hand, the remaining phenols form structurally sound resins. p-Cresol tends to form powdery resins because of the location of its reactive sites on the ring. Polymer formation through the two sites ortho to the single hydroxyl group leads to primarily linear, and so

softer, polymers. The offset nature of the reactive sites on the other phenols produce more three-dimensional frameworks. The only seeming exception to this reasoning is 2,4-DHBA; perhaps the meta-directing influence of the carboxylic acid group produces sufficient substitution at the hindered site between the hydroxyl groups to form a strong polymer.

The softer nature of the glutaraldehyde resin is probably due to the longer carbon chain present in the cross-linking group, although the influence of reaction temperature on this polymerization is still not clear. The furfural cross-linking group is much more rigid than the extended carbon chain in glutaraldehyde, and the resulting resins are therefore much more durable.

Powdery resins form particles that are too small and fragile to incorporate a template solid and maintain a macroporous structure. In addition, powders are generally unsuitable for column use. The very small particles tend to pack under pressure, causing either channeling in the resin bed or plugging of the column, with a resulting buildup of back pressure. In light of these considerations, further detailed studies of resins whose final forms were powders were not undertaken.

Polymers forming brittle solids do not have any of these disadvantages. The templates are occluded easily as the polymer forms, and the mechanical stability of the final resin

state preserves the porosity very well. These resins can be readily ground and sieved to any desired particle size, and they perform well under column conditions. In fact, the porous resins produced in this work seemed to show improved flow characteristics compared to nonporous polymers of similar structure.

The physical nature of the prepolymer mixture ranged from a liquid to a soft gel, and appeared to depend both on the phenol and on the reaction temperature used. Most of the resins containing resorcinol and synthesized at reflux temperature gave a gelatinous prepolymer, as did the m-cresol mixture under the same conditions. At a reaction temperature of 60°C (or, as was later determined, any temperature below reflux) the prepolymer mixture in every case was a liquid. After rotary evaporation of most of the water solvent the remaining viscous liquid could be cured under vacuum to a brittle solid. This would indicate that condensation (cross-linking) only occurs readily at high temperature. In the aforementioned study by Sebenik et al. (126) the authors concluded from thermal data that condensation between hydroxymethylated resorcinols set in at temperatures above 70°C. However, in this work, noticeable gelation of the polymers during the reaction period was only observed at temperatures above reflux. Further examination of the effects of reaction temperature on the sorption characteristics of

these polymers for cesium-137 and strontium-90 will be discussed in a subsequent subsection.

Finally, it should be noted that the general physical descriptions of most of the polymers produced in this study are in good agreement with those of similar resins manufactured industrially.

RE:F:IDA Resins Synthesized with Different Templates

Template materials were chosen taking the following considerations into account:

- 1) The material had to be relatively insoluble in basic solution.
- 2) In spite of this base stability, the substance had to dissolve easily under suitable conditions.
- 3) The solid should be chemically inert towards the reaction mixture.
- 4) Potential templates had to be readily available in a finely divided form.
- 5) Inexpensive materials would be the most attractive.

A number of solid materials which met these general criteria were tested as templates for RE:F:IDA polymers. Resorcinol resins were used because they have proven to be the

most consistently effective resins for the uptake of cesium-137 and strontium-90 in the previous study of nonporous P:F:IDA polymers (77). Table 5 gives distribution coefficient data for resins synthesized with all of the template solids examined. Values for a typical nonporous resin are included for reference. Measurements with a photomicroscope showed that each template considered had a particle size range of 5-10 μm .

Although silica gel powder mixed well with the prepolymer to form a thin slurry, its use as a template produced resins with reduced affinities for the ions of interest compared to a typical resin synthesized without a template. This reduction in affinity undoubtedly resulted from the conditions used for dissolution of the template. A high degree of degradation of the resins treated with HF or strong caustic was evident from physical examination. A large number of fine particles and extensive darkening of these resins were apparent. Further evidence for the degradation of these resins were the very low distribution coefficients for cesium-137. Since the phenolic polymer backbone is the primary site for sorption of cesium-137, a low K_d value for cesium-137 would indicate inadequate incorporation of phenolic functional groups into this backbone. This could result from either poor polymer formation or a subsequent breakdown of the polymer structure.

Table 5. Distribution coefficients of resorcinol-formaldehyde-
iminodiacetic acid resins with different templates^a

Template	$K_d, {}^{137}\text{Cs}^+$ b	$K_d, {}^{90}\text{Sr}^{2+}$ b
NONE	350	890
SiO_2 (HF) ^c	105	320
SiO_2 (NaOH)	20	665
Porasil (HF)	20	1200
Porasil (NaOH)	70	1400
CaCO_3	710	2485
Na_2CO_3	450	870
Cs_2CO_3	60	365
$\text{Cs}_2\text{CO}_3/\text{CaCO}_3$	25	280
$\text{Ca}_2\text{P}_2\text{O}_7$	750	2400
$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$	495	2600
$\text{Mg}(\text{OH})_2$	640	2650
Fe_2O_3 (conc. HCl)	290	4900

^a All resins synthesized at 60°C reaction temperature.

^b K_d values determined in simulated salt solution.

^c Dissolution of templates by treatment with 2 N HCl except where noted in parentheses.

Resins that were cured within porous silica formed fine grains, compared to the chunks of polymer produced with internalized silica powder. Unfortunately, similar cesium-137 distribution coefficients were obtained for both resins. However, the distribution coefficients for strontium-90 were considerably better for the Porasil resins than for those resins synthesized with silica gel powder. The poor cesium values are probably again the result of the harsh dissolution procedure. The rationale for the improved strontium values is not clear. Nonetheless, the generally poor resin sorption characteristics for cesium that resulted dissuaded any further study of silica as a template material.

The next solids tried as templates were a variety of base-insoluble salts. A series of carbonate salts, namely calcium carbonate, sodium carbonate, and cesium carbonate were tested. Also examined were the compounds tribasic calcium phosphate, calcium pyrophosphate, iron oxide (hematite) and magnesium hydroxide. Although generally insoluble in basic solution, all of these compounds except iron oxide could be readily dissolved by treatment with dilute aqueous acid. Concentrated hydrochloric acid was required for the dissolution of iron oxide. Calcium carbonate was considered the most promising choice, because it changed the pH of the reaction mixture by only a small amount (approximately 0.2 pH units). The other solids altered the reaction pH to varying

degrees. The effect of the added template on the reaction pH was minimized by adding the solid just prior to evaporation of the solvent for the lower temperature syntheses. Judging from the K_d data, and the physical properties of the resulting resins, these effects of any pH change were not considerable. It was later determined from the literature that base catalyzed reaction mechanism is observed above pH=5 (98,103). In the case of each template studied, the final pH of the reaction mixture was above this value.

Calcium carbonate, the first such salt tried, produced the desired result. The salt was added as a powder just prior to the addition of formaldehyde. An overnight reaction period was followed by evaporation of the solvent and heat curing. The calcium carbonate remained suspended in solution throughout the procedure. A highly porous material was produced after dissolution of the calcium carbonate with 2 N hydrochloric acid. This effect can be seen in Figure 13. Figure 13a is a scanning electron micrograph of a typical nonporous RE:F:IDA resin at 1000x magnification. Note that the polymer appears glassy, with a relatively featureless surface. Figure 13b is a similar micrograph of a resin produced utilizing the calcium carbonate template. The porosity and improved surface area is readily apparent. An overall improvement in surface area of better than a factor of two was realized. A more complete discussion on the

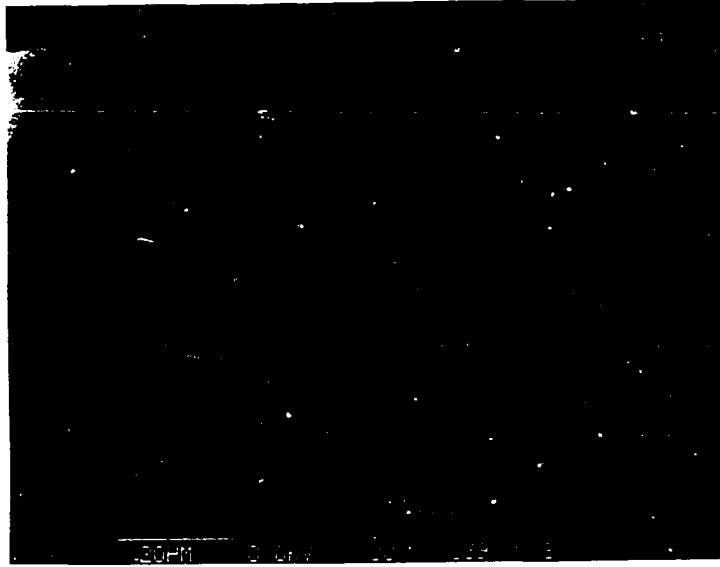
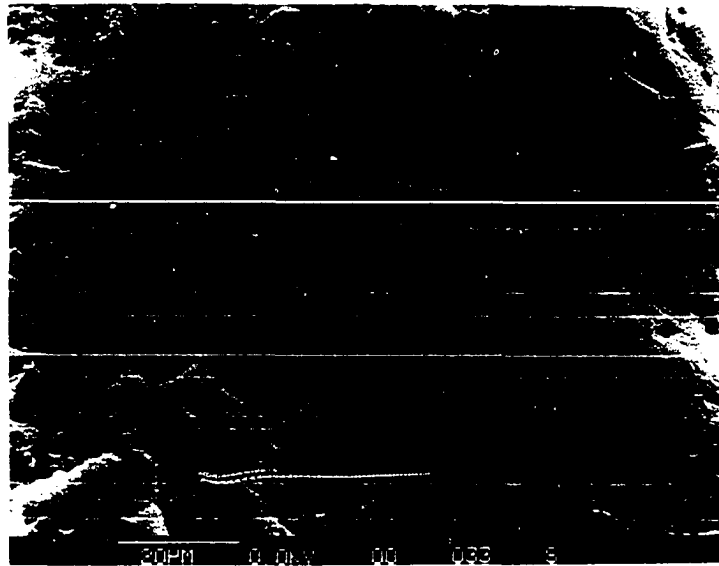
A
~**B**
~

Figure 13. Scanning electron micrographs of resorcinol-formaldehyde-IDA polymers. 1000x magnification.
A) without CaCO_3 B) with CaCO_3

relationship of the amount of added template, surface area, and relative affinities for cesium-137 and strontium-90 will be presented later. However, Table 5 shows that this increase in porosity was accompanied by significant increases in affinity for both cesium-137 and strontium-90.

Resins produced with other carbonate salts were less successful. Sodium carbonate proved to be too soluble at pH=9 and produced a resin with affinities similar to those of the nonporous resin. Cesium carbonate was tried in an attempt to produce resins with pores of suitable size and also exchange sites tailored for cesium ions (by coordination to any soluble cesium). However, this salt was also too soluble under the reaction conditions and produced a very poor resin. The very low K_d for cesium-137 could be partially due to Cs^+ present in the reaction mixture poisoning some of the active sites of the resin by irreversible adsorption. A mixed $CaCO_3/Cs_2CO_3$ template also produced a poor resin. Poisoning may have reduced the cesium-137 affinity here as well, but the low K_d value for strontium-90 remains unexplained.

When acidified, calcium carbonate produces carbon dioxide gas. While this provided a useful indicator for the completion of the dissolution step (i.e. outgassing of CO_2 ceased), some fracturing was caused by the expansion of the gas within the resin. Therefore, several other solids were tried as templates that were soluble under acid conditions but

did not produce gaseous products. Table 5 shows that calcium pyrophosphate and magnesium hydroxide both produced resins with improved affinities for the ions of interest. In fact, both of these polymers had affinities comparable to those of the resin made with calcium carbonate. Additionally, the tribasic calcium phosphate template gave a resin with reasonable affinities for both ions. The resin synthesized with Fe_2O_3 showed an extremely high distribution coefficient for strontium-90. However, elemental analysis of this resin showed that it contained 13% Fe (by weight) after extensive treatment to remove the template. Thus, this very high K_d value is probably a result of the incomplete removal of the hematite. Hematite shows some adsorptive properties for both cesium and strontium (128). Because of the initial success achieved with calcium carbonate, it became the template of choice for further studies of P:F:IDA polymer properties. Future work on resins made with some of the other solids might prove beneficial.

Studies of Various P:F:IDA Polymers Containing CaCO_3

In order to find resins with the highest possible affinities for both cesium-137 and strontium-90, a series of P:F:IDA polymers based on different phenols were synthesized at two different reaction temperatures, using the calcium

carbonate template. Distribution coefficient data for these resins are given in Table 6. The data clearly indicates that the resins with the highest affinities for the ions of interest are the resorcinol based resins and resins synthesized with 2,4-DHBA. Resorcinol-formaldehyde-IDA polymers had the highest overall affinity for strontium-90, while maintaining a reasonably high attraction for cesium-137. Resins based on 2,4-DHBA produced balanced affinities for both ions of interest. This was undoubtedly due, to a large extent, to the presence of a second ion-exchange group. The carboxylic acid group of 2,4-DHBA should also exchange cesium-137 ions, thus increasing the distribution coefficient values for that ion. Polymers based on these two resins were used in selected for further study.

In each case, the resins showed an inversion of affinities between reaction temperatures. Resins synthesized at 60°C showed a generally higher affinity for strontium-90, while those synthesized at reflux temperature showed a greater attraction for cesium-137. The inverse relationship between the distribution coefficients for cesium-137 and strontium-90 was seen consistently in resins made from resorcinol. The effect was less pronounced in 2,4-DHBA:F:IDA polymers.

Initially, it was thought that this relationship resulted from competition for the two ions of interest by the two sequestering groups present, especially by the phenols.

Table 6. Distribution coefficients of various porous phenol-formaldehyde-iminodiacetic acid polymers^a

Phenol	60°C		100°C	
	K_d, Cs^+	K_d, Sr^{2+}	K_d, Cs^+	K_d, Sr^{2+}
Resorcinol	710	2485	2085	450
2,4-DHBA ^b	1465	1430	1600	580
3,5-DHBA	0	0	dec. ^c	dec. ^c
m-Cresol	50	940	45	870
p-Cresol	1	315	110	360
Phloroglucinol	0	4	---	---
1:3 p-Cresol/Resorcinol	365	1400	2550	405
1:1 2,4-DHBA/Resorcinol	1100	2200	3100	380

^a All resins synthesized with $CaCO_3$ template and K_d s measured in simulated salt solution.

^b DHBA = dihydroxybenzoic acid.

^c dec. = decomposed during testing.

Besides acting as an ion-exchange site for monovalent cations, the meta hydroxyl groups on resorcinol can form a six-membered ring chelating site with divalent metals. Formation of this site should be especially favorable under basic conditions, with the phenols being present primarily as phenolates. If so, perhaps the phenolic sites were competing for strontium-90 with the iminodiacetic acid sites. Likewise, a competition for monovalent cesium-137 between phenolate sites and the carboxylic acid groups of IDA would be possible. Such a competition could produce the cooperative relationship between the distribution coefficients that was observed.

This hypothesis was tested by measuring the resin distribution coefficient for one ion in the presence of steadily increasing amounts of the other. As the amount of analyte ion present increases, the exchange sites on the resin should eventually become loaded. The observed result is a rapid decrease in distribution coefficient value at high analyte ion concentrations. If the two sites present on these resins are competing for the same analyte ion, then a concerted drop-off in K_d s for both ions should be observed as the concentration of only one ion is increased. The results of this experiment are depicted graphically in Figure 14.

In Figure 14a the distribution coefficients are plotted for increasing cesium concentration. Note that while the anticipated decrease in cesium-137 K_d is seen at high cesium

concentration, the distribution coefficient for strontium-90 remains constant regardless of the the cesium concentration. A similar plot is shown in Figure 14b for increasing strontium concentration, with the same results. The cesium-137 K_d is constant throughout the entire range of strontium concentrations. The conclusion drawn is that the exchange or chelating sites for each ion of interest work independently of one another. Thus, competition for sites cannot explain the observed relationship between the distribution coefficients. As will be described in a succeeding subsection, this relationship appears to be merely a consequence of the reaction temperature used, and the amount of IDA that was incorporated into the resin at each temperature.

It is perhaps appropriate at this point in the discussion to put forth some possible explanations for the observed selectivity of these resins for cesium-137 and strontium-90. The selectivity of these resins for strontium-90 is undoubtedly due to the selectivity of the chelating group present. Iminodiacetic acid and related compounds (such as EDTA) have long been known to show high affinities for divalent cations, especially the alkaline earths (76,129). The formation constant for sodium with EDTA is several orders of magnitude lower than that for strontium. A similar situation should exist with iminodiacetic acid. The low levels of strontium-90 present in the waste supernatant, and

the general lack of other divalent species, produces a very favorable situation. The chelating group should be primarily present as the dianion (or the disodium salt) in the strongly basic supernatant.

The observed selectivity for cesium-137 in a high-sodium matrix is probably due to a combination of effects. According to both the data presented here and other work pertaining to the affinity of EDTA for alkali metals, it is clear that the IDA moieties are not involved in cesium-137 adsorption. The phenolic groups, or more correctly, the phenolate groups, are the primary exchange groups for the monovalent cations, including cesium-137. Resins of this type display the classical selectivity characteristics found for most cation exchangers. Cesium is preferred over sodium, because of its smaller hydrated volume (130). This effect is somewhat diminished by the high degree of cross-linking present in phenol-formaldehyde type condensation resins, but is increased because of the small amount of cesium-137 present compared to sodium.

In a similar vein, the selectivity of these resins for cesium-137 may be partially due to entropy effects. Prior to adsorption, the resins are converted from the H^+ to the sodium form. The matrix is brine consisting of solvated anions and cations. The cationic "structure" consists almost entirely of

sodium ions, with small amounts of other cations. The overall internal structure of the brine is disrupted by the presence of cations other than sodium. Therefore, cesium-137 ions would be forced out of the matrix onto the resins site to be replaced in the brine by sodium counterions from the resin. The exchange phenomena thus restores the internal regularity of the brine solution, minimizing its internal energy. This idea is somewhat similar to the theory proposed by Diamond and Whitney (131), where a restoration of the internal solvent structure of water is a driving force for ion exchange and helps determine selectivity.

Lastly, some of the selectivity may be due to the internal structure of the polymer itself. Macrocylic polyphenols called "calixarenes" have been synthesized and used to as liquid membranes to transport cesium ions (132). These compounds consist of a number of substituted phenol molecules (typically, p-tert-butyl phenol) joined into a ring by methylene bridges. The hydroxyl groups point towards the inside of the ring because of the steric hindrance of the substituent alkyl groups. This produces an electron-rich ring with high selectivity for cesium ions. The low hydration energy of cesium has again been proposed as the primary effect responsible for the observed selectivity, but the size of the ring that is produced may also have a small effect. Similar structures may form during phenol-formaldehyde

polymerizations, such as those being discussed here. This could lead to improved selectivity for cesium-137.

Column Studies

Based on the data described in the preceding subsections, the resorcinol resins synthesized at both reaction temperatures and the 2,4-DHBA resin synthesized at 60°C were tested for their usefulness under dynamic (i.e. column) conditions. Breakthrough curves for both cesium-137 and strontium-90 in simulated supernatant on each of these resins are shown in Figures 15 and 16. Curves for those nonporous Re:F:IDA with the best distribution coefficients for each ion are also included for reference. If resin capacity can be estimated from the point of 50% breakthrough, then the capacity of a typical "low temperature" porous resin is about one-half the cesium-137 capacity of the best nonporous resin, and the "high temperature" has approximately the same capacity (see Figure 15). However, most of the porous polymers being considered were only about half as dense as a typical nonporous resin (0.16 g/mL versus 0.32 g/mL). Thus, on a weight basis (i.e. meq/g), the low temperature porous resin has the same cesium-137 capacity (~0.1 meq/g) as the best nonporous resin, and the high temperature porous resin has double the cesium-137 capacity of the best nonporous resin.

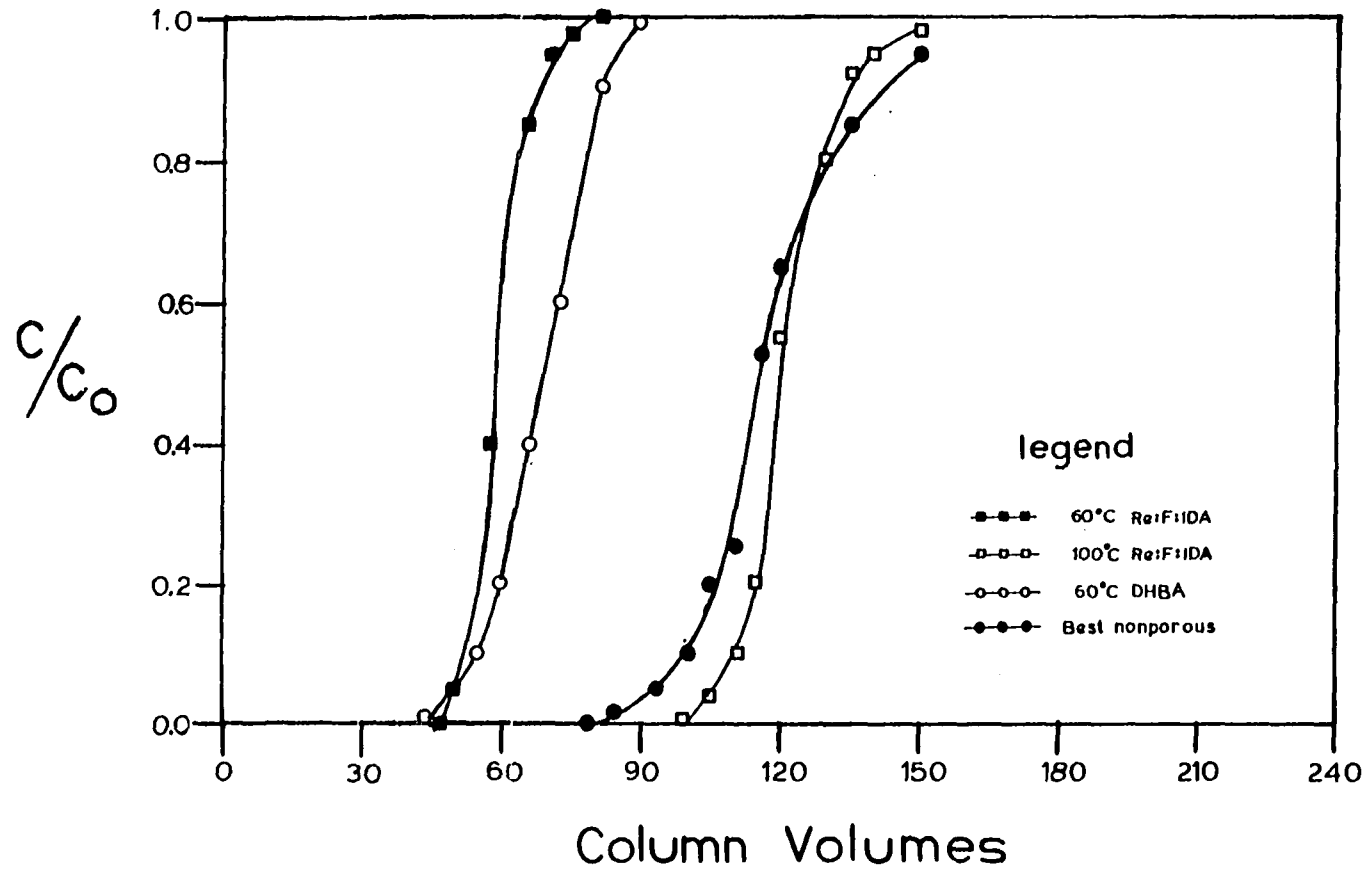


Figure 15. Cesium breakthrough curves for various resins. All runs using simulated supernatant and +100/200- resin.

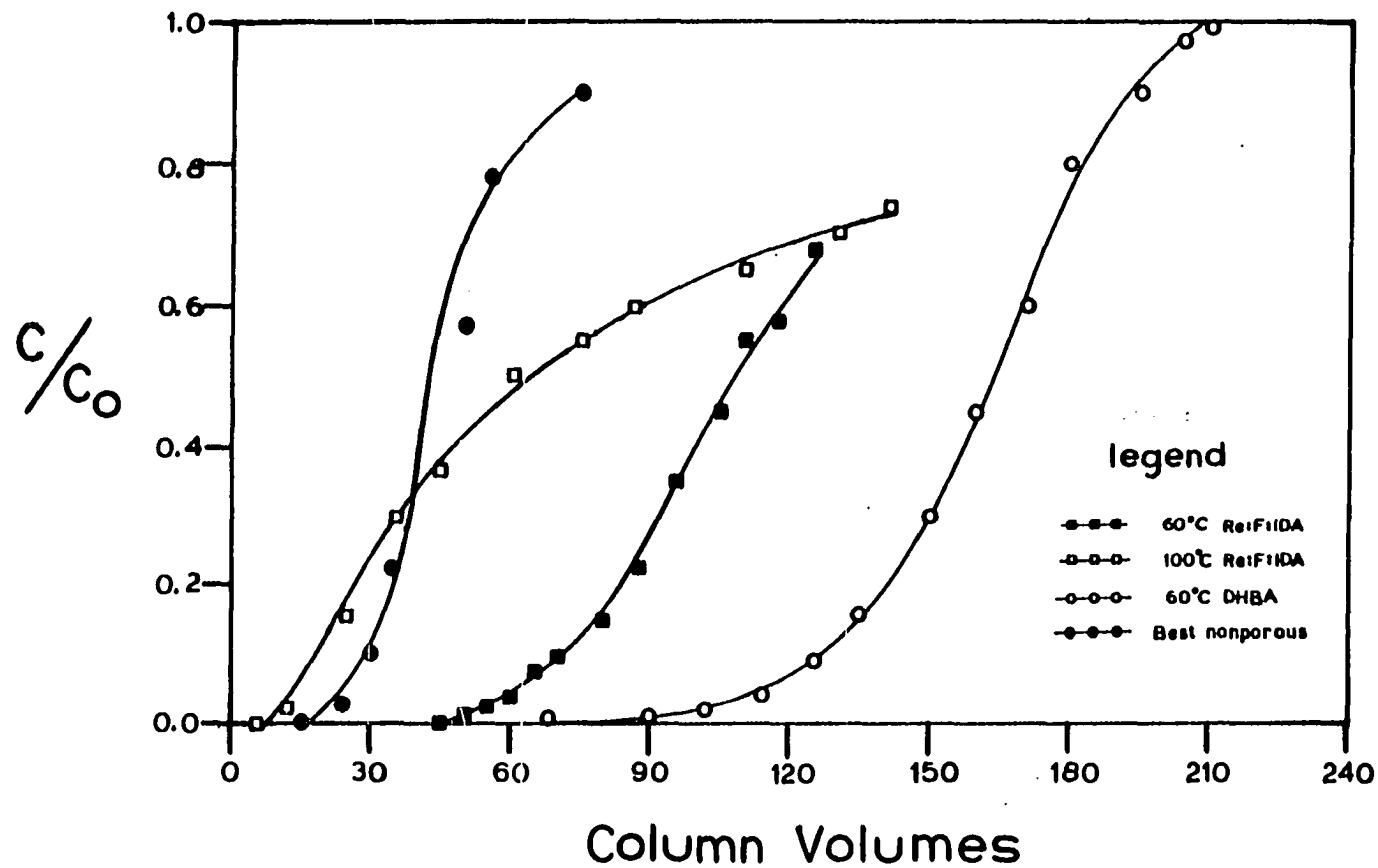


Figure 16. Strontium breakthrough curves for various resins. Same conditions as Figure 15. DHBA curve somewhat exaggerated due to lower flow rate.

For the strontium-90 breakthrough curves shown in Figure 16, the volume basis capacity of the low temperature resin is more than twice that of the best nonporous resin. On a weight basis, this corresponds to an over four-fold increase in capacity. The strontium-90 breakthrough curve for the high temperature porous resin is very poor. This seems to indicate that only a small amount of IDA is present in this resin. The breakthrough curves for the 2,4-DHBA resin closely resembled those of the low temperature resorcinol resin, despite the differences in their distribution coefficients. As yet this unexpected result remains unexplained. Perhaps this result is merely a consequence of the inherent inaccuracy of K_d values. Despite apparently large differences in K_d , the differences may not be large enough to significantly effect the overall resin capacity.

Columns of these resins can be easily regenerated, as seen in Figure 17. A 2 N solution of formic acid will elute a typical column in 5-10 column volumes, with an overall recovery of better than 90 percent for both ions.

Synthetic Reproducibility and Scale-up Studies

Before studying the effect of various reaction parameters on resin affinity for cesium-137 and strontium-90, the reproducibility of the polymer synthesis was examined.

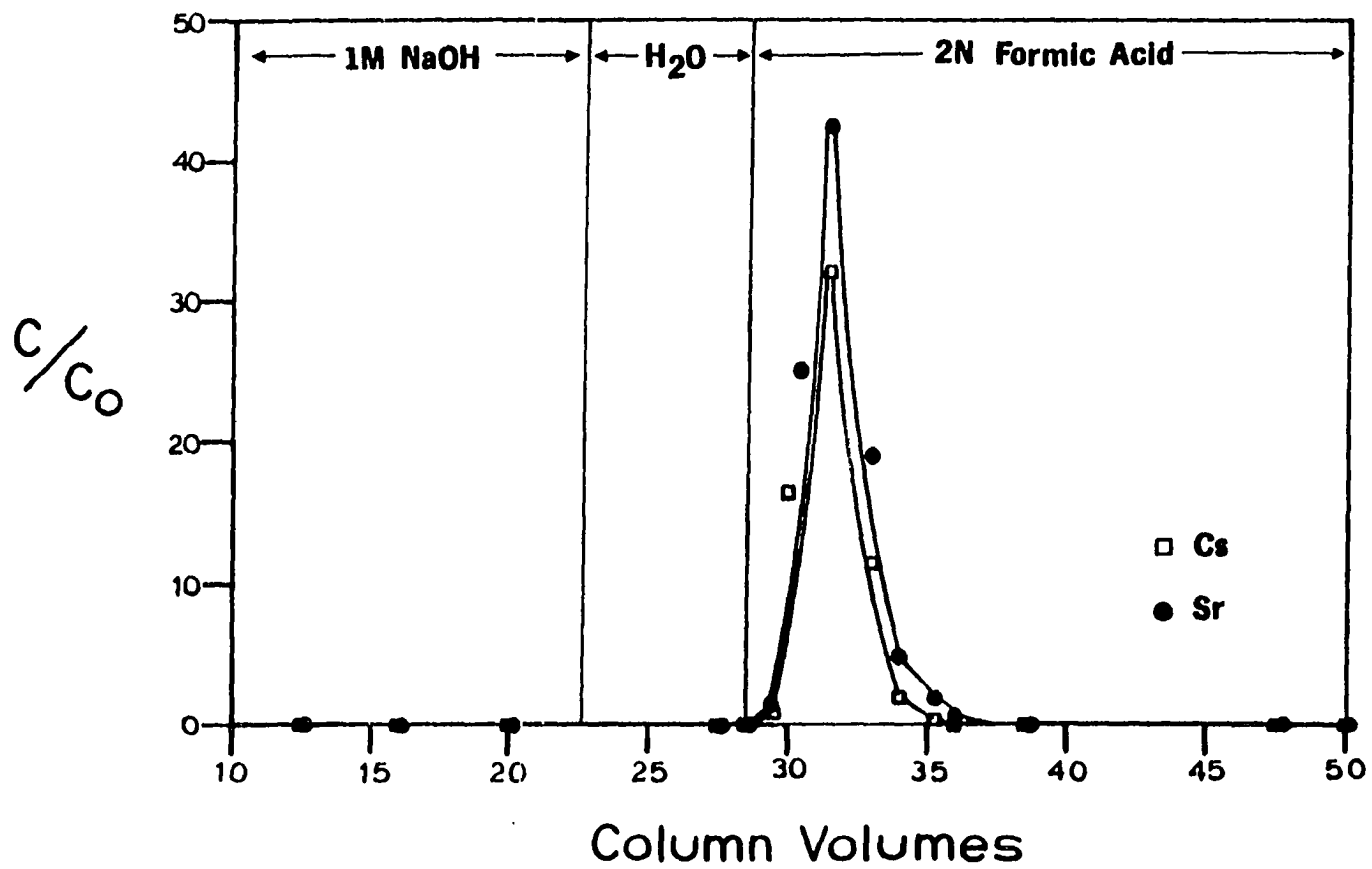


Figure 17. Elution curves for resorcinol-formaldehyde-IDA resin.

Studies were made to check both the compositional duplication and the reproducibility of distribution coefficient data.

Table 7 gives a summary of the data.

Nitrogen analysis of resins synthesized under the same conditions was used to determine the amount of iminodiacetic acid present. This is reasonable, since IDA would be the only potential source of nitrogen. Considering that undue care was not taken in performing the syntheses, and the extensive number of possible reactions that could take place in a one-pot synthetic scheme such as the one used, a percent relative deviation in nitrogen content of 8% for the seven resins synthesized at 60°C is quite respectable. Equally good results were obtained for the other resins studied.

The reproducibility of K_d data for the various resins was considerably worse than that for the compositional studies. Percent relative deviations of between 20% and 45% were seen. However, it is the nature of distribution coefficients to be excellent indicators of relative affinity, but not necessarily of absolute capacity. They are typically inexact but useful figures. A very small change in the amount of analyte ion determined to be sorbed by the resin (itself a source of error) can result in large differences in the calculated distribution coefficient. In fact, often only changes in K_d of orders of magnitude are considered significant. In light of the inherent inaccuracy of K_d s, the results in this study

Table 7. Synthetic reproducibility for phenol-formaldehyde-
iminodiacetic acid polymers

Resin	$K_d, {}^{137}\text{Cs}^+$ a	$K_d, {}^{90}\text{Sr}^{2+}$ a	Wgt % N
RE:F:IDA (60°C;1X) ^b	635 ± 260 ^c	2690 ± 800	1.90 ± 0.16
RE:F:IDA (60°C;2X)	820 ± 335	2180 ± 500	1.65
RE:F:IDA (60°C;all)	710 ± 290	2485 ± 710	-----
RE:F:IDA (60°C;10X)	1400	1500	-----
RE:F:IDA (100°C;1X) ^d	2050 ± 875	400 ± 100	0.70 ± 0.06
RE:F:IDA (100°C;2X) ^d	1590 ± 415	535 ± 35	0.52
RE:F:IDA (100°C;1X) ^e	3165 ± 815	490 ± 15	-----
RE:F:IDA (100°C;all)	1880 ± 750	450 ± 100	-----
DHBA:F:IDA (60°C;1X)	1465 ± 500	1430 ± 715	1.16
DHBA:F:IDA (60°C;10X)	1400	1500	-----

^a All K_d s determined in simulated salt solution.

^b RE = resorcinol; DHBA = 2,4-dihydroxybenzoic acid; F = formaldehyde; IDA = iminodiacetic acid. Last number stipulates batch size, with "all" meaning all batch sizes.

^c Data is reported as a mean and standard deviation for measurements involving three or more samples. Figures reported without standard deviations are averages determined from less than three samples.

^d Used heating mantle as heat source.

^e Used constant temperature oil bath as heat source.

are reasonable. Based on this reproducibility data, a two-fold change in distribution coefficient was considered to be a significant change in subsequent studies. A review of the data presented prior to this study shows that all of the conclusions reached are in accord with this criterion.

Several reflux temperature syntheses were performed using an oil bath for heating the reaction mixture, rather than a heating mantle. Maintenance and control of a homogeneous reaction temperature is much easier with the oil bath than the mantle heater. Distribution coefficient results were used to test the effect of careful temperature control on the reproducibility of the synthesis. Although the mean K_d values were higher for the oil bath resins, the standard deviations were large enough to make the differences insignificant. However, application of the F-test (133) to these sets of data indicates that the standard deviations of the strontium-90 K_d data sets are significantly different at the 90% confidence level. The variations in the cesium-137 data sets are not significantly different. It would be advisable, therefore, to maintain some measure of temperature control under any conditions, to ensure reproducible incorporation of IDA. Excellent temperature control was obtained in the lower temperature reactions through the use of a circulating water bath as a heat source. Reaction temperatures using this device were reproducible to $\pm 0.1^\circ\text{C}$.

Reproducible resin affinities for the ions of interest does not necessarily ensure reproducible response under column conditions. Therefore, how closely the breakthrough curves for several columns of resins produced under similar conditions would resemble each other was checked. As seen in Figure 18, both the cesium-137 and strontium-90 curves for a series of 60°C resins appeared to be nearly the same. Figure 19 shows this to be true for a series of reflux temperature resins, as well.

Another conclusion drawn from this study is that scaling up the polymerization had an insignificant effect on the affinity of the resulting resin for either cesium-137 or strontium-90. Nitrogen analysis of double and ten-fold batches of resins under all of the conditions examined showed them to be close to those obtained for the respective single batches. Comparison of the standard deviations of the affinity (K_d) data for single and double batches of resin synthesized at 60°C and 100°C by the F-test showed that they were the insignificantly different for both 90% and 98% confidence intervals. Admittedly, these scale-ups are small compared to any that may eventually be used for industrial applications, but the data are encouraging nonetheless. Tests of larger scale-up processes can be made at a later time, if necessary.

One final consideration in judging the accuracy of

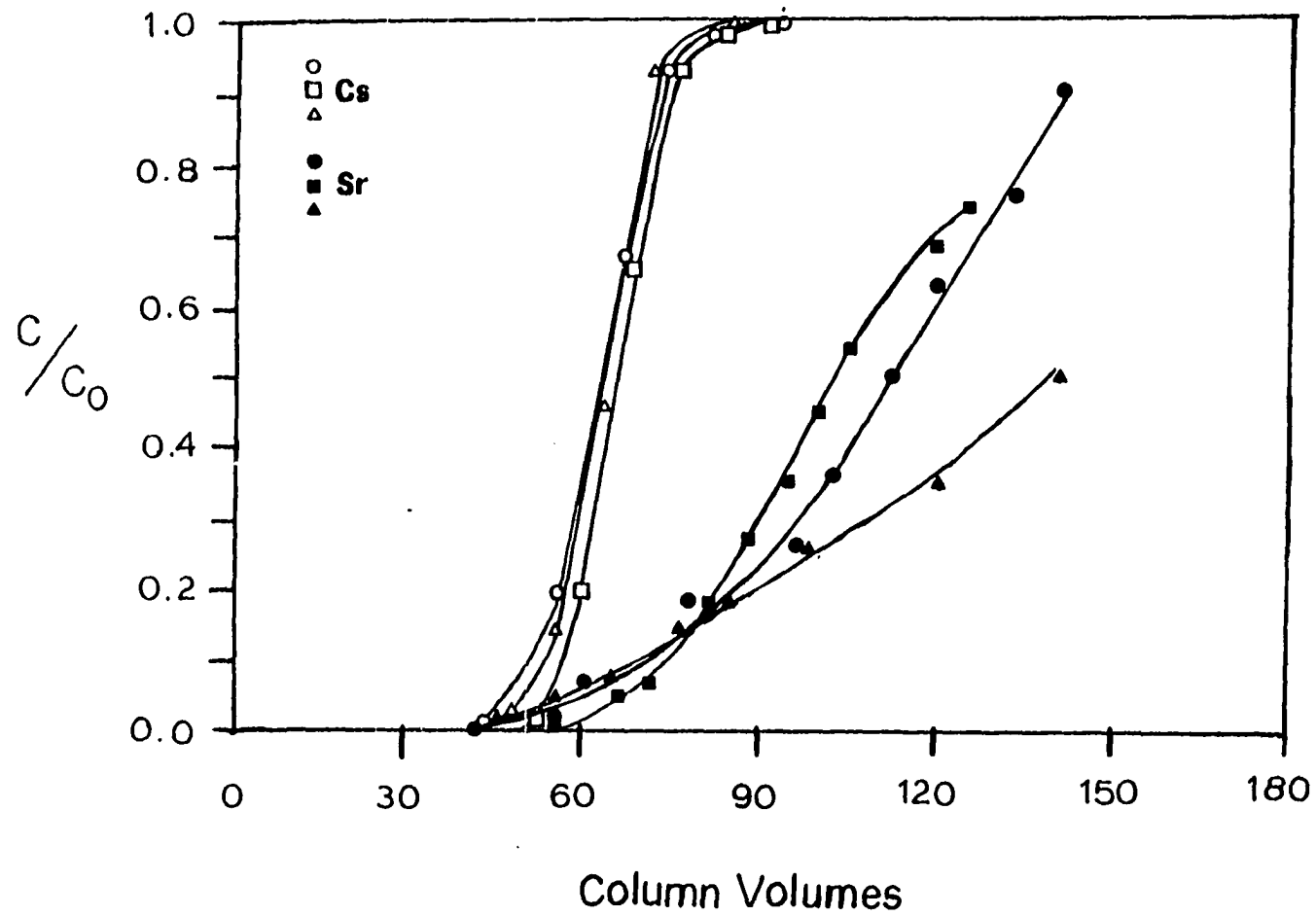


Figure 18. Breakthrough curves for three different batches of RE:F:IDA resin synthesized at 60°C.

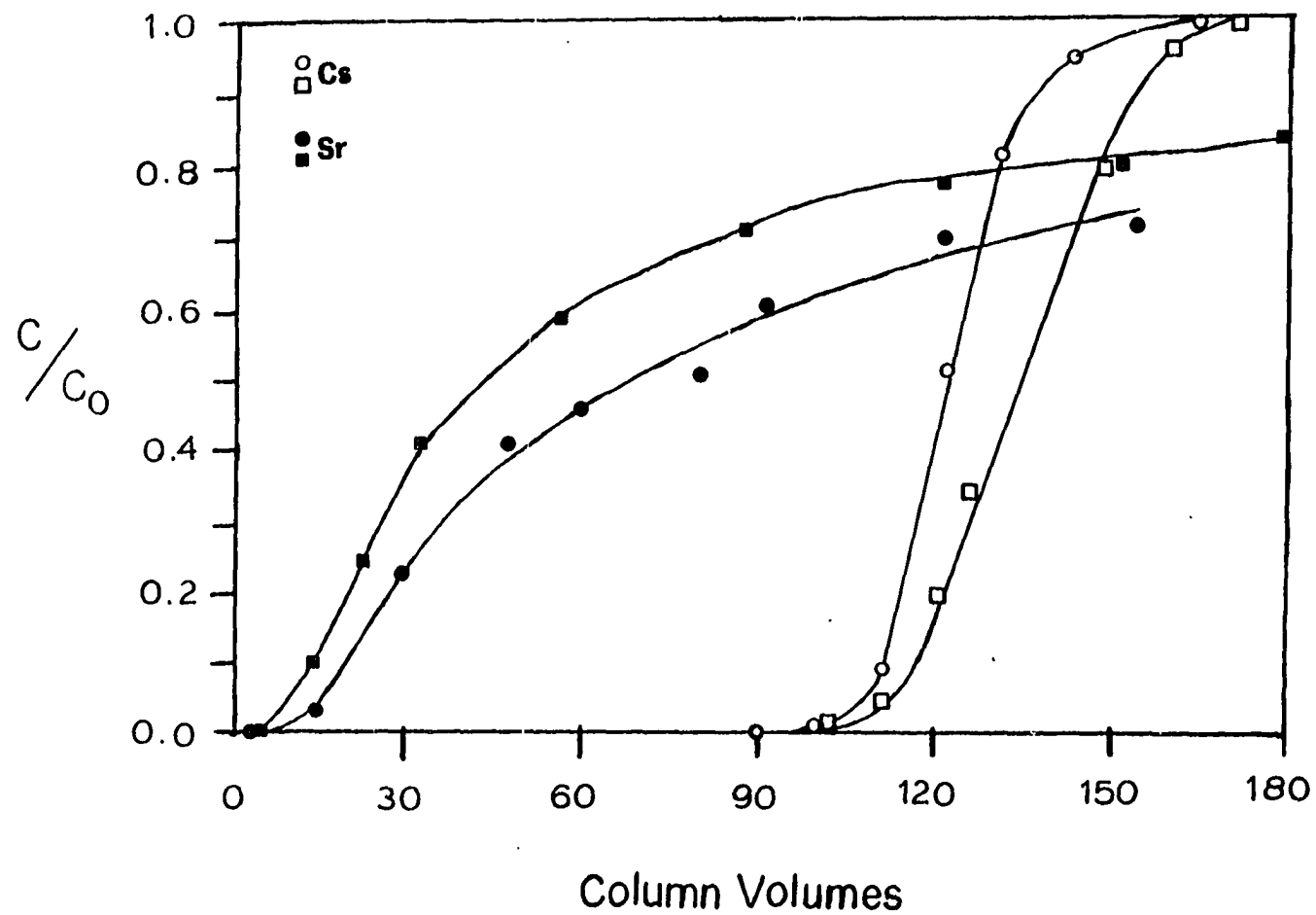


Figure 19. Breakthrough curves for two different batches of RE:F:IDA resin synthesized at 100°C.

distribution coefficient measurements is any effect of the particle size of the resin on these determinations. This effect is illustrated in Table 8. It is obvious from the data that there was essentially no change in the distribution coefficients over a substantial particle size range. This is a somewhat surprising result. Gel-type resins typically display increased K_d values with decreasing particle size as a result of the increased surface area available for exchange in smaller particles. The trend observed here is generally seen for high surface area macroporous exchangers, where much of the total surface area is internal. In such cases, decreasing the particle size produces only small changes in the overall surface area. The surface areas of the resins in this study were lower than $5 \text{ m}^2/\text{g}$, which is several orders of magnitude smaller than those of typical macroporous polymers. Thus, it would be expected that their properties would more closely resemble those of gel-type resins rather than macroporous exchangers. Nonetheless, the data seem to indicate that the internal surface area of the porous polymers was a significant enough fraction of the total to negate the effect of particle size. To maintain consistency in the K_d measurements used in this work, all determinations were carried out on +100/200-mesh (75-150 μm) resin, despite the negligible effect of particle size on the distribution coefficients. This particle size range was convenient for use in column applications.

Table 8. Effect of grinding on distribution coefficients^a

Mesh Size	$K_d, {}^{137}\text{Cs}^+$ b	$K_d, {}^{90}\text{Sr}^{2+}$ b
<u>Single Resin Batch</u>		
+40/60-	480	1700
+80/100-	530	2700
+140/160-	630	2200
<u>Ten-fold Resin Batch</u>		
>40	1500	1700
+40/60-	1500	1800
+60/80-	1600	2000
+80/100-	1500	1900
+100/200-	1600	2000
+200/325-	1600	1700

^a Using resorcinol-formaldehyde-IDA resin synthesized at 60°C reaction temperature.

^b All K_d s measured in simulated salt solution.

Effect of Reaction Temperature

The temperature at which the Re:F:IDA polymers were synthesized was found to have a pronounced effect on their relative affinities for cesium-137 and strontium-90. Distribution coefficient and nitrogen analysis data for a series of resins manufactured at different temperatures is presented in Table 9.

A gradual and regular increase in affinity for cesium-137 is seen with increasing reaction temperature. The distribution coefficient values for strontium-90 appear to be relatively independent of reaction temperature below reflux temperature. A drastic decrease in strontium-90 affinity is seen for resorcinol resins synthesized at temperatures exceeding 100°C. This drop-off in strontium-90 affinity is accompanied by a sharp decrease in the nitrogen content of the resin, which would indicate poor incorporation of IDA into the polymer. Further evidence for this observation are the generally poor strontium-90 breakthrough curves exhibited by resins manufactured at this temperature, as previously mentioned.

These results can best be explained by mechanistic considerations. As was described in the overview portion of this dissertation, both Mannich condensation of IDA with a phenol and the initial hydroxymethylation step leading

Table 9. Effect of reaction temperature on distribution coefficients for resorcinol-formaldehyde-imino-diacetic acid polymers

Temperature	$K_d, {}^{137}\text{Cs}^+$ a	$K_d, {}^{90}\text{Sr}^{2+}$ a
25°C	260	2125
40°C	510	2150
60°C	710	2485
80°C	1375	2150
100°C (reflux)	1880	450

^a All distribution coefficients are the average of two runs measured in simulated salt solution.

to polymerization produce ortho adducts. Thus, the two reactions must compete for reactive ortho sites on resorcinol. Under acidic conditions, the competition is between the formaldehyde electrophile and the carbonium ion form of the base. In basic media, the competition is between hydroxymethylation and formation of the hydroxylamine followed by displacement. The amount of IDA incorporated into any resin would depend on the Mannich condensation reaction's ability to compete effectively for sites under the conditions used. From the data, it would appear that Mannich condensation competes favorably with prepolymer formation at temperatures below 100°C (although the total amount of IDA added is still low). Since it can be reasonably assumed that sufficient formaldehyde is present to form adequate amounts of hydroxylamine, displacement and hydroxymethylation are probably the primary competitive reactions here. However, at reflux temperature, hydroxymethylation seems to be so facile that formation of the Mannich base is almost totally excluded. This would account for the inverse relationship between the distribution coefficients noted earlier. The less IDA product that forms, the more prepolymer molecules that can be produced. Resorcinol should polymerize more effectively under these conditions. Therefore, it would be reasonable to assume that the high temperature resins simply contain more resorcinol groups, resulting in a higher overall affinity for

cesium-137. Likewise, the gradual increase in cesium-137 K_d with reaction temperature can be explained by more efficient hydroxymethylation at higher temperature. Some of the results described in the next subsection will expound upon this hypothesis.

The low cesium-137 affinities and poor physical properties of the resins synthesized below 60°C excluded them from further consideration. However, because of the equivalency of the cesium-137 and strontium-90 K_d s observed for Re:F:IDA resins synthesized at 80°C, several column runs were performed using these resins. Comparison of the breakthrough curves seen in Figure 20 with those for the low temperature resorcinol resin shown in Figures 15 and 16 shows little difference in capacity or exchange kinetics between the two resins. A strict interpretation of the K_d data again appears to have been somewhat misleading.

Resins Synthesized Under Special Conditions

As a further examination of the effects of various reaction condition changes on the resins produced, a number of polymers were synthesized using special procedures. Distribution coefficient data for these resins are presented in Table 10.

Although oligomer formation cannot be ruled out, it is

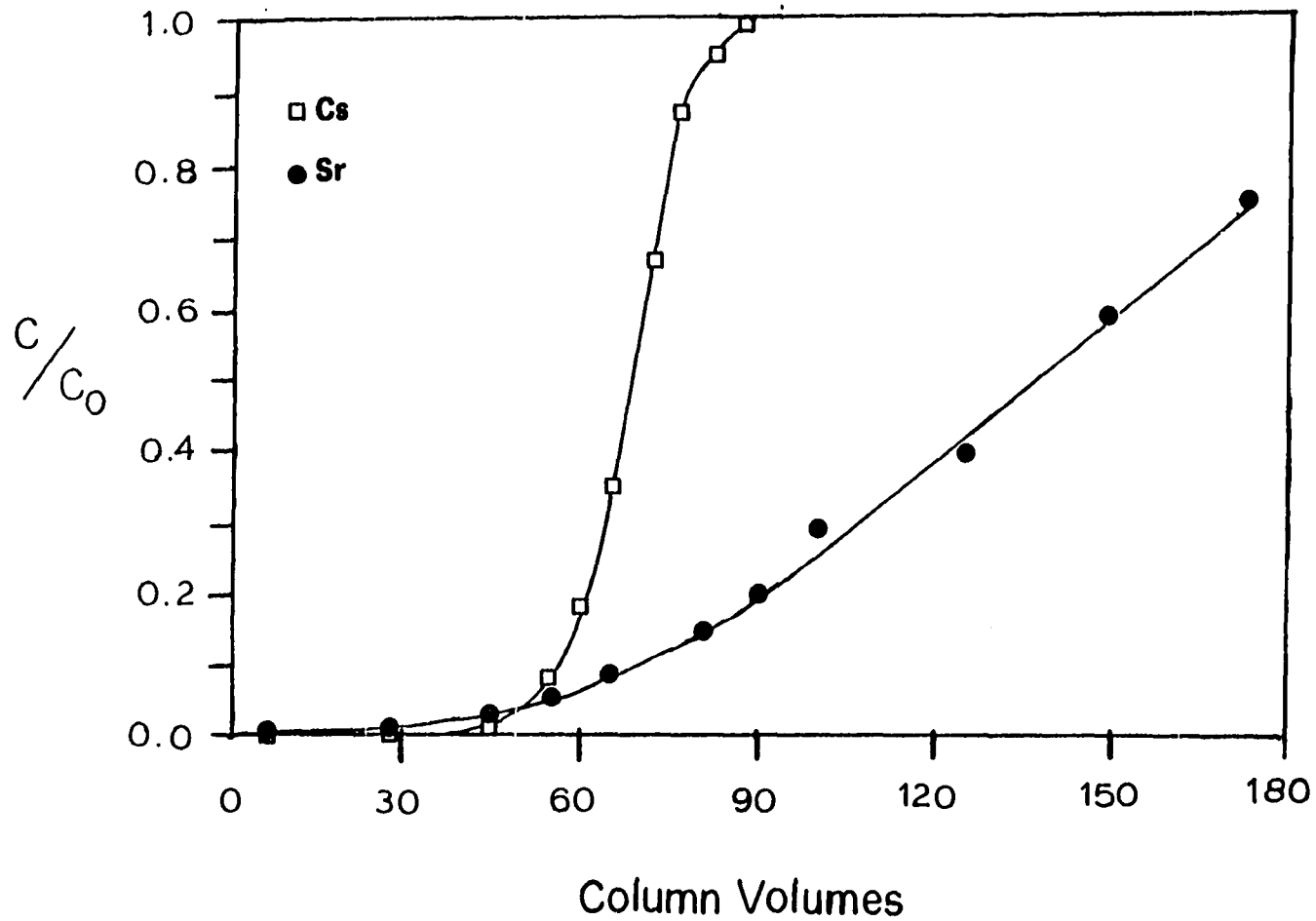


Figure 20. Breakthrough curves for RE:F:IDA polymer synthesized at 80°C. Simulated supernatant and +100/200- resin were used.

Table 10. Cesium-137 and strontium-90 distribution coefficients for resins synthesized under special conditions

Reaction Conditions	$K_d, {}^{137}\text{Cs}^+$ a	$K_d, {}^{90}\text{Sr}^{2+}$ a
Normal/60°C	710	2485
Normal/reflux	1880	450
Late template add'n/60°C	415	2150
Dropwise F add'n/reflux	1100	510
1xF @ 60°C/6xF @ reflux	1050	500
Long procedure 60°C/reflux	1000	2000
Normal 60°C/cured at 110°C	1200	790
Time study/reflux	2750	295
Surface functionalization	300 (930) ^b	835 (335) ^b

^a All K_d s measured in simulated salt solution.

^b Number in parentheses represents the distribution coefficient for the original resin (w/o IDA) prior to surface functionalization.

doubtful that substantial polymer formation occurs during the reaction period for reactions below reflux temperature. This conclusion is supported by the fact that the distribution coefficients for a resin where the template was added to the prepolymer liquid just prior to rotary evaporation did not differ significantly from resins synthesized in the usual fashion. Therefore, provided that a low reaction temperature is used, the point at which template is added to the mixture is not critical.

Dropwise addition of formaldehyde to a refluxing prepolymer mixture produced a resin with affinity characteristics resembling those of typical high temperature resins. With an excess of both substrates present (phenol and amine), very little IDA was incorporated into the resulting polymer. This indicates that hydroxymethylation of the phenol is greatly favored over Mannich condensation at this temperature. A similar resin was produced when one molar equivalent of formaldehyde was added to a mixture of IDA and resorcinol at 60°C, heated to reflux, and the remaining excess formaldehyde added thereafter. Apparently, hydroxymethylation is favored over Mannich condensation even at temperatures below reflux, if a large excess of substrate is present. However, should the formaldehyde be in large excess, Mannich condensation can compete with hydroxymethylation to some extent, as shown by the higher strontium-90 K_d 's in the typical

low temperature resins. It seems reasonable to propose, then, that hydroxylamine formation is slow compared to hydroxymethylation, even at lower temperatures, when the two reactions must compete for formaldehyde. Excess formaldehyde is therefore required to produce enough of this intermediate to give significant amounts of Mannich condensation. Even more interesting are the distribution coefficients for a resin manufactured by a somewhat more detailed reaction scheme.

From the data for the previous two resins, it became obvious that an excess of phenol over formaldehyde had to be avoided for a significant amount of Mannich condensation to occur. Rapid hydroxymethylation prevented any of the amine intermediate from forming. Therefore, one molar equivalent of formaldehyde was added to an equivalent of IDA at pH=9 and 60°C, and this mixture was allowed to stir for a short period of time. This, it was hoped, would induce formation of the hydroxylamine. Resorcinol was then added in a dropwise fashion (as an aqueous solution), to maintain an excess of hydroxylamine in solution. After addition of the resorcinol was complete, the reaction mixture was heated to near reflux temperature, the CaCO₃ template stirred in, and another 6 molar equivalents of formaldehyde added. After reacting overnight, the resin that was produced showed affinities similar to those of a low temperature polymer. A high strontium-90 K_d , and a lower distribution coefficient for

cesium-137 were seen (refer to Table 10). This result strongly supports the proposed mechanistic explanation for the observed affinities of P:F:IDA polymers.

The deleterious effect of high temperatures was even seen during the curing stage. Curing a portion of low temperature resin at 110°C produced a low strontium-90 K_d value and a high value for cesium-137. Curing a second portion of the same resin at 60°C gave the normal distribution coefficient pattern. Perhaps elimination of IDA occurred during high-temperature curing, or, more probably, the reaction was incomplete prior to this step. Note that the reverse situation does not produce low-temperature type resins, since most of the resins produced at reflux temperature were cured at 60°C. Future examinations of the curing step may provide insight into the mechanism of this process.

A time study of the high temperature reaction was performed using simple observation of the solution to determine when polymerization was more or less complete. From this study, it was concluded that a reaction period of at least 12 hours was required for a substantial amount of gelation to occur. On this basis, and from determinations made in an earlier study (77), a overnight reaction period was used for most of the polymerizations. A future series of experiments to examine changes in the low temperature reaction mixture with time may show that a shorter reaction period is

possible, but for this work overnight reactions were both convenient and ensured complete reaction.

Close examination of the breakthrough curve for strontium-90 shown in Figure 16 for the low temperature resin shows that, while the capacity is high, the curve has a low slope and is fairly drawn out. This is in marked contrast to the very sharp breakthroughs for cesium-137 seen in Figure 15. The gradual breakthrough implies that the resin exchange kinetics for this particular ion are somewhat slow. This may be caused by a combination of slow diffusion within the resin and the nature of the IDA chelating group, which tends to wrap itself around the metal ion. To reduce the diffusion required, and hopefully, improve the sharpness of the breakthrough curve for strontium-90, surface functionalization of a resorcinol-formaldehyde polymer with IDA was attempted. A porous P:F polymer was synthesized in the usual manner, utilizing a CaCO_3 template. Some of this resin was treated with IDA and formaldehyde at 60°C to try to induce Mannich condensation of the IDA just at the surface of the polymer. Table 10 shows that the resulting resin did show a slight improvement in strontium-90 K_d over the original polymer, but not enough to support further testing. Additionally, a decrease in cesium-137 affinity was also observed. This unexpected result is not readily rationalized. Since the majority of the ortho reactive sites in the polymer are

occupied by methylene cross-links, some addition of IDA between the hydroxyl groups may have occurred. This, in turn, may have caused a reduction in cesium-137 adsorption by steric hindrance of the hydroxyl exchange groups. Nonetheless, the results for this resin were not considered promising enough to merit more detailed study.

Resins Synthesized with Different Reactant Ratios

In order to determine if there was an optimal ratio of reagents for the production of high affinities for both ions of interest, a number of different resins were synthesized at two different reaction temperatures. Distribution coefficient data for these resins is presented in Table 11.

With a single exception, a large increase in strontium-90 affinity is seen at the 60°C reaction temperature for resins containing IDA over those containing none. This corresponds to incorporation of IDA into the polymers, as evidenced by the nitrogen analysis results listed in Table 7. However, at 100°C, no significant increase in strontium-90 affinity was seen for any resin. Again, this shows that very little IDA adds at this temperature.

Interestingly, even resins containing no IDA showed some attraction for strontium-90. This was also thought to be produced by the dual hydroxyl groups on resorcinol chelating

Table 11. Distribution coefficients of porous resorcinol-formaldehyde-iminodiacetic acid polymers^a synthesized using different initial reactant ratios^a

RE:IDA:F Ratio	60°C		100°C	
	K_d, Cs^+	K_d, Sr^{2+}	K_d, Cs^+	K_d, Sr^{2+}
1 : 0 : 3.5	480	520	1350	445
1 : 0 : 7	420	490	930	335
1 : 1 : 3.5	590	2800	920	780
1 : 1 : 7	710	2485	1880	450
2 : 1 : 14	705	495	1600	960
3 : 1 : 21	300	2400	1200	920
3 : 2 : 21	535	1500	1900	540
4 : 1 : 28	260	1500	1000	600
1 : 1 : 14	635	1950	1500	420
1 : 2 : 7	580	2200	3000	660

^a All resins synthesized with $CaCO_3$ template and K_d s measured in simulated salt solution.

to the divalent metal. However, loading experiments similar to those mentioned previously did not indicate the presence of site competition. The source of this strontium sorption remains undetermined. The generally higher K_d s for cesium-137 seen at the higher reaction temperature is probably due to increased amounts of resorcinol being included in the polymer, as described earlier.

It should also be noted that, with a single exception, the distribution coefficients did not change appreciably with the initial amount of IDA used. The exception, where half the initial amount of IDA was used, showed a unique decrease in the K_d for strontium-90. Considering the results obtained for the other resins where less IDA was used, this decrease is probably caused by a random synthetic inefficiency, rather than the effect of the reactant ratio.

To produce the observed K_d s values, the overall yield of Mannich addition would have to be less than 25% (the smallest ratio of IDA/Re used). From the elemental analysis data, the actual yield appears to be 15-20%, or 1 IDA group for every 5.5 phenol rings or so. The overall polymer structure is therefore probably a number of short chains which are either intermeshed or cross-linked together. Increasing or reducing the amount of formaldehyde used also seemed to have little effect on affinity, as long as an excess was used.

Effect of the Amount of Template Added

The overall surface of the porous resin would be expected to be a direct consequence of the amount of template added to the prepolymer. Therefore, some variability in affinities may occur for polymers containing differing amounts of template. This would be especially true if surface area were the predominant factor determining the relative affinity of a resin for various ions. Resins containing various amounts of CaCO_3 were synthesized and their distribution coefficients for cesium-137 and strontium-90 measured. These data are presented in Table 12. In addition, the surface area for each of these resins was determined and correlated with the measured affinities.

For low temperature reactions, where the prepolymer was a liquid, a steady increase in resin surface area is seen for increased amounts of added calcium carbonate. However, the affinity of the resin for the ions of interest did not increase appreciably with increasing amounts of template. Beyond the initial increase in surface area of about a factor of two, the absolute surface area does not appear to have a strong influence on affinity. Thus, about 2 g of CaCO_3 could be used for most of the other studies to induce porosity without having a major effect on the measured K_d values. Additionally, this amount was far enough out on the plateau to

Table 12. Distribution coefficients and surface areas for RE:F:IDA polymers containing different amounts of CaCO₃ template^a

Amt of CaCO ₃	60 °C			100 °C		
	K _d ,Cs ⁺	K _d ,Sr ²⁺	Surface Area (m ² /g) ^b	K _d ,Cs ⁺	K _d ,Sr ²⁺	Surface Area (m ² /g) ^b
0 g ^c	460	740	0.489	835	480	0.256
1 g	925	1900	0.746	2875	430	0.386
2 g	775	2050	0.992	1250	505	0.468
4 g	700	1375	2.477	2100	425	0.867
8 g	475	2075	4.442	1675	630	0.528

^a All K_ds are the average of two samples measured in simulated supernate.

^b Surface areas measured on +100/200- mesh resin.

^c 0 g data courtesy of D. D. Walker, Savannah River Laboratory.

prevent significant changes in K_d from occurring with small variations in the mass of template used.

The increase in surface area observed for the high temperature porous polymers was very slight over the original nonporous resins. There was little effect on the measured affinities as well. Apparently, the template was not as well incorporated into the polymer if it gelled during the reaction period. Unexpectedly, there was virtually no change in the surface area of these resins with increasing amounts of template. A possible explanation is that during gelation, the template solid was occluded in large pockets, rather than homogeneously. Such heterogeneity of template within the resin mass would produce fewer pores, but of larger size. If the occluded pockets of material were large enough, and increased as more template solid was added to the mixture, then very little increase in overall surface area might result. With the low temperature procedure, the liquid prepolymer and rotary evaporation step would keep the template more evenly dispersed within the resin mass, producing the observed variation in surface area. Use of a mechanical stirrer, rather than a magnetic device, in the high temperature syntheses might alleviate this problem.

Effects of Different Basic Catalysts

In an earlier section of this dissertation, the effect of certain basic catalysts in producing higher amounts of ortho substitution was described. A study was therefore initiated to examine whether or not basic catalysts other than sodium hydroxide would produce resins with altered affinities for cesium-137 and strontium-90. Distribution coefficient data for this series of resins is shown in Table 13. A variety of hydroxide salts, organic amines, and NaOH plus zinc acetate were used as catalysts for the production of resins at 60°C and 100°C (reflux).

From Table 13 it can be seen that polymerization catalyzed by any of the alkali metal hydroxides produces resins with approximately the same affinity characteristics. Catalysis by ammonium hydroxide, however, results in a very different resin. Formation of aminomethyl cross-links probably occurs, and at 60°C a powdery material is produced. Polymers synthesized at either temperature with NH_4OH showed poor affinities for either ion of interest, especially cesium-137. Inclusion of zinc acetate with the NaOH catalyst did not have a noticeable effect on the resins produced.

Resins synthesized using a barium hydroxide catalyst had interesting affinity properties. At either reaction temperature, the resulting resin had a high affinity for

Table 13. Distribution coefficients of porous resorcinol-formaldehyde-iminodiacetic acid polymers synthesized using different basic catalysts^a

Catalyst	60°C		100°C	
	K_d, Cs^+	K_d, Sr^{2+}	K_d, Cs^+	K_d, Sr^{2+}
NaOH	710	2485	1880	440
KOH	710	2200	4900	520
CsOH	660	3000	900	690
NH ₄ OH	40	995	30	480
Ba(OH) ₂	230	2600	260	3230
NaOH + Zn(OAc) ₂	825	1900	1750	400
Diethylamine	50	850	115	435
Triethylamine	210	1650	255	450

^a All resins synthesized with CaCO₃ template and K_d s measured in simulated salt solution.

strontium-90, but a poor affinity for cesium-137. The high strontium-90 K_d for the 100°C polymer was unique among the resins synthesized at that temperature. The reason for this result is unclear. If ortho addition had been catalyzed by the formation of a chelate with Ba^{2+} , this would be more likely to produce a higher cesium-137 K_d and a lower strontium-90 distribution coefficient. Previously reported results of increased ortho substitution have been exclusively for the hydroxymethylation reaction. Increasing the rate of ortho hydroxymethylation for resorcinol should severely limit the amount of Mannich condensation that occurs, and increase the resorcinol content of the polymer. Some other, as yet undetermined, factor in the reaction is therefore necessary to explain the observed results. Affinity data notwithstanding, both resins are powdery in nature, so their usefulness as ion exchangers is severely limited.

The organic bases tested, diethylamine and triethylamine, have been used before in the manufacture of P:F polymers (97). The best resin of the group was synthesized at 60°C with triethylamine. However, all of resins produced in this study utilizing organic base catalysts had poorer affinities for the ions of interest than those catalyzed by alkali metal hydroxides.

Use of Other Cross-linking Agents

As has been mentioned previously, the most promising P:F:IDA polymers produced for application as ion exchangers were brittle solids. While a certain amount of physical stability is desirable, solids that are too brittle tend to be friable. By forcing large amounts of liquid over the resin bed under pressure, shear forces develop that tend to fracture the resin particles. This produces a large number of fine particles which will eventually plug the column and limit its useful lifetime. Any pliability that could be induced into the resin, without making it soft, would be advantageous for long-term considerations. For this reasons, a number of additives were mixed with resorcinol in an effort to produce more pliable porous resins. Generally, these additives were cross-linking agents. It was hoped that the formation of longer or larger cross-links within the polymer would generate the desired flexibility. Affinity data for these resins are shown in Table 14.

The solid form of formaldehyde, paraformaldehyde, was utilized as a cross-linking agent to see if any physical changes in the resin resulted. Not surprisingly, the resin produced had physical and chemical properties similar to those of the resins produced with Formalin. Thus, paraformaldehyde can be readily substituted for the aqueous reagent.

Table 14. Distribution coefficients of porous resins synthesized with different cross-linking agents^a

Cross-linking Agent	60°C		100°C	
	K_d, Cs^+	K_d, Sr^{2+}	K_d, Cs^+	K_d, Sr^{2+}
Formaldehyde (Formalin)	710	2485	1880	440
Paraformaldehyde	600	2000	2565	635
Glutaraldehyde	75	165	310	120
2-Furaldehyde	590	760	800	390
p-Cresol ^b	365	1400	2550	405

^a All resins synthesized with $CaCO_3$ template and K_d s measured in simulated salt solution.

^b Ratio of p-cresol:resorcinol:formaldehyde of 1:3:21; all others synthesized with a seven fold excess of aldehyde.

Two other aldehydes, glutaraldehyde and 2-furaldehyde (furfural) were also tested as cross-linking agents. It was thought that the five-carbon chain present in glutaraldehyde as a cross-linking group might permit enough free rotation to give a flexible polymer. In fact, glutaraldehyde resins produced under both 60°C and reflux conditions were extremely soft. This, coupled with generally poor affinities observed for both cesium-137 and strontium-90, discouraged further study of these resins.

The inclusion of a large furan cross-linking group might also improve the pliability of the resulting resin. The more linear polymerization pattern of 2-furaldehyde should produce a more "open" structure, while still permitting three-dimensional cross-linking. Resins synthesized with this reagent were dark in color and somewhat softer than Re:F:IDA resins, although they could still be categorized as brittle solids. Despite their promising physical characteristics, the affinity data for these resins were disappointing. Neither of the reaction temperatures used produced a resin with affinities as high as those for resorcinol resins polymerized with formaldehyde. Resins of this type were also not considered further.

p-Cresol was mixed with resorcinol and polymerized with IDA and formaldehyde to produce linkages similar to those with furfural. Since p-cresol polymerizes in a linear manner, a

somewhat open lattice structure would be produced where it was substituted for resorcinol. Resins produced from a mixture of resorcinol and p-cresol bore a strong physical resemblance to Re:F:IDA resins, and the affinity data showed good attraction for both ions of interest. The polymers were still not particularly pliable, however. The amount of p-cresol added was small (25%), so it is possible that the addition of more of this phenol might produce a resin of the desired softness. It should be noted however, that the presence of p-cresol in the reaction mixture made rotary evaporation more difficult. Both these resins and polymers produced from p-cresol alone foamed terribly upon evaporation of the solvent. These procedural difficulties must be overcome before further studies can be completed.

Structural Studies

Although not essential in proving their effectiveness as ion exchangers, it was felt that the elucidation of the structure of the resins produced in this study might prove useful. Any significant structural details determined for these polymers might correlate in some way with the affinity data, and with the reaction condition variables. Once these relationships are known, it might then be possible to design polymers of any given physicochemical characteristics to suit

a particular application. With this in mind, several exploratory experiments were performed. Unfortunately, in actual practice, obtaining satisfactory analytical data about the structure of Re:F:IDA resins proved very difficult, and very little useful information could be determined.

Those techniques that were tried were chosen based on their ability to provide structural information. These techniques included NMR and IR spectroscopy, mass spectrometry, and, only recently, X-ray techniques. Whereas the polymer synthesis is performed in aqueous solution, it was necessary to transfer the prepolymer material into an organic solvent for examination by proton nuclear magnetic resonance. The reddish prepolymer material was too polar and would not extract from water into any of the common organic solvents. Those tried included diethyl ether, methylene chloride, benzene, and ethyl acetate. Acidification of the aqueous layer with HCl and reextraction produced an orange precipitate which also remained in the aqueous layer. The formation of this gelatinous precipitate was reversible with the addition of base. Attempts to dissolve the uncured gel and the cured polymer also failed. The uncured material was somewhat soluble in both water and a water-dimethylsulfoxide mixed solvent. The cured material was completely insoluble in strong mineral acid, strong aqueous base, water, and organic solvents. However, hot concentrated nitric acid or alcoholic

KOH could be used to dissolve the polymers. Thus, proton NMR was ruled out as a suitable technique. Proton NMR of the solid material was performed, but did not produce any definitive results.

¹³Carbon NMR has been used successfully to study phenol-formaldehyde polymers and their precursors (126,127,134). Preliminary experiments in the use carbon-13 NMR to study the polymers synthesized in this study were performed. A spectrum of the 60°C prepolymer reaction mixture was taken in D₂O solvent, d₆-DMSO as a reference. The crude spectrum showed 10 sharp peaks, plus two broad signals. The sharp resonance signals appeared at 44.1 ppm, 53.0 ppm, 58.2 ppm, 60.3 ppm, 80.8 ppm, 83.5 ppm, 87.4 ppm, 172.2 ppm, 172.6 ppm, and 175.2 ppm respectively. The two broad signals occurred between 115-125 ppm and 150-155 ppm. This spectrum was matched to a possible prepolymer structure consisting of resorcinol with ortho, para hydroxymethyl and ortho, para IDA substituents. The chemical shifts of the two broad resonances correlate with those of aromatic ring carbons in phenols (135,136). Since they are not sharp, the number of different carbons that can be accounted for by these bands cannot be determined. In carbon-13 NMR, the resonances are usually sharp and represent a single type of carbon. The broadness of these bands therefore indicates that some polymerization may have occurred, causing the signals to be smeared out because

of small changes in the electronic environments of similar carbons. The three downfield resonances represent carbonyl carbons, with shifts resembling those of ethylenediaminetetraacetic acid (136). However, the presence of three resonances would not be expected. The two carbonyl carbons on IDA should be equivalent and produce a single peak. One of the remaining peaks could be due to unreacted IDA, showing a different chemical shift (these would probably be the two peaks that are close together). The last peak might indicate lactone ring formation in the prepolymer. Lactone carbonyls have similar chemical shifts to carboxylic acid carbonyls, and the proximity of the IDA to the chain to the aromatic could produce a six-membered ring lactone, which is a stable structure. Further NMR studies may shed light on this anomaly. The peaks at 53.0 and 60.3 correlate well with the methylene bridge between the phenol and the IDA nitrogen, and the methylene groups in IDA, respectively. The peak at 58.2 ppm may represent methylenes in unreacted IDA or the methylene group in the hydroxymethyl substituent. The peak at 44.1 is somewhat upfield to be assigned to hydroxymethyl methylene, and may represent methylene bridges or ether bridges between resorcinol molecules, since some polymerization is indicated by the aromatic resonances. The final grouping of peaks in the 80-90 ppm range could represent unreacted formaldehyde as polymethylene glycol (127), or methylene groups on the phenols

that have been shifted by the presence of the IDA group. These peaks occur in an frequency range that contains fewer common carbon-13 resonances, and their assignment to a particular compound is at best tentative.

Many of the peaks in this spectrum cannot be unambiguously assigned to a given structure. However, examination of the crude mixture using carbon-13 NMR has produced encouraging results, and has shown that this technique has great potential use in determining the structures of the these polymers and their precursors. These studies will be continued in the future, with the hopes of providing clear structural information on the polymers and their precursors. This technique may also eventually provide a means of determining the mechanism and progression of polymer formation in this system. Solid-state carbon-13 NMR was unavailable at the time of this preliminary work, but it may be applied to the cured polymers at some future date.

The combined insolubility and thermal stability of the resins also limited the usefulness of mass spectrometry. A large number of very small peaks were found in the mass spectrum of the cured solid, but no conclusions could be drawn. The large amount of water associated with the prepolymer interfered with mass spectrometric analysis of this material. Attempts to concentrate the material sufficiently to produce interpretable spectra were unsuccessful.

A useful way of obtaining infrared spectra of insoluble solids such as polymers is the technique of photoacoustic spectroscopy (PAS) (137). This technique has been used to examine poly(styrene-divinylbenzene)s (138). The advantages of applying PAS to samples such as the ones being discussed will be outlined briefly here. The interested reader can obtain theoretical and experimental details from the cited references.

The primary advantage in using PAS to study solid materials is in ease of sample preparation. Except for drying the sample thoroughly and grinding it to a small particle size, no further special preparation was required. Techniques such as FT-IR generally require the formation of a KBr pellet to examine solid materials, which can often be troublesome. In addition, although the resolution obtained in PAS is usually much less than that for other infrared techniques, the functional group information that can be determined from the spectrum is the same as that in a standard IR spectrum. Thus, this technique can quite suitable for qualitative analysis, where high resolution is usually not required.

Photoacoustic spectra for resins synthesized at 60°C and 100°C are shown in Figures 21 and 22. Comparison of the spectra shows that they are very similar. Initial interpretation of the spectra was as follows. The broad, intense peak covering from 3500-2500 cm^{-1} represents the OH

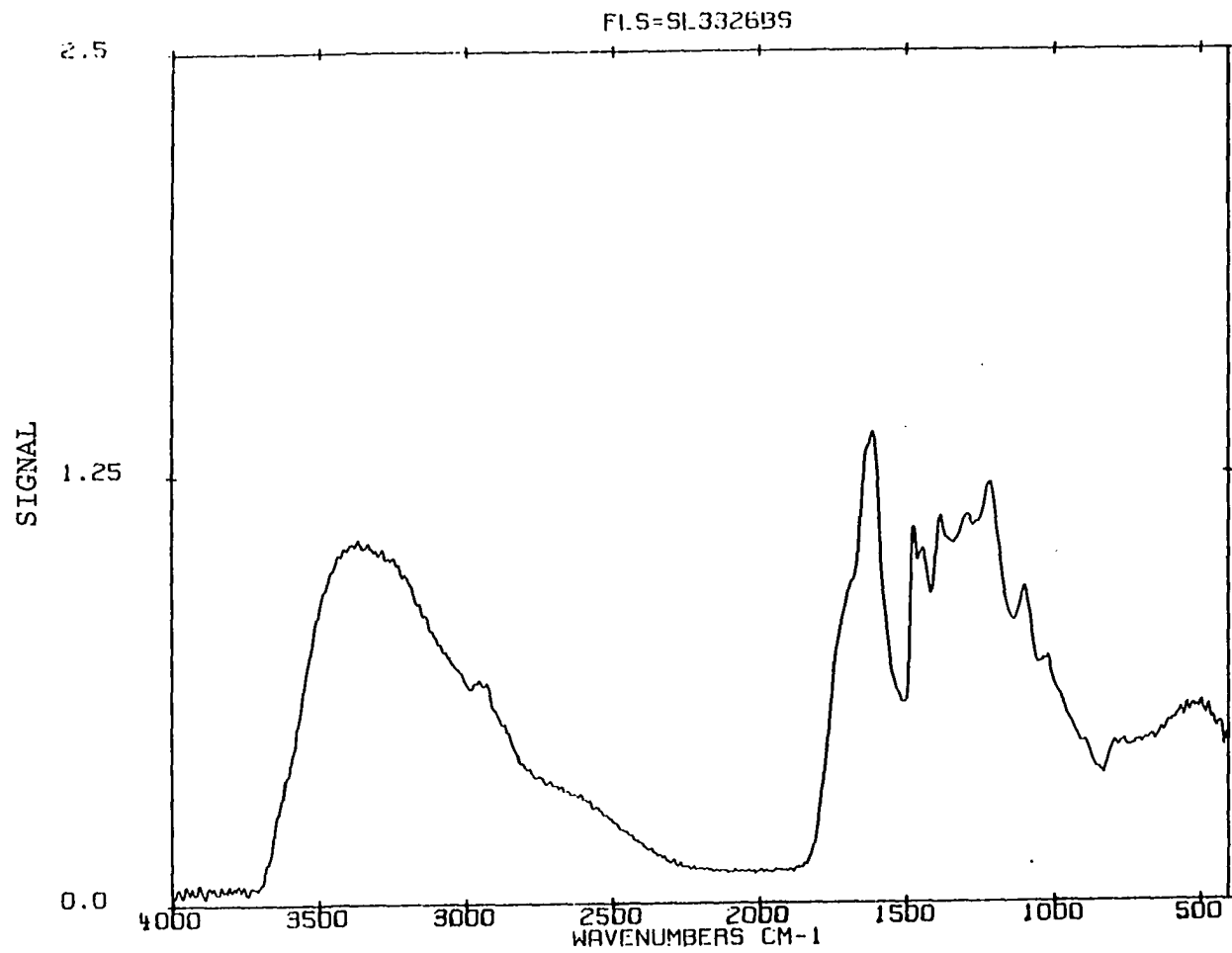


Figure 21. PAS spectrum for 60°C synthesized RE:F:IDA polymer.

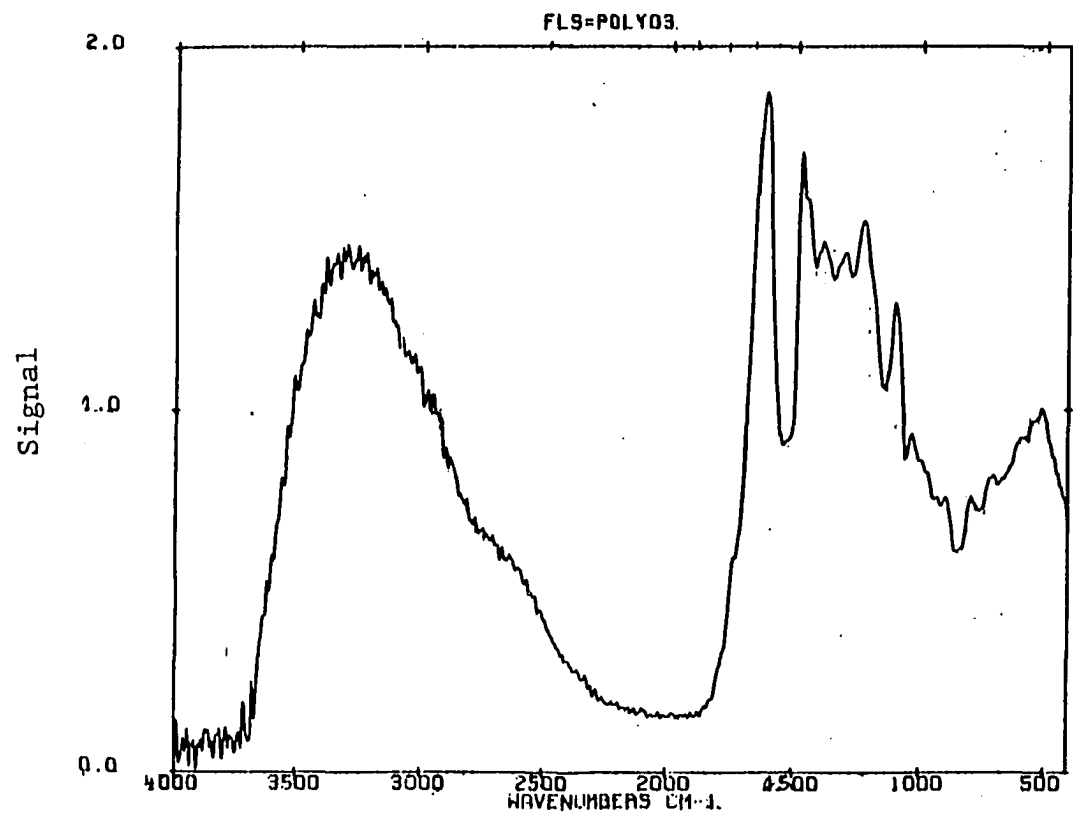


Figure 22. PAS spectrum of RE:F:IDA polymer synthesized at 100°C.

stretching present. Careful examination of this peak reveals a broad shoulder at lower wavenumbers. Therefore it was considered likely that two superimposed peaks were actually present, a low broad signal, and a sharper, more intense one. This was consistent with the presence of both carboxylic acid hydroxyl (the low, broad signal) and the hydroxyls in resorcinol (the more intense peak).

The sharp peak at $\sim 1600 \text{ cm}^{-1}$ was consistent with a carbonyl stretch, such as that in IDA, although it appeared at somewhat higher frequency than was shown by the infrared spectrum of iminodiacetic acid.

Finally, the peaks at $1100\text{-}1200 \text{ cm}^{-1}$ in the 60°C resin spectrum were thought to indicate the presence of aliphatic ether groups. This could mean that insufficient curing of the polymer was occurring, with incomplete conversion of ether linkages into methylene cross-links. However, the presence of similar absorbances in the high-temperature resin spectrum contradicted this conclusion.

The PAS spectrum of a resin synthesized without IDA was run and showed that many of the initial peak assignments made were incorrect. In fact, this spectrum resembled the first two very closely, as seen in Figure 23. Closer examination of the IR spectra of some phenols led to the conclusion that the spectra essentially represent only the polymerized resorcinol. The abundance of the phenol compared to the amount of IDA

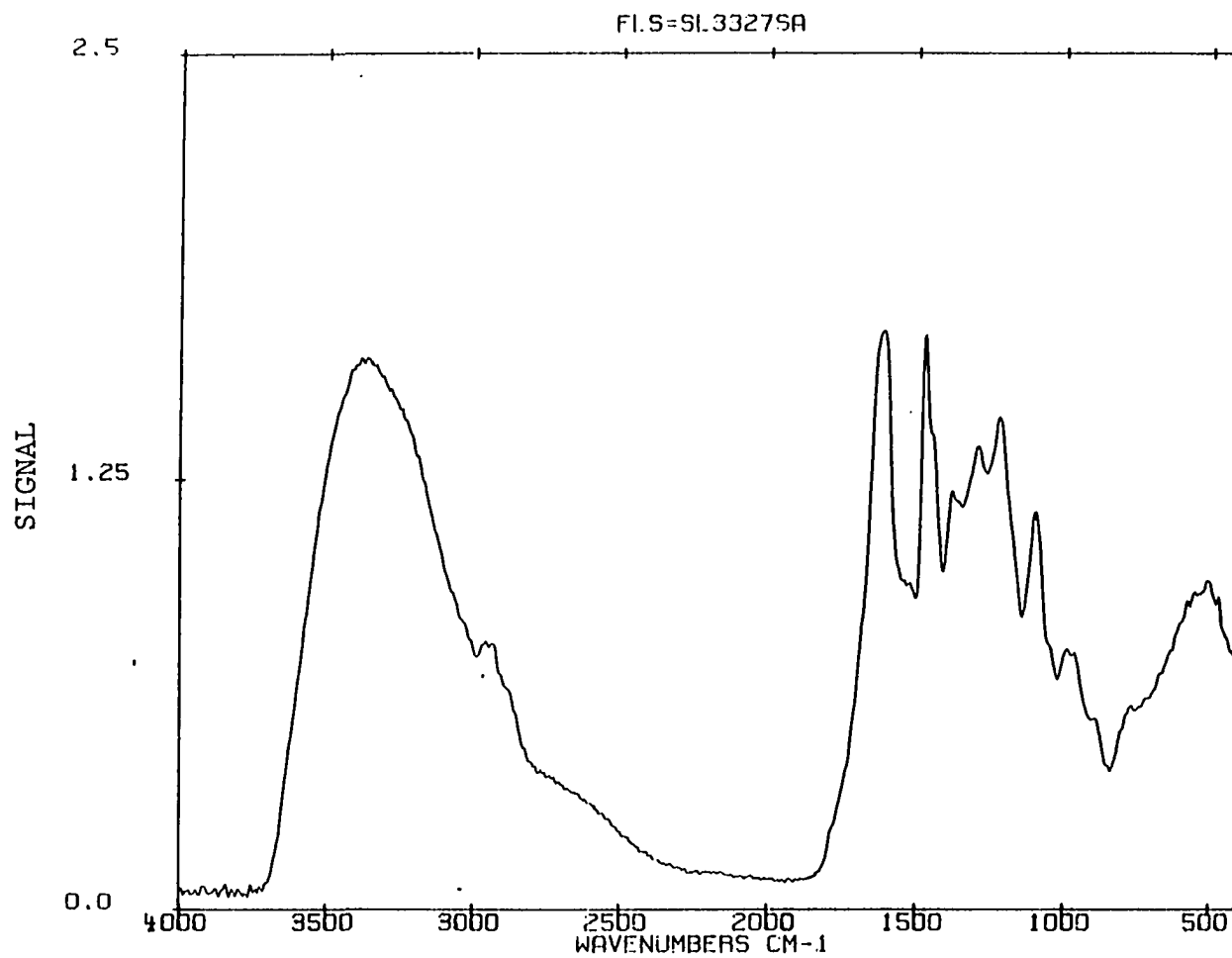


Figure 23. PAS spectrum of 60°C RE:F resin containing no IDA.

present (refer to the nitrogen analysis performed on these polymers) apparently swamps any absorptions resulting from this group, with one exception to be mentioned later. This conclusion seems to best rationalize all of the information in the three spectra.

The intense peak at high wavenumbers does indeed represent the hydroxyl stretches in the phenolic polymer. However, the shoulder occurring at 2800 cm^{-1} is probably due to a combination of phenol hydroxyl stretches and aromatic C-H stretching. Phenol and substituted resorcinols exhibit broad OH absorptions that often include shoulders. An absorption from the acid hydroxyl groups may be present, but it would not be distinguished from the other signals. 4-Alkyl resorcinols also show intense absorptions in the 1600 cm^{-1} range.

The single absorption that can be tentatively assigned to IDA is the shoulder seen at approximately 1710-1725 wavenumbers. This peak is definitely not present in the resorcinol-formaldehyde polymer spectrum, but is clearly seen in the 60°C resin spectrum. A smaller shoulder appears in the reflux temperature resin spectrum. This absorption is at an appropriate frequency for the carboxylic acid carbonyl in iminodiacetic acid, which is among the most intense in its spectrum. In addition, the relative size of the peak in each of the spectra is in general agreement with the amount of IDA determined to be present in each case.

Further evidence of these PAS spectra being primarily that of polymerized resorcinol is seen in the spectrum of a furfural cross-linked resin, shown in Figure 24. Again, the spectrum bears a strong resemblance to the others. This is reasonable, since any distinctive peaks from the furan groups would undoubtedly be lost in the aromatic absorptions of the phenolic resin backbone. In fact, it is quite probable that the aromatic furan groups could not be clearly distinguished by their infrared absorptions from resorcinol groups in a polymer of this type.

Subtraction of the spectrum of the non-IDA polymer from the others verified the presence of the peak at 1725 cm^{-1} , but not provide much other useful information. At the present time, PAS has been able to indicate the incorporation of IDA into the Re:F polymers, but has provided little else in the way of structural information. Continued investigations of these polymers using this technique may improve upon this situation, and help to more clearly determine the overall structure of these chelating resins.

Preliminary X-ray diffraction studies on the polymeric material synthesized at 60°C indicated that it was an amorphous, rather than a crystalline solid. Considerable further testing must be done before any direct structural information can be obtained. Future work in this area will include attempts to determine the chelate bond distances by

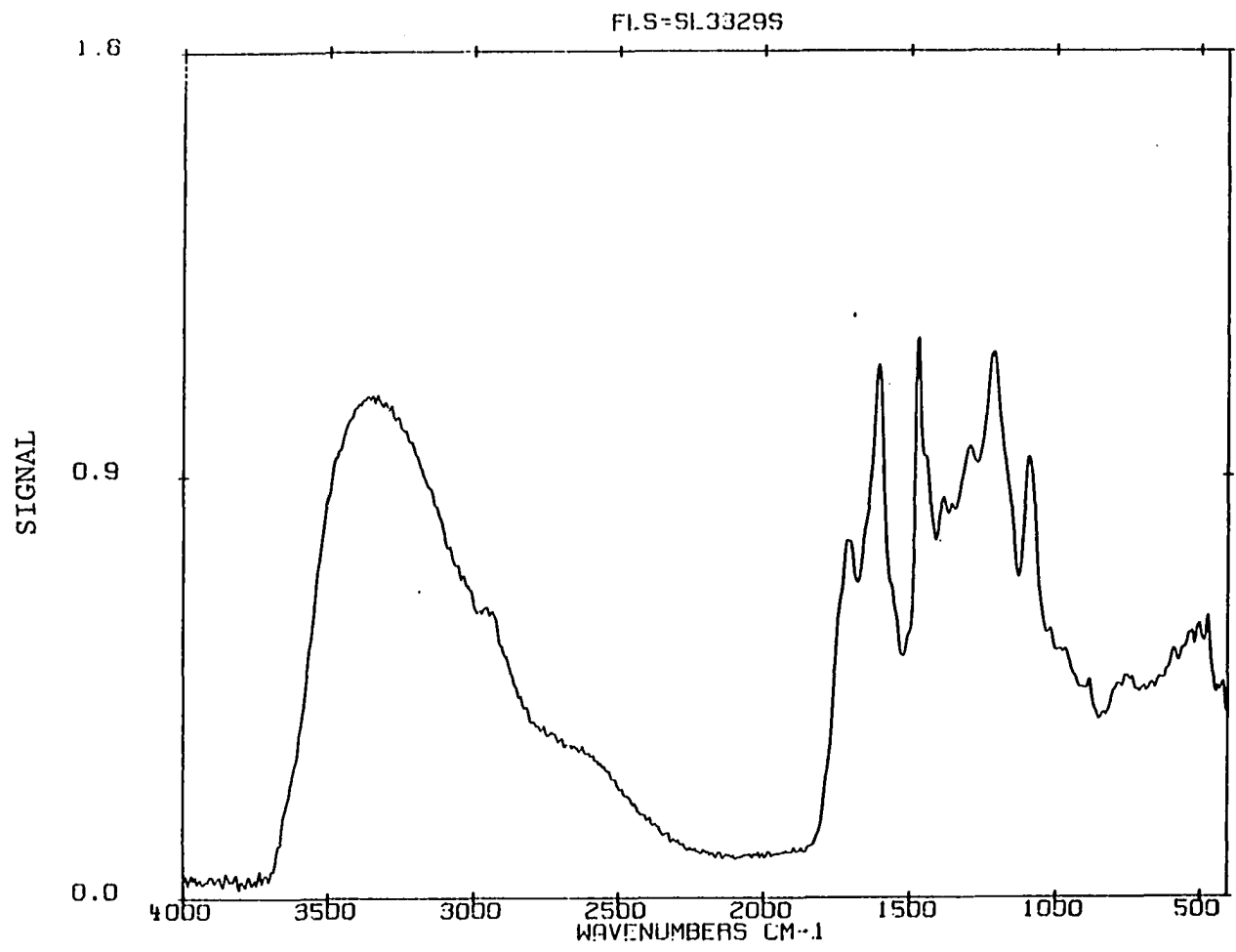


Figure 24. PAS spectrum of Resorcinol:furfural:IDA polymer.

examining the spectra of H⁺-form resin and the same resin in the Cu²⁺ form.

Affinity of P:F:IDA Resins for Other Metals

Iminodiacetic acid is known to complex with a number of different metals, most notably the alkaline earths (76), divalent transition metals (139-142) and uranyl ion (143). This selectivity has been used to advantage in the development of a number of chelating resins containing various IDA-type groups (78,81,82,144,145). Similarly, resins based on phenols such as salicylic acid have been used to sorb the heavy metals and uranium (146). With this in mind, examination of the affinities of some of the porous P:F:IDA polymers synthesized in this work for metals ions other than cesium and strontium was undertaken.

A number of common or important metal ions were chosen for study. The distribution coefficients of these ions in aqueous solution at various pHs were measured for samples of 60°C Re:F:IDA polymer and 60°C 2,4-DHBA:F:IDA polymer. In addition, the K_d of each metal in an aqueous solution containing 200 ppm each of Ca²⁺ and Mg²⁺ at pH=5 were measured. This matrix was used to represent a typical "hard" water solution. The results for all of these studies are shown in Tables 15 and 16.

Table 15. Distribution coefficients of various metals at different pHs with porous RE:F:IDA resin

Metal Ion	Distribution Coefficients ^a				
	pH=1	pH=3	pH=5	pH=7	Hard Water ^b
Cu ²⁺	40	740	1270	---	1160
Fe ²⁺	15	35	4455	---	1050
Fe ³⁺	5	95	---	---	125
Ni ²⁺	5	75	110	85	25
Pb ²⁺	10	510	750	1465	245
Hg ²⁺	20	15	15	15	15
Cd ²⁺	25	15	20	5	20
UO ₂ ²⁺	15	20	25	---	20

^a Duplicate determinations using 1×10^{-3} M solutions of each metal.

^b Hard water solution is simulated by an aqueous solution containing 200 ppm each of Ca(II) and Mg(II) at pH=5.

Table 16. Distribution coefficients of various metals at different pHs with porous 2,4-DHBA:F:IDA resin

Metal Ion	Distribution Coefficients ^a				
	pH=1	pH=3	pH=5	pH=7	Hard Water ^b
Cu ²⁺	30	950	995	---	965
Fe ²⁺	20	30	755	---	505
Fe ³⁺	5	205	---	---	160
Ni ²⁺	5	50	70	65	20
Pb ²⁺	10	535	535	1305	295
Hg ²⁺	15	20	20	25	20
Cd ²⁺	30	20	25	15	30
UO ₂ ²⁺	15	20	25	---	10

^a Duplicate determinations using 1×10^{-3} M solutions of each metal.

^b Hard water solution is simulated by an aqueous solution containing 200 ppm each of Ca(II) and Mg(II) at pH=5.

Both the resorcinol and 2,4-DHBA resins showed poor affinities for all of the metals tested at pH=1. This is probably caused by strong protonation of the iminodiacetic acid groups. Various values of pK_1 for iminodiacetic acid between 2.5 and 3.0 have been reported, both for the reagent in solution and in a resin matrix (139,147,148). Since the divalent metals have been found to displace at least one H^+ when undergoing chelation, at low pH the chelating capabilities of the resins should be severely restricted. However, at pH=3 and above, both resins had significant affinities for Cu^{2+} , Pb^{2+} , and Fe^{3+} . The resins also took up Fe^{2+} at solution pH of 5. The K_d values for Ni^{2+} were surprisingly poor at all pH values. Very poor affinities were seen for Hg^{2+} , Cd^{2+} , and UO_2^{2+} ions.

To some extent, these results are in general agreement with the properties of IDA as a chelating agent found in the literature. Studying the IDA-group containing resin Dowex A-1, Leyden and Underwood (147) determined that most divalent metals exhibited a maximum distribution coefficient between pH 4-5. The data in Tables 15 and 16 show a general increase in K_d with increasing pH, for those metals that are significantly adsorbed. No maxima were seen within the pH range studied, however, the values for Cu^{2+} and Fe^{2+} at pH=5 may very well be the highest values obtainable. These metals precipitated above pH=5 and K_d measurements could not be made.

The resins seemed to perform best for Cu^{2+} and Pb^{2+} ions. Copper(II) forms strong chelates with IDA, displacing two H^+ ions (139). Iminodiacetic acid is generally regarded as an excellent chelating group for Cu^{2+} , and resins containing this group have been used to sorb this metal in a variety of applications (82,149). Nickel(II) has also been reported to form strong complexes with the IDA, although not as strong as copper (139,147,148). The relatively poor performance of both the RE:F:IDA and 2,4-DHBA:F:IDA resins for this metal is therefore curious, and no reasonable explanation is readily apparent.

Cadmium (II) forms a relatively weak complex with IDA, compared to nickel and copper. Nonetheless, resins containing IDA chelating groups can be used to sorb cadmium at trace levels (144,149). In their original study (139), Chabarek and Martell found that the Cd-IDA complex does not form below pH 5.5. Thus, the poor affinities of the porous resins being studied for this metal are reasonable, although the low affinities extend beyond this pH range. Mercury (II), being in the same group as cadmium, is consistent in showing similarly poor adsorption. It should be noted that the concentrations of analyte ion used in these screening experiments were relatively high, in order to simplify the final measurement. Distribution coefficients are dependent upon the initial amount of analyte present. Reevaluation of

these resins for the sorption of trace level amounts of these same metals may produce more positive results.

Lead (II) has an IDA complex formation constant between those of copper and nickel (140). Therefore, the high affinities seen for this ion would be expected. Both iron species have IDA complex formation constants similar to that of cadmium (141,142). The good affinities observed are therefore somewhat surprising. However, as with cadmium, resins containing this group have been used previously to sorb both ferric and ferrous iron. Although a phenolic resin containing IDA groups has been used for cadmium (144), the phenolic backbone may be partially responsible for the difference in the affinity data for cadmium and the iron species. A resin based on salicylic acid polymerized with formaldehyde showed a reasonable affinity for iron(III) (146). No data on cadmium were reported.

Although a salicylic acid-formaldehyde polymer was found to be highly selective for UO_2^{2+} (146), both of the resins in this study performed poorly in sorbing uranyl ion. Although uranyl ion has been reported to form a 1:1 complex with IDA when uranyl ion is in excess (143), the preferred structure appears to be a 2:1 complex. For example, uranyl ion was considered to form a complex with two mer units in the salicylic acid polymer. This may not be a favorable situation with the porous resins being examined, because of the

relatively low amount of IDA present. Nonetheless, the resin based on 2,4-DHBA might have been expected to show improved results, considering its similarity to salicylic acid. No such improvement compared to the resorcinol resin was observed, however.

The inclusion of Ca^{2+} and Mg^{2+} in the test solution only decreased the affinity values for two metal ions, lead (II) and iron (II). (Note: precipitation of Fe(III) did not occur in the pH=5 solution containing calcium and magnesium, but did occur in the simple pH=5 aqueous solution. The reason for this is not clear.) Even the two observed decreases may not be significant, considering the accuracy of distribution coefficient measurements. The effect on Fe^{2+} with the resorcinol resin is probably somewhat exaggerated, because the average distribution coefficient reported at pH=5 included one very high value. Neither calcium nor magnesium would be expected to reduce the affinities of these resins for divalent transition metals to any great extent. The alkaline earths form very weak complexes with IDA compared to most of the transition metals, and so should not interfere. One possible explanation for the reduction in the K_d values for Pb (II) is its tendency to form mixed chelates (140). Lead will form complexes with the monoprotonated iminodiacetic acid species and even the neutral species, as well as the dianion. This tendency is not so prevalent with other metals. The overall

affinity of the resins for Pb^{2+} may therefore result from the formation of all of these species, and the Ca^{2+} and Mg^{2+} may interfere with one of the formation of one of these complexes, producing the observed decrease in K_d values. The interference would most probably occur in the formation of the complex with the monoprotonated species. The sorption of the alkaline earths by iminodiacetic acid has been postulated to involve the displacement of one proton, similar to the binding of cadmium (148).

Functionalized PS-DVBs and Coated Resins

Distribution coefficient data for both functionalized PS-DVB resins, and various coated resins are presented in Table 17. Although the results obtained were generally negative, some of the data could be considered encouraging.

Among the catalysts used for the Friedel-Crafts alkylation of macroreticular poly(styrene-divinylbenzene) were aluminum chloride ($AlCl_3$), zinc chloride ($ZnCl_2$), and later, titanium chloride ($TiCl_4$). Zinc chloride was fused according to the method of Feinberg and Merrifield (150), and $TiCl_4$ was distilled before use. Because of the limited solubility of resorcinol in chlorinated solvents and carbon disulfide, nitromethane became the solvent of choice. Tetrahydrofuran (THF) also proved to be a useful solvent, especially since the

Table 17. Cesium-137 and strontium-90 distribution coefficients for functionalized PS-DVB resins and various coated resins

Resin	$K_d, {}^{137}\text{Cs}^+$ a	$K_d, {}^{90}\text{Sr}^{2+}$ a
<u>Functionalized PS-DVBs</u> ^b		
ZnCl ₂ /THF/reflux	4	0
After treatment w/IDA & F	6	160
AlCl ₃ /CH ₃ NO ₂ /reflux/3 hrs	3	32
After treatment w/IDA & F	6	90
AlCl ₃ /CH ₃ NO ₂ /25°C/12 hrs	3	4
<u>Coated Resins</u>		
DHBA octyl ester on XAD-4	3	0
RE:F:IDA on glass	3	25
RE:F:IDA on Chromosorb G	3	155

^a All distribution coefficients are averages of dual determinations measured in simulated salt solution.

^b Functionalization consisted of addition of resorcinol by Friedel-Crafts alkylation using the conditions indicated.

ZnCl₂ preparation procedure included final dissolution in this solvent. The reactions were generally carried out at either room temperature or in refluxing solvent. In a later adaptation of the procedure the reaction was maintained under dry conditions to preserve the catalyst.

During the alkylations, the color of the solution changed drastically upon addition of the Lewis acid catalyst. The reaction began as a very light brown solution, and changed to any of several colors, ranging from maroon to deep brown, depending upon the catalyst used. This was taken as an indication of the formation of the metal complex intermediates, which are typically reported as being intensely colored (119). After completion of the reaction, almost all of the color was washed away by rinsing with methanol, leaving resins whose color ranged from tan to light yellow. In some of the early synthetic attempts where the reaction mixture was heated, the resulting resins were dark brown in color. However, a great deal of resin degradation was also apparent, and filtering the resinous product was difficult.

The resins with the highest oxygen contents utilizing the first two catalysts were chosen for distribution coefficient determinations. These included chloromethylated XAD-4 refluxed in THF with ZnCl₂ for 8 hours (4.66 % by weight O), chloromethylated XAD-4 stirred overnight with AlCl₃ in nitromethane (2.13 % O), and chloromethylated XAD-4 refluxed

for 3 hours with AlCl_3 in nitromethane (12.07 % O). A resin produced by refluxing chloromethylated XAD-4 with AlCl_3 for six days in nitromethane had a substantial oxygen content, but the resin was too badly degraded to be tested.

The reaction procedure was later adapted to maintain dryer conditions. The modifications included using freshly distilled and dried solvents, freshly prepared catalysts, and performance of the reaction under a dry nitrogen atmosphere. Titanium chloride was also added as a potential catalyst, being intermediate in reactivity between aluminum chloride and zinc chloride. Resins produced by overnight room temperature reaction of chloromethylated XAD-4 with TiCl_4 and AlCl_3 under the dry conditions were tested as sorbents for cesium-137 and strontium-90. The distribution coefficients for these resins are shown in Table 17.

Despite the encouraging oxygen analysis data, which predicted capacities of as high as 4 meq/g, the K_d values for all of the resins were poor. The generally poor results for strontium-90 are not surprising, since IDA is not present on these resins. The poor K_d values seen for cesium-137 may be a result of the matrix. The general preference of phenolic-type resins for cesium over sodium has been mentioned previously. Selectivity rules can be violated, however, if there is a vast preponderance of one ion (i.e. the less preferred ion) compared the other. Resins such as the various

resorcinol-formaldehyde polymers discussed earlier are composed entirely of phenolic sites. In this situation, a large amount of sodium from the matrix can be taken up and still leave enough phenolic exchange sites available to display their usual selectivities. This fact is supported by the relatively low cesium-137 capacities exhibited by the Re:F:IDA resins in simulated supernatant. Obviously, a large fraction of the total sites are still occupied by Na^+ ions. The situation is much different for the functionalized PS-DVB resins. Their equivalent capacities, which are relatively low (1-2 meq/g), represent the total number of phenolic sites present on the resin. Despite favorable selectivity, the amount of cesium present in the simulated supernatant could be too small to compete with the large amount of sodium present for a limited number of resin sites. The anticipated result would be low distribution coefficients for cesium-137 for resins of this type.

Even though the functionalized resins gave low K_d values, several of them were reacted with formaldehyde and iminodiacetic acid to see if Mannich addition would occur, and realized as an increase in affinity for strontium-90. The results in Table 17 indicate that some Mannich addition probably occurred. Sizable increases in affinity for strontium-90 appeared in both ZnCl_2/THF and $\text{AlCl}_3/\text{CH}_3\text{NO}_2$ reacted with IDA under Mannich reaction conditions. This

result encourages further pursuit of optimal reaction conditions for the addition of resorcinol to PS-DVBs, since it implies that subsequent addition of IDA will occur readily. The improved strontium-90 K_d s also indicate that some resorcinol has been added to each of the polymers. Mannich addition requires the presence of an active hydrogen, such as those ortho to the hydroxyl groups of resorcinol. The hydrogens present on alkyl-substituted benzene rings, such as those in the poly(styrene-divinylbenzene), are not sufficiently reactive.

Attempts were also made by the author to produce a number of different types of ion exchangers in which the active functional groups were coated, rather than bonded, onto an inert solid support. Ion exchangers of this type have been used to separate metal cations (151), and have several advantages. Capacity can be modified, within limits, by adjusting the amount of material that is coated on the support. Selectivity can be varied in a similar manner, by altering the nature of the exchange group. Such changes can be made rapidly and relatively easily, by stripping and recoating the same support, saving time and materials. Unfortunately, the overall capacity of coated resins is typically somewhat limited, and they are generally more suitable for analytical separations columns than for concentrator columns.

Four different coated exchangers were examined. These included n-octyl-3,5-dihydroxybenzoate on PS-DVB (XAD-4), tetraphenylboron on XAD-4, and resorcinol-formaldehyde-IDA prepolymer on glass beads and a diatomaceous earth chromatographic support (Chromosorb G). Esterification of 3,5-dihydroxybenzoic acid with n-octanol produced the first reagent. After dissolution of the ester in acetone, the ester was coated onto XAD-4 by sonication and flushing with water. The ester appeared to coat the hydrophobic resin very well, and the resulting exchanger was tan in color. Some of the exchanger bled from a resin column when water was forced through it, but this bleeding was not severe. Lengthening the hydrophobic chain to perhaps C_{18} or C_{24} would reduce this problem. Unfortunately, the distribution coefficients for this coated resin were disappointingly low, as seen in Table 17. The poor affinities are probably a result of factors similar to those mentioned for functionalized resins.

Although an exchanger of tetraphenylboron-coated Kel-F for cesium-137 has been reported (84), unsatisfactory results were obtained for tetraphenylboron coated on macroreticular poly(styrene-divinylbenzene). Sodium tetraphenylboron could be coated on XAD-4 by first wetting the support with acetonitrile, then adding the reagent as a solution in the same solvent. Copious amounts of water were then added to drive the reagent onto the hydrophobic surface of the resin.

While the reagent seemed to initially coat the support satisfactorily, it bled profusely during subsequent column rinsing with deionized water (precipitation with Cs^+ was used to check the column effluent for the presence of tetraphenylboron). Qualitative column studies showed that the coated resins retained very little cesium, and what was retained formed a precipitate within the resin bed. Further studies of this resin were discontinued, because of its poor overall performance.

The last two coated resins were produced by adding the inert support to an aqueous solution of the 60°C Re:F:IDA prepolymer discussed earlier. Rotary evaporation for removal of the aqueous solvent also served to coat the polymeric material onto the support. Both coated resins were then cured overnight at both 60°C and 110°C.

If vacuum drying was performed at 60°C, the Re:F:IDA coating bled heavily from both supports under aqueous column conditions. Apparently, the polymer did not cure properly under these conditions. The coating was much less soluble when cured at 110°C, and bled only slightly, during the initial water rinse. Microscopic examination revealed that the support was not actually coated, but that the Re:F:IDA polymer formed in pockets between the individual support particles, or in patches on the particle's surface. The surfaces of the support do not seem to be homogeneously polar

enough to give an even coating of the prepolymer. The inclusion of a surfactant or long-chain alcohol into the coating mixture might improve this situation.

As seen in Table 17, the distribution coefficients for these coated ion exchangers were also low, especially for cesium-137. Undoubtedly, the same limitations that applied to functionalized resins apply here as well, with the limited amount of phenolic sites present accounting for the poor cesium-137 selectivity. The higher strontium-90 affinities for these coated supports show that the selectivity of the IDA sites is not as strongly affected by the high sodium matrix as that of the phenolic sites.

Despite the disappointing results obtained in this study using coated supports as concentrator columns, these materials might be useful in analytical separation columns at some future time. The low capacities that severely restricted their use in concentrating trace level ions, would not be as crucial to their success as stationary phases for analytical separations involving cesium-137 or strontium-90.

Liquid Ion Exchangers

Liquid ion exchangers are generally molecules that contain both a hydrophilic exchange or chelating functional group, and a large, nonpolar organic substituent, such as a long-chain

alkyl group (152). The presence of the hydrophobic groups on these molecules typically makes them immiscible with water. Therefore, displaying their normal selectivity, they can act as extracting agents for aqueous metal ions. Two long-chain carboxylic acids and two alkylphenols containing long-chain substituents were tested as liquid ion exchangers for cesium-137 and strontium-90 from brines and alkaline brines. The reagents examined included n-hexanoic acid, 2-ethylhexanoic acid, 4-hexylresorcinol, and p-nonylphenol. These compounds were used both neat and in a toluene solution. The acids were first converted to the salt form using either NaOH (Na^+ salt) or Allamine 336 (quaternary ammonium salt). Conversion to the salt using NaOH was accomplished by washing the organic layer with a 1.0 N aqueous base solution prior to extraction. Allamine 336 was added directly to the organic layer prior to extraction.

Qualitative results using Ni^{2+} showed that toluene solutions of both of the acidic reagents would extract this green colored ion from NaCl saturated (approximately 5 M) aqueous solution. Unfortunately, neither Cs^+ nor Sr^{2+} were extracted under the same conditions. However, Sr^{2+} was about 80% extracted with neat 2-ethylhexanoic acid and Allamine 336 when the composition of brine solution was changed to 50% NaCl/50% NaClO_4 . This result can be explained by the fact that ClO_4^- is a large ion with diffuse charge density. This

promotes ion-pair formation with the quaternary ammonium group, whereas the presence of an anion such as chloride does not. The formation of ion pairs frees up both the exchange sites on the reagent and the analyte cation in the brine. Uptake of analyte ion is therefore enhanced. The solution of 2-ethylhexanoic acid in toluene did not extract strontium from this matrix, probably because ion-pair formation was inhibited by the presence of the organic solvent. Matrices more closely resembling waste supernate gave equally poor results. The solution of the acid reagents did not extract either of the analytes of interest from either a 4.5 M NaCl/0.2 M NaNO₃ or a 1.0 M NaOH/1.7 M NaNO₃/2.0 M NaCl brine. Obviously, neutralization of the neat acid prevented its use in extraction of the basic brine.

Similar experiments were performed using the phenolic extraction agents. Attempts to extract either Cs⁺ or Sr²⁺ from the NaCl/NaNO₃ brine were made with both 4-hexylresorcinol and p-nonylphenol in toluene, and neat p-nonylphenol. In each case, the phenol was converted to the phenolate salt prior to extraction by shaking the reagent with 1 N NaOH.

Each of the reagents failed to extract either of the ions of interest. Both the neat p-nonylphenol and the 4-hexylresorcinol reagents formed precipitates after washing with sodium hydroxide. In the case of 4-hexylresorcinol, the

salt was actually taken up into the aqueous phase. Obviously, these reagents will be inappropriate for extractions from alkaline brines.

These particular reagents were chosen because of their semblance to the functional groups of the bifunctional resins also being studied. Although the results observed for these compounds were generally disappointing, they are by no means the only reagents that can be used. The variety of possible reagent reagent-solvent combinations is practically limitless, and further study of liquid exchangers in the decontamination of nuclear waste might prove both interesting and fruitful.

CONCLUSIONS

Improved affinities of bifunctional chelating resins for cesium-137 and strontium-90 are obtained by introducing porosity into the polymers. A phenol, formaldehyde, and iminodiacetic acid were reacted together to give resins with the desired selectivity for the ions of interest. The phenolic backbone gives the resin selectivity for cesium-137, while iminodiacetic acid serves as a good chelating group for strontium-90. Base-insoluble solid "templates" were added to the reaction mixture prior to polymerization and heat curing. Subsequent removal of the template material, typically by dissolution in dilute acid, produced brittle macroporous resins that had higher surface areas than nonporous polymers synthesized in a similar manner, and so improved capacities for cesium-137 and strontium-90.

Calcium carbonate was found to be the most suitable template of the various solids tried. Resins synthesized at 60°C and using a calcium carbonate template showed a nearly three-fold increase in strontium-90 affinity over nonporous resins. Resins manufactured at reflux temperature gave higher cesium-137 distribution coefficients than nonporous material, but reduced values for strontium-90. Calcium pyrophosphate, tribasic calcium phosphate, and magnesium hydroxide also showed promise as potential templates, and do not form gaseous

products upon dissolution. Other solids, most notably silica, were less successful as templates. The failure of silica was primarily because of the more drastic conditions (HF or strong caustic) required for its dissolution.

Polymers based on a number of different phenols were tested for their relative affinities for the ions of interest. Resins using resorcinol and 2,4-dihydroxybenzoic acid were found to have high affinities for both analytes. The affinities of resorcinol resins were strongly related to reaction temperature, with higher strontium-90 values for "low-temperature" resins, and higher cesium-137 distribution coefficients for "high temperature" material. Resins based on 2,4-dihydroxybenzoic acid were more balanced, displaying moderately high affinities for both ions. This balance was accounted for by the presence of the carboxylic acid group in the dihydroxybenzoic acid, which would act as a second monovalent exchange site. All remaining studies were completed using one of these two resins made porous by a calcium carbonate template.

In order to examine the relative capacities of these two resins, tests under column conditions were performed. The results showed that the high temperature porous resorcinol resins gave a two-fold increase in cesium-137 capacity over nonporous resins, when considered on a weight basis. Unfortunately, a sacrifice of strontium-90 capacity

accompanied this improvement in cesium-137 capacity. Low temperature porous resorcinol resins gave a four-fold increase in strontium-90 capacity over nonporous materials without loss of cesium-137 capacity. The 2,4-dihydroxybenzoic acid resins gave similar results, despite their somewhat different affinity characteristics. Elution of analytes of interest from the resins was easily accomplished using 2 N formic acid. Regeneration of the resin column was 90-95% complete within ten column volumes of acid.

Both the physical form of the prepolymers and the affinity characteristics of the resulting resins were found to be dependent upon several experimental parameters, most notably the reaction temperature. At temperatures below reflux (100°C), the prepolymers were liquids, and the resulting resins showed high strontium-90 K_d values, with lower cesium affinities. The disparity in the K_d values decreased as the reaction temperature was raised. At reflux temperature, gelation of the reaction mixture occurred, and the cured resins had high cesium-137 K_d values, but showed very poor affinity for strontium-90. Since the two types of exchange sites present were determined to act independently of each other, competition between formaldehyde and the Mannich electrophile for reactive sites ortho to the phenolic hydroxyl group was proposed as an explanation for this result. Hydroxymethylation appeared to be less favored at lower

temperature, and therefore more Mannich condensation occurs. Nitrogen analysis of resins produced at each reaction temperature showed a two- to three-fold increase in IDA content for the lower temperature polymer over the resin synthesized at reflux temperature. Further supportive evidence for the proposed mechanism was seen when a procedure was used in which the electrophile was allowed to form at 60°C prior to polymerization at 96°C. The resin produced had affinities resembling those of a low temperature polymer. Very little actual polymerization appeared to occur at 60°C since the template can be added just prior to solvent removal with no change in affinity characteristics. The formation of oligomers during the reaction period could not be ruled out, however.

The reproducibility of the resin synthesis was determined to be reasonably good, especially considering that one-pot syntheses were typically performed. Multiple resin batches synthesized at both 60°C and reflux temperature showed relative errors of only 8% in their nitrogen content. The reproducibility of the distribution coefficient values was poorer, giving relative errors of between 25% and 40% for multiple resin batches synthesized under the same conditions. Much of this variability was due to the inherent inaccuracy of distribution coefficients. Nonetheless, even this reproducibility was an improvement over the original work done

at the Savannah River Laboratory. In addition, the resin synthesis could be scaled up by at least a factor of ten, without any observable loss in affinity for the ions of interest.

The effect of a number of reaction parameters on the affinities of the resulting resins were tested. Reaction temperature was found to have a strong effect on resin affinity. Cesium-137 affinity gradually increased with increased reaction temperature, presumably due to greater incorporation of the phenol into the polymer backbone. Strontium-90 affinity was relatively independent of reaction temperature below reflux temperature, but dropped off dramatically above this point. As was mentioned previously, high rates of hydroxymethylation in this temperature range is a probable explanation.

The affinity of resorcinol resins for strontium-90 did not change much as long as at least a 1:4 ratio of IDA:resorcinol was used. Calculations based on nitrogen content showed that approximately one IDA group was present for every 5 or 6 phenol rings in the polymer. Thus, any amount of IDA greater than 20% of the number of moles of resorcinol was an excess, and the reaction seemed to proceed equally well in all the cases examined. Reflux temperature resins showed poor strontium-90 affinities regardless of the amount of IDA added. In each case, the final strontium-90 K_d value was

approximately the same as that for a resin containing no IDA at all. This was taken as a further indication of poor IDA addition at high temperature. The fact that resins synthesized without IDA at either temperature had significant affinities for strontium-90 was surprising, and a satisfactory explanation for this occurrence has not yet been found.

The amount of calcium carbonate template added to the reaction mixture also had little effect on resin affinity, although it produced distinct changes in the surface areas of the various resins. Any amount of template above 1 g produced the desired increase in affinities. Apparently, reaction temperature was the more significant factor affecting affinity. As expected, a steady increase in surface area was noted in the "low temperature" resins as the amount of added template increased. However, very little increase in surface areas were seen for the "high temperature" resins. Possibly, the template was more homogeneously occluded during the low temperature synthesis, because of the rotary evaporation necessary before heat curing. During the gelation seen in the high temperature synthesis, the template might be occluded in large pockets, rather than as small particles. A large reduction in potential surface area would result.

All of the alkali metal hydroxides performed equally well as catalysts for the polymerization. In each case, brittle solids with similar adsorption characteristics were produced.

Ammonium hydroxide, however, produced powdery resins with poor overall affinities. Organic base catalysts likewise gave poorer resins, in both form and function, than the alkali metal hydroxide catalysts. The use of a barium hydroxide catalyst produced resins at both 60°C and reflux temperature that had high strontium-90 affinities, a unique result. Unfortunately, both resins were too mechanically unstable to be useful. The addition of a transition metal to the sodium hydroxide catalyst (so-called "high ortho" substitution conditions) produced no significant changes in resin affinity compared to the use of sodium hydroxide alone.

Attempts to soften the resorcinol resins slightly by the incorporation of other cross-linking agents were generally unsuccessful. Paraformaldehyde, not surprisingly, produced resins similar to those cross-linked with formalin. Glutaraldehyde as the cross-linking agent gave soft resins, but with very poor affinities for the ions of interest. The physical properties of resins cross-linked with furfural were intermediate between those of the glutaraldehyde resins and the typical resins cross-linked with formaldehyde. However, the affinities of the resulting resins were not high enough to warrant further consideration. Resins based on a mixture of p-cresol and resorcinol, with IDA added and cross-linked with formaldehyde, had adequate K_D values, but were not noticeably different physically from simple RE:F:IDA polymers.

Aside from their affinities for cesium-137 and strontium-90 in high sodium alkaline medium, RE:F:IDA and 2,4-DHBA:F:IDA resins were both found to have significant affinities for some transition metals in aqueous solution. Copper(II), lead(II), and iron(II), were taken up well by both resins at pH=3 and above. Iron(III) and nickel(II) were taken up only poorly; uranyl ion, mercury(II), and cadmium(II) were hardly taken up at all throughout the pH range studied. The inclusion of excess calcium(II) and magnesium(II) did not significantly affect the affinities of either resin for any of the metals tested at pH=5, with the possible exception of lead(II). The tendency of this ion to form mixed complexes with IDA may be partially responsible. These studies portend the possibility of using these resins to sorb some of the heavy metals in a variety of applications.

Attempts to add resorcinol to poly(styrene-divinylbenzene) resins by Friedel-Crafts alkylation met with only limited success. A variety of solvents and catalysts were tested. Oxygen analysis of several of the functionalized resins indicated the presence of resorcinol, but subsequent distribution coefficient determinations showed essentially no uptake of either cesium-137 or strontium-90. However, attempts to add IDA to two of the functionalized polymers using Mannich reaction conditions gave encouraging results. Significant increases in strontium-90 K_d values were observed

for these resins. Relatedly, surface functionalization of a resorcinol-formaldehyde polymer with IDA was unsuccessful, probably due to a lack of available reactive sites.

Various resins coated with reagents that were potentially selective for either cesium-137, strontium-90, or both showed generally poor affinity characteristics. The octyl ester of 3,5-dihydroxybenzoic acid was easily synthesized and coated readily onto the macroporous resin XAD-4. Some bleeding of the reagent was observed, but it did not pose a serious problem. Distribution coefficient values for this resin, however, were very poor. Likewise, RE:F:IDA prepolymer liquid coated and then cured on glass beads and diatomaceous earth gave low K_d values for both ions, although they were somewhat higher than those for the octyl ester coated resin. Attempts to coat tetraphenylborate onto XAD-4 were totally unsuccessful. The reagent bled profusely and tended to form a precipitate with the cesium analyte in the resin bed. The poor performance of these resins was proposed to be caused by inherently low resin capacity. A resin containing phenolic exchange groups throughout the polymer mass should have a sufficiently high capacity to allow trace levels of Cs^+ to compete successfully with the large excess of Na^+ present for exchange sites. However, when small amounts of exchange sites are present, as in the cases of both the functionalized PS-DVBs and the thinly coated resins, Cs^+ does not compete as

successfully, and a drop-off in affinity is observed. Apart from the unusual matrix involved in these studies, these resins might work well for the analytes in question.

Preliminary applications of two types of liquid ion exchangers, long-chain carboxylic acids and long-chain alkyl substituted phenols, to the removal of cesium-137 and strontium-90 from simulated nuclear waste were made. Both types of compounds were found to be generally ill-suited for removing these ions under the stipulated conditions. The acid reagents were unsuccessful because of neutralization with the alkaline matrix. The phenolic reagents either precipitated during the extraction process or did not extract the ions of interest to any great extent. However, these reagents were tested only because their exchange groups most closely resembled those of the bifunctional chelating resins being studied concurrently, and they by no means represent all of the potentially applicable reagents. Liquid ion exchangers have been used successfully for the selective removal of ions (primarily anions) from aqueous brines. Further studies on the removal of cesium-137 and strontium-90 from nuclear waste utilizing other liquid ion exchangers may produce positive results.

FUTURE WORK

Interesting areas for future work on the resins developed in this section of the dissertation can generally be grouped into four categories. First, although many of the reaction conditions have been studied here, further exploration and optimization of the polymerization procedure might be pursued. This would include further development of resins using some of the other promising templates rather than calcium carbonate. Additionally, a better (more reproducible) procedure for suspending the template in the reaction mixture might be a beneficial step. Other means of inducing porosity into phenol-formaldehyde polymers could be explored as well. Control of the the reaction conditions to a sufficient degree to produce resins with preordained affinity characteristics should also be an eventual goal, in the event these resins find widespread application.

Second, more extensive attempts at determining the structure and process of formation of these resins should prove interesting. Continuation of ongoing studies using X-ray techniques and carbon-13 NMR are good starting points. Solid state NMR might be an ideal means of obtaining structural information on the cured polymers. Although gas chromatographic analysis of the prepolymer reaction mixture was hampered by its aversion for organic solvents, the

usefulness of high-performance liquid chromatography or gel permeation chromatography has not been thoroughly explored. Development of methods for analyzing these resins and their precursors utilizing these techniques may prove troublesome. The highly polar nature of the proposed precursors could cause extensive adsorption problems under typical HPLC or GPC conditions. These analytical techniques were not pursued by the author because of the poor preliminary results found with both normal-phase and reversed-phase thin layer chromatography. However, more concentrated efforts in this regard could yield techniques of general utility for polymers of this type.

Third, expanded application studies for these P:F:IDA polymers should be pursued, most notably in the area of heavy metal sorption. The presence of transition metal impurities is a problem in many industrial and environmental situations, and chelating resins with unique selectivity characteristics are always potentially useful. A further application of these bifunctional resins in the nuclear industry might be in the sorption of trace levels of uranyl ion from various process and waste streams. Studies of the affinity of these polymers for metal ions other than those already examined may also generate new areas of interest and application.

Finally, the functionalization of already formed polymers with cesium and strontium selective groups should not be

abandoned. The reproducible synthesis of selective chelating resins by this means is still a fundamentally sound idea. However, more extensive studies are required to determine the optimal reaction scheme for the addition of resorcinol and IDA to matrices such as macroreticular PS-DVBs, if one exists. Studies of this type could be broadened in scope, with the examination of a wide variety of selective chelating groups for the ions of interest and the chemical means to anchor them to a resin support. One such group of potentially useful reagents are crown ethers and similar macrocyclic molecules. Currently, they are often expensive to produce and use on a widespread basis. However, anchoring them to a resin support, with the possibility of regeneration and reuse, might make them economically more attractive.

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AFTERWORD

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"Research is to see what everyone else has seen,
and to think what nobody else has thought"

---Albert Szent-Gyorgyi

"They can, because they think they can"

---Virgil

"Faith is the substance of things hoped for;
the evidence of things not seen"

---St. Paul

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"If I have been able to see farther than others
it was because I stood upon the shoulders of giants"

---Sir Isaac Newton

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every man is a piece of the continent, a part of the main"

---John Donne

"They say that these are not the best of times
but they're the only times we'll ever know"

---Billy Joel

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"There's a divinity which shapes our ends
Rough-hew them how he will"

---William Shakespeare

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kindness and generosity.

"All the world's a stage, and
all the men and women merely players"

---William Shakespeare

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