DEVELOPMENT OF ION EXCHANGE RESIN METHODS FOR DIRECT ANALYSIS OF ENVIRONMENTAL RADIONUCLIDES

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Paul Allan Blakeslee

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ABSTRACT

DEVELOPMENT OF ION EXCHANGE
RESIN METHODS FOR DIRECT ANALYSIS
OF ENVIRONMENTAL RADIONUCLIDES

by Paul Allan Blakeslee

This thesis examines the development and evaluation of an upflow ion exchange column for the concentration and subsequent direct gamma analysis of radionuclides from environmental samples. The column has been developed specifically for optimum counting geometry in the well of a three-inch sodium iodide (thallium activated) scintillation well detector; however, modification to other crystal detection systems is possible.

The investigation of column characteristics and performance was conducted using a mixed bed consisting of Dowex 50W-X8 and Dowex 1-X8 resins. Physical and chemical factors affecting column performance are discussed and observations of column uniformity and capacity are presented.

An evaluation of column performance is given with respect to both actual isotope removal from prepared samples and the existing method of concentrating liquid environmental samples by evaporation on plastic film followed by gamma analysis of the plastic film.

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By

Paul Allan Blakeslee

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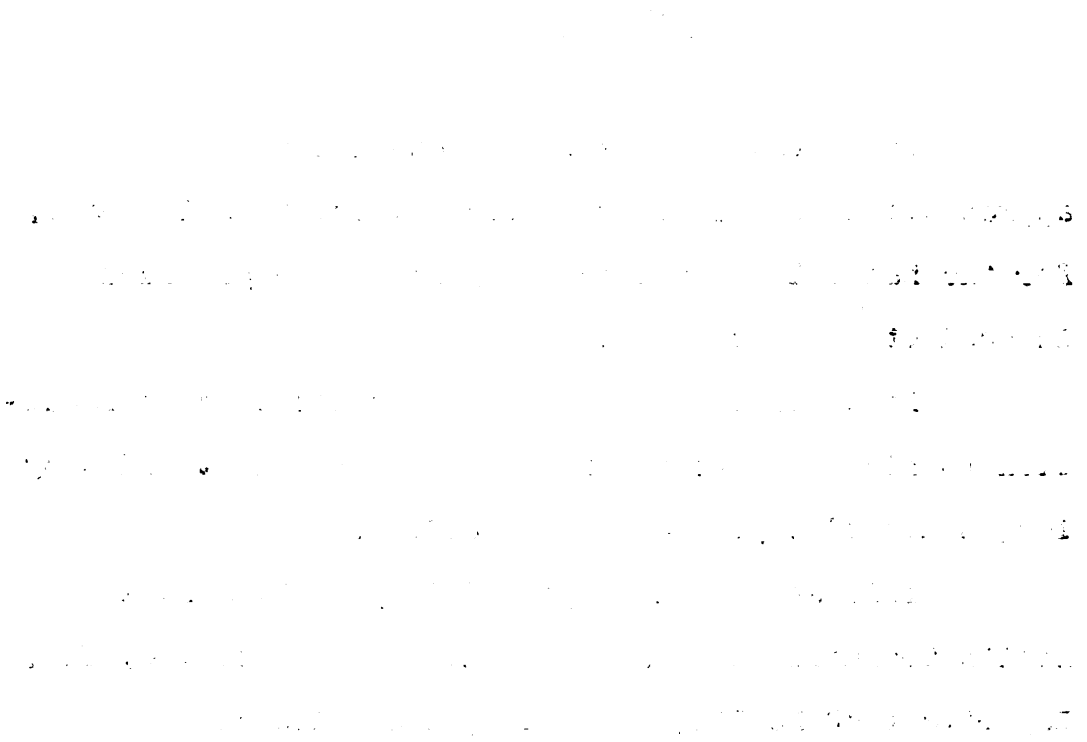

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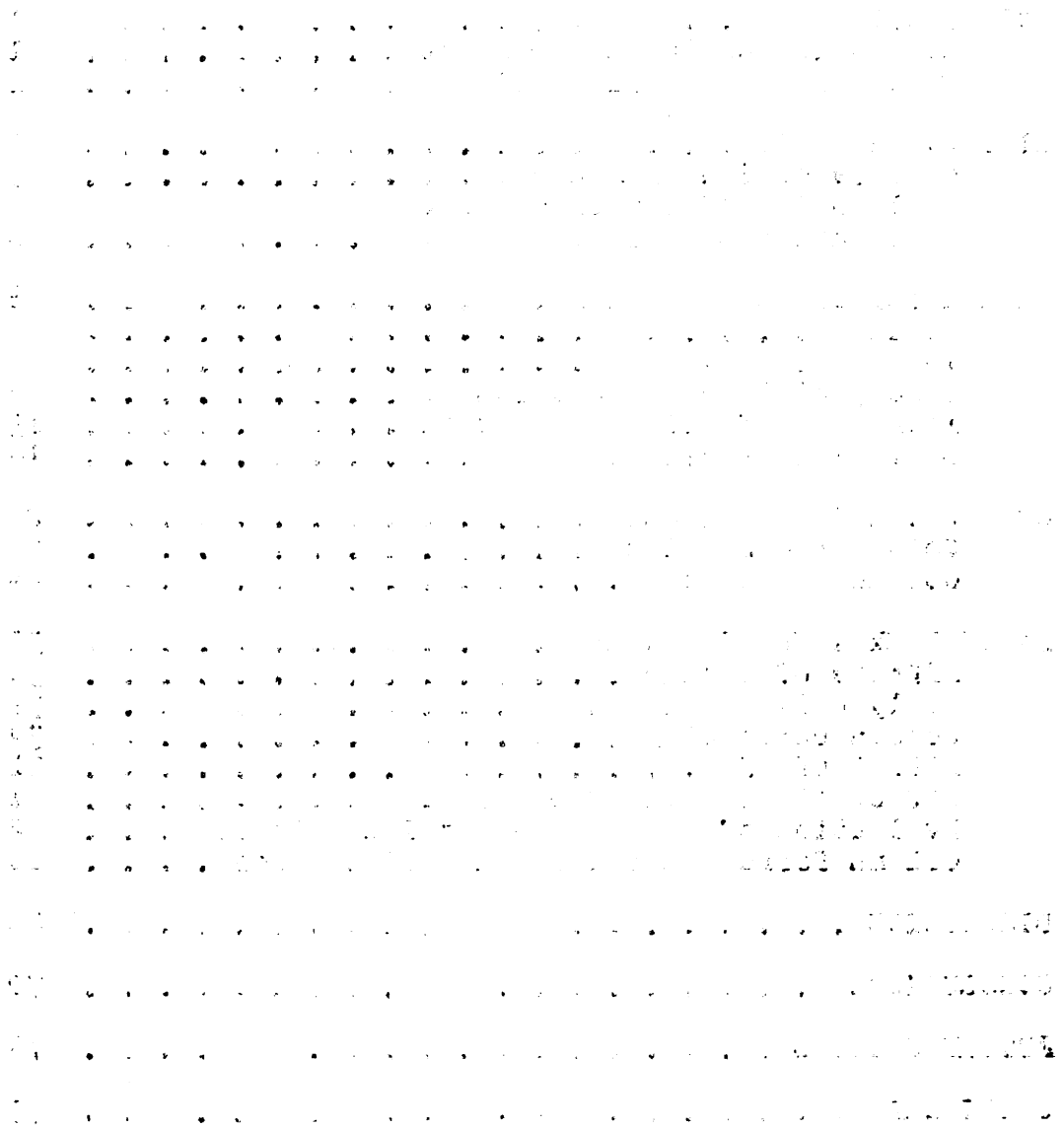

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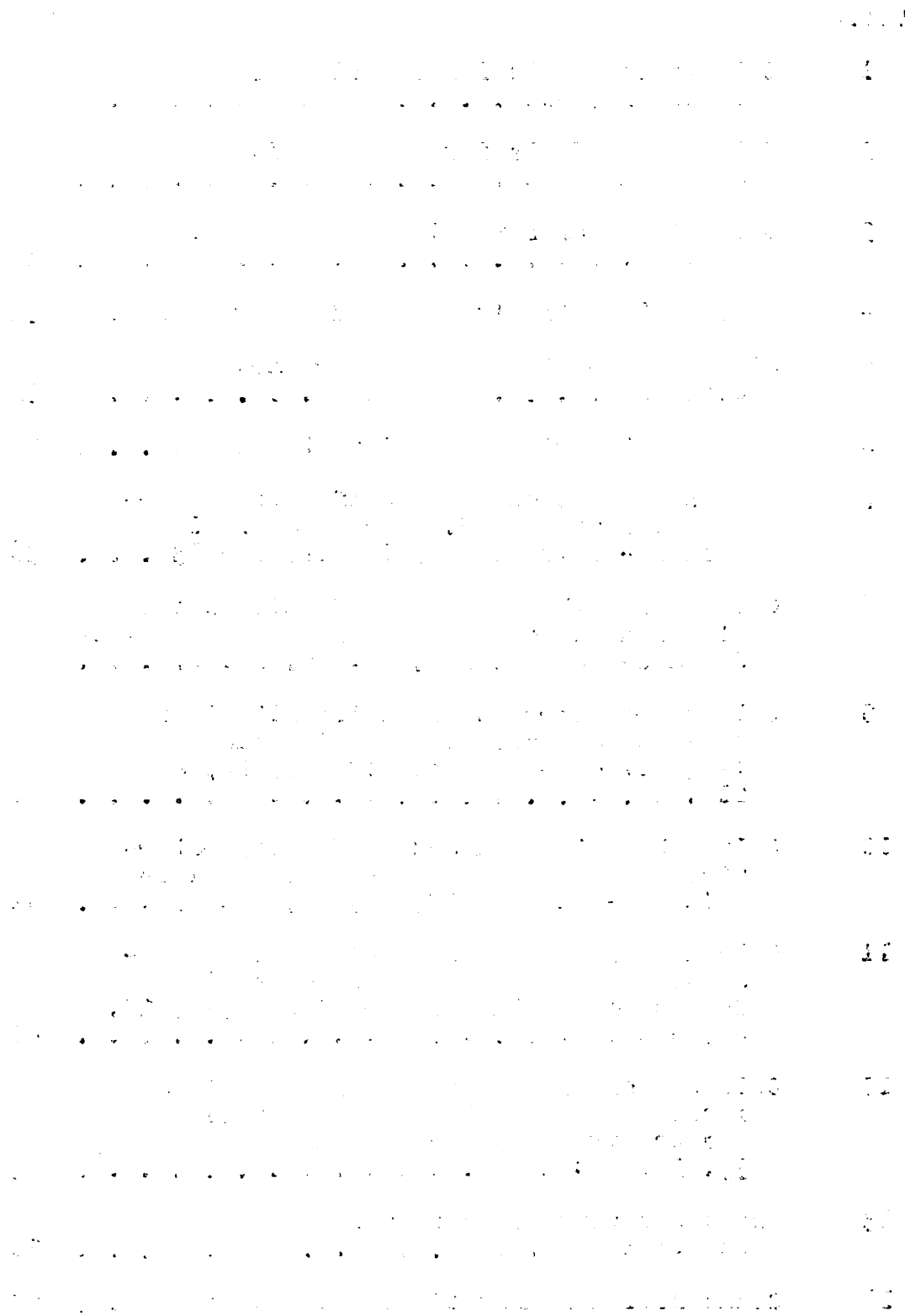

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INTRODUCTION

Monitoring of Our Environment

The presence of man made radioisotopes in rainwater and surface waters is a phenomenon created by the age of nuclear technology in which we live. The major sources of this potentially hazardous contamination are nuclear weapons testing, nuclear power reactor operations, and wastes from nuclear research operations.

The potential hazard to the health and safety of man has become an item of international concern, as witnessed by the nearly worldwide acceptance of the Nuclear Test Ban Treaty of 1963. Although environmental pollution from weapons testing has decreased significantly over the past few years, there still exists an urgent need for the development of improved systems for monitoring radioactivity present in our environment.

It is hoped that this investigation will be one step in the development of a monitoring system capable of rapid and quantitative analysis of the radionuclides present in liquid environmental samples.

The use of ion exchange resins for the concentration of radionuclides for direct gamma analysis is by no means a new technique, but it is hoped that the modifications in apparatus and procedure presented in this paper will make this method more applicable to routine sample monitoring. The concentration of environmental samples on ion exchange resins can result in a significant saving

in time and space involved as compared with evaporation methods. Skillful and precise laboratory technique is not required as with radiochemical methods.

Although completely quantitative analysis of mixed isotope samples is not possible using present spectrographic methods, it is hoped that in the near future the combination of gamma and beta spectrographic analysis will place this method on an equal footing with the more tedious and time-consuming procedures of radiochemical analysis. When this day arrives the methods of ion exchange concentration will become very useful techniques.

Development of Upflow Column

Conventional ion exchange column operation consists, in its simplest form, of a packed column of ion exchange resin which receives a feed solution at the top of the column. Flow through the column is downward, aided by both gravity and hydrostatic pressure from the fluid above. Several investigators [Boni (1) and (2); Krieger, Gilchrist, and Gold (12)]; and others have used the downflow column method of ion exchange for the removal of radionuclides from environmental samples.

The low activity levels found in environmental water samples preclude any process of direct counting with equipment presently available. Background levels on the order of 10 $\mu\mu$c/l are common, particularly in

surface waters--Grune (8). Concentration on ion exchange resins of ionic forms of the radionuclides present is one of several methods which has proven to be of value in increasing sample counts to a level where statistical reliability can be obtained within reasonable counting periods.

One of the unique features of environmental samples is the presence of suspended solids in the sample to be investigated, particularly in rain or stream water. These solids can be treated in one of two ways: the sample may be prefiltered to remove the solids, or the gross sample may be analyzed. Filtration results in the removal of a relatively large portion of the radionuclides found in rain and stream samples. For some applications this separation may be desirable; however, for routine monitoring activities a gross analysis of the sample may give a more adequate picture of the condition of the sample. In such a case it is desirable to concentrate both particulate and dissolved portions in one container for counting. The downflow column designed by Boni (1) and (3) has been used for this purpose.

One of the limitations of this column was the stoppage of flow caused by the buildup of particulate matter over the upper surface of the resin. The upflow column introduced by the author in this paper eliminates this form of flow obstruction. Flow enters at the bottom of the column and diffuses upward through the resin bed.

Large solid particles are retained in a void volume at the bottom of the column and thus cannot form a mat on the resin surface capable of blocking flow.

Solid particulate matter concentrated from rain and stream water samples has been shown (22) to contain a significant fraction of the radioactivity found in such samples. The concentration of suspended solids at the bottom of the upflow column provides optimum counting geometry when the column is placed in the well of the scintillation detector for analysis.

The downflow column designed by Boni (1) and (3) was significantly larger than the upflow columns investigated in this paper. The crystal well available to Boni for gamma analysis of his samples measured 3-1/4 inches in diameter by 6 inches deep, whereas the crystal well available for this investigation measured 1-1/8 inches in diameter by 1-3/4 inches deep. With this size limitation it has been necessary to design a column which most effectively utilizes the space available.

LITERATURE STUDY

History of Ion Exchange

Records as far back as 755 A.D. indicate that man has recognized and utilized certain beneficial properties of natural soils and sands for the purification of water. Nachod and Schubert (17) trace the development of ion exchange technology beginning with the first observations of the phenomenon of ion exchange by H. S. Thompson in 1850. It was observed by Thompson that certain soils had the ability to absorb ammonium sulfate with the release of calcium sulfate from the soil. The mechanism of this exchange reaction was visualized by J. T. Way as being:

$$Ca\text{-soil} + NH_4SO_4 \rightleftharpoons NH_4\text{-soil} + CaSO_4.$$

The first ion exchange process, developed by F. Harm in 1896, utilized a natural cation exchange of silicate for the removal of sodium and potassium from sugar beet juice. The first successful large-scale application of cation exchange was by R. Gans, who synthesized inorganic exchange materials capable of exchanging Na^+ for other cations. This material was used successfully for water softening and sugar treatment.

The inorganic exchange materials developed by Gans and others were limited by the fact that they were acid sensitive and therefore could not be utilized in exchange reactions involving acid solutions. The discovery of exchange capacity of humus and other natural organic materials led to the development of sulfonated coals which

were durable and inexpensive.

Only within the past thirty years has the development of ion exchange processes brought ion exchange to the point of being considered a unit operation. This recent development in application has resulted from the discovery of the ion exchange properties of certain synthetic resins by Adams and Holmes. Holmes was the first to synthesize both anion and cation exchange resins.

The modern era of ion exchange technology began in 1944 with the synthesis of exchange resins from preformed polystyrene by G. D'Alelio of General Electric Company. From these first polystyrene resins, the presently available resins with greatly improved capacity and mechanical stability have developed.

Application of Ion Exchange to Radiation Studies

The literature presented each year on the topic of ion exchange and its applications is summarized briefly by Kunin in the publication "Industrial and Engineering Chemistry". The number of papers presented annually has increased almost exponentially since the end of World War II. Developments are continually expanding in the application of ion exchange methods in the areas of water conditioning, inorganic chemistry and hydrometallurgy, organic chemistry, food technology, biochemistry, waste treatment, and related fields.

Of particular interest in this investigation are

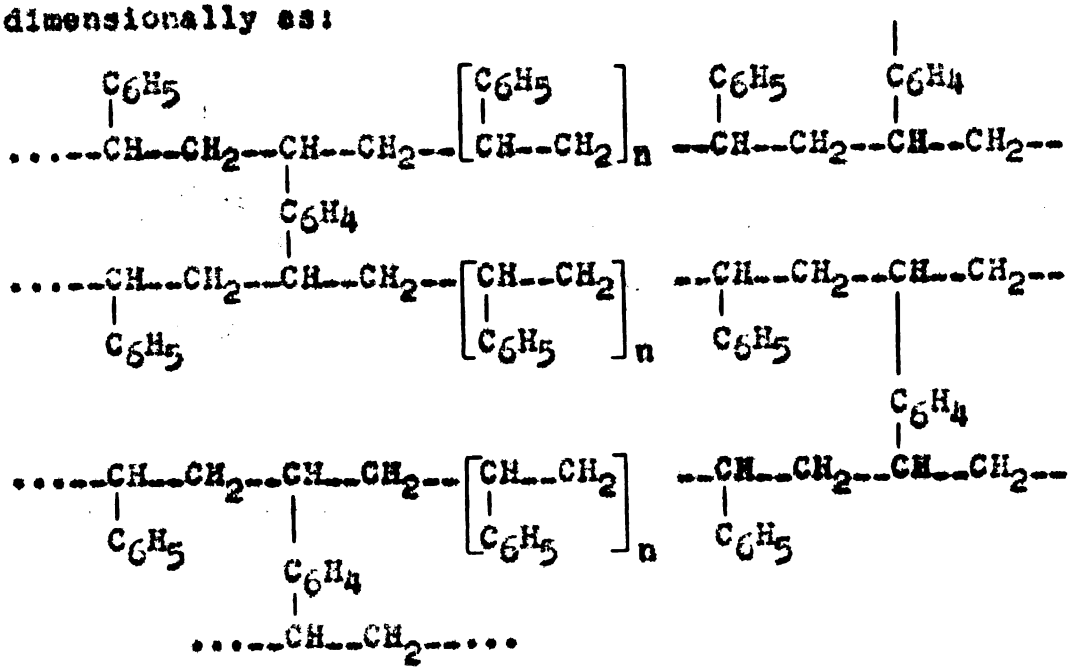
the areas of hydrometallurgy and waste treatment. Within these broad fields much work has been done on the concentration and separation of the various radionuclides for purposes of waste treatment and purification.

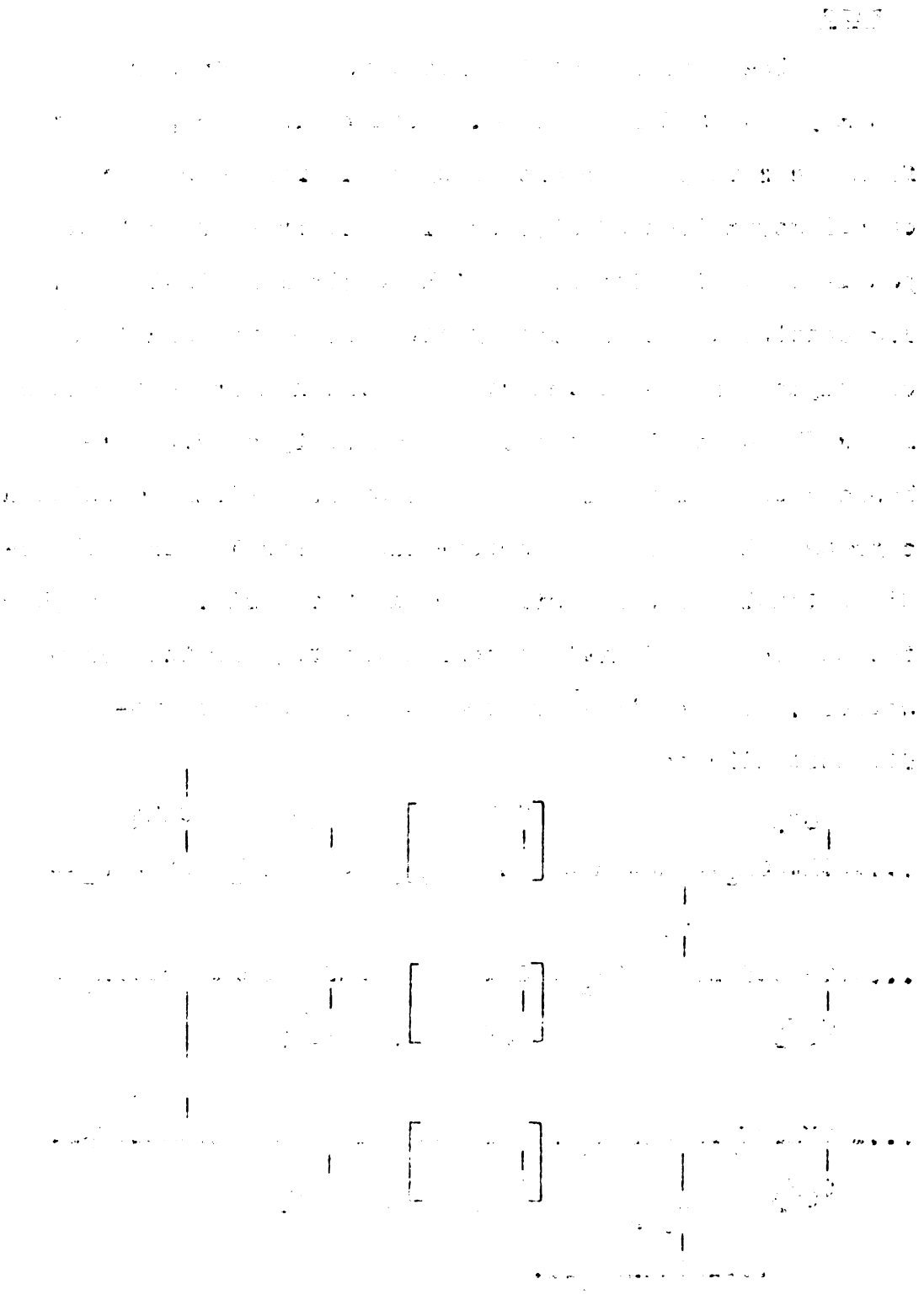
The technique of removal of radioisotopes by ion exchange from dilute solutions has been investigated by Swope (23) using nuclear reactor process waters. Application of the same principles for the concentration of radionuclides from environmental samples has been carried out by Boni (1) and (3) and by Krieger, Gilchrist, and Gold (12). Krieger, Gilchrist, and Gold have concentrated radionuclides from rainwater in a two-column ion exchange process. Boni has developed a column containing alternate layers of cation and anion resin which he has used to concentrate radionuclides from rain and stream samples. The column developed by Boni is suitable for direct gamma analysis using a large well scintillation crystal.

PRINCIPLES OF ION EXCHANGE

Resins

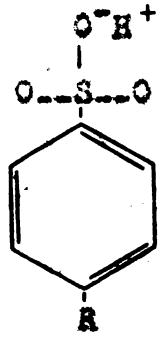
The resins used in this investigation were Dowex 50-X8 and Dowex 1-X8. Both resins are prepared from the same polymer matrix which is formed by the co-polymerization of styrene with divinylbenzene in a pearl-polymerization from which nearly spherical beads are obtained. The amount of divinylbenzene used in the co-polymerization is indicated by the number "-X8" which means "8% divinylbenzene". The quantity of divinylbenzene used dictates the degree of cross-linkage between styrene polymers. This cross-linkage results in a three-dimensional "network" structure in the resin. The higher the percentage of divinylbenzene the tighter the resin network. The resin structure can be pictured two-dimensionally as:



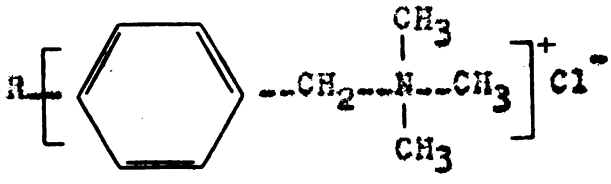


Dowex 50W-X8 is a strongly acedic, nuclear sulfonated, styrene-divinylbenzene cation exchange resin. Nuclear sulfonation is carried out using sulfuric acid, with the resultant introduction of approximately one sulfonic acid group per benzene ring. Dowex 1-X8 is a strongly basic, quaternary ammonium type, styrene-divinylbenzene anion exchange resin. The ionogenic quaternary ammonium groups are introduced by treatment of the co-polymer matrix with chloromethyl ether followed by treatment of the chloromethylated resin with trimethylamine. The resulting product is a quaternary ammonium salt (the chloride form of a strongly basic anion exchange resin).

Considering only the benzene ring to which the exchangable groups are attached, the two resins may be represented as:



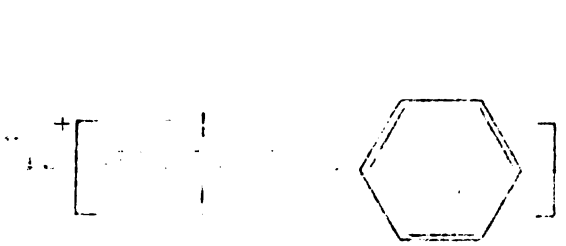
Cation Exchange Group
Hydrogen Form

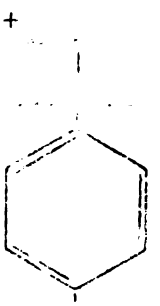


Anion Exchange Group
Chloride Form

Ion Exchange Theory

Since the first investigation of the phenomenon of ion exchange by Way in 1850, scientists have attempted to





define a theory of ion exchange which would accurately explain the observed facts about this type of reaction. Three general classes of ion exchange theories have been proposed:

(1) the Donnan membrane theory;

(2) the double-layer theory; and

(3) the crystal lattice exchange theory.

For the most part all three theories are quite similar in that the exchange of ions must satisfy the law of electroneutrality. The major difference in the three theories is the position and origin of the exchange site. In each case the exchange site is in effect a fixed, non-diffusible, ionic group capable of forming an electrostatic bond with a small diffusible ion of opposite charge.

The Donnan membrane theory, as applied to ion exchange, considers the interface between the solid phase resin and the liquid phase ionic solution as a semi-permeable membrane. The exchange of ions through this "membrane" takes place in such a way as to satisfy conditions of solution equilibrium.

The double-layer theory as applied to ion exchange is a modification of the explanation of the electrokinetic properties of colloids. This theory proposes the existence of a double layer of electrical charge surrounding the resin. The inner layer of charge is fixed (the resin matrix), while the outer layer consists of a mobile, diffuse layer of charged ions (the counter ions). It is

this outer layer of ions which are pictured as taking part in exchange reactions.

The most easily visualized picture of the ion exchange process, especially with respect to the structure of polymeric organic resins, is probably the crystal lattice theory. Although organic resins do not have the crystal structure with definite lattice points found in inorganic minerals exhibiting exchange properties, the resins do have exchange sites created by sulfonation, ammonation, or similar treatment of the co-polymer. At these exchange sites a diffusible ion is electrostatically bound to the resin polymer network. Exchange occurs (depending on solution concentration and selectivity) when an ion of like charge diffuses into the resin and approaches the exchange site.

The crystal lattice theory accounts adequately for the observation that certain large molecules can be effectively eliminated from exchange reactions by virtue of the fact that they are too large to diffuse through the matrix of the polymer network. This screening effect can be controlled by using resins of proper cross-linkage. The higher the degree of cross-linkage, the smaller the network in the polymer.

Kunin (13, p. 12) has shown that the exchange capacity of both anion and cation resins can be accurately predicted from the known content of nitrogen or sulfur in each resin type. The quantity of nitrogen and sulfur

indicates the number of possible exchange sites, and it is thus evident that exchange occurs throughout the resin matrix rather than as a surface reaction such as simple surface adsorption.

Theory of Column Operation

Samuelson (13, p. 103) has stated that, "A detailed theoretical study of column operation is quite an involved task, and at present there exists no theory in which all factors are taken into consideration. Fortunately, such a complete study is not essential to the proper application of ion exchange separations . . .".

When rigorous investigation is undertaken, however, analysis can be based on one of two established theories:

(1) the plate theory, or

(2) the theory based on continuous variables.

The plate theory was originally developed as a theory for solvent extraction and distillation. Later, it was modified somewhat for application to chromatographic columns. For purposes of calculation and prediction of column performance, the column under investigation is divided into a series of plates or layers of exchange resin. Each plate is then considered to come to equilibrium with the portion of solution in contact with the plate.

The theory based on continuous variables is the

more precise of the two and in non-mathematical terms can be explained as being a consideration of idealized assumptions about the kenetics of the ion exchange process. The theory is essentially based on the principles of mass transfer and utilizes a form of material balance--Selke (20, p. 77).

The shape of the breakthrough curve for a given exchange reaction in a particular column is governed by the type of exchange involved, i.e., favorable, neutral, or unfavorable. These conditions correspond to systems in which the selectivity coefficient for the ion present in the feed solution is greater than unity, equal to unity, or less than unity, respectively.

Within the exchange zone of the column, local equilibrium (required for theoretical prediction of column performance) will be improved by such factors as low flow rate, reduced particle size, and increased temperature. These conditions therefore lead to a sharpening of breakthrough curves and increased column efficiency.

Mechanism of Column Operation

Normal ion exchange column operation utilizes a cylindrical column of ion exchange resin in a relatively dense, uniform state of packing charged with one type of exchangeable ion (neglecting for the moment the condition of mixed bed ion exchange). A feed solution of uniform concentration is introduced at one end of the column. This solution passes through the resin column and diffuses

into the matrix of the resin particles where exchange takes place between the ions present in the feed solution and the counter ions of similar charge originally attached to the resin. Equilibrium is established within each differential element of depth of the column according to the conditions of selectivity, flow rate, temperature, and concentration. The conditions are such that at the top (inlet end) of the column the counter ions are displaced by ions from the feed solution, establishing equilibrium at that concentration. The feed solution passes through the column, establishing an equilibrium state at each level of the column corresponding to the feed concentration at that level. Gradually the uppermost levels of the column become saturated with the ions picked up from the feed solution. This condition of saturation proceeds down the column, preceded by a band of partial saturation. As the band of partial saturation reaches the bottom of the column, the concentration of the ionic form originally found in the feed solution increases until at complete saturation the composition of the effluent solution is identical to that of the influent.

Resin Selectivity

The equilibrium constant used in physical chemistry is not completely applicable to resin systems, and it is therefore customary to define a term known as the selectivity coefficient. For a resin in ionic form B, placed in a solution of ion A and allowed to come to equilibrium, the

selectivity coefficient is defined as (6, p. 8):

$$(k)\,{}^{A}_{B} = \frac{\left[\begin{matrix}\text{Conc. of Ion A}\\ \text{in the Resin}\end{matrix}\right] \times \left[\begin{matrix}\text{Conc. of Ion B}\\ \text{in Solution}\end{matrix}\right]}{\left[\begin{matrix}\text{Conc. of Ion B}\\ \text{in the Resin}\end{matrix}\right] \times \left[\begin{matrix}\text{Conc. of Ion A}\\ \text{in Solution}\end{matrix}\right]}$$

In terms of a reaction equation:

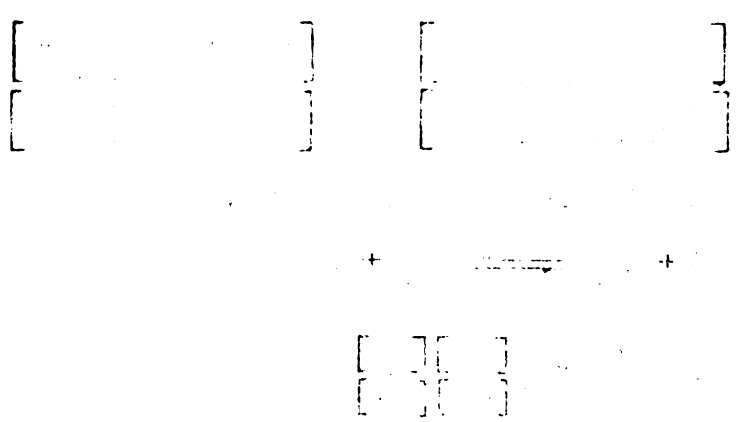
$$A + B_r \rightleftharpoons A_r + B$$

$$(k)\,{}^{A}_{B} = \frac{[A_r][B]}{[A][B_r]}$$

A more rigorous definition of the selectivity coefficient includes the activity coefficients of the ions involved in the reaction--Samuelson (18, p. 65). Such a definition is required for precise analytical work, but in the present investigation the composition of the samples to be analyzed is too complex to allow rigorous investigation. A simple understanding of the basis for exchange reactions will, however, aid in explaining the observed behavior of the waters investigated.

Being a form of equilibrium constant, the selectivity coefficient is dependent upon many factors. Temperature and pressure have a minor effect and are of little concern under normal operating conditions. For a given type of resin the factors which have the greatest effect on the selectivity coefficient are the valence, concentration, and nature of the exchanging ions.

Kunin (13, p. 32) has suggested the following set of imperical relationships which can be used to relate ion selectivity:



(1) At low concentrations and ordinary temperatures, in an aqueous medium, the extent of exchange increases with increasing valency of the exchanging ion.

(2) At low concentrations and ordinary temperatures, in an aqueous medium and with constant valence, the extent of exchange increases with increasing atomic number of the exchanging ion.

Another general rule which is used in predicting ionic selectivity is that within a given series, as defined in (1) or (2) above, the affinity for a given resin decreases as the size of the hydrated ion increases (5, p. 9).

Donner (4) has reported two series of selectivity coefficients (k) for univalent and divalent ions on Dowex 50-X8 resin:

Table 1. Selectivity Scale for Univalent Ions on Dowex 50-X8.

	k		k
Li	1.00	Rb	3.16
H	1.27	Cs	3.25
Na	1.98	Ag	8.51
NH_4	2.55	Tl	12.4
K	2.90		

Table 2. Selectivity Scale for Divalent Ions on Dowex 50-X8.

	k		k
UO_2	2.45	Ni	3.93
Mg	3.29	Ca	5.16
Zn	3.47	Sr	6.51
Co	3.74	Pb	9.91
Cu	3.85	Ba	11.5
Cd	3.88		

The selectivity of Dowex 1 resin for certain anions can be seen from the following partial listing of values reported by Wheaton and Bauman (27).

Table 3. Selectivity of Dowex 1 for Monovalent Anions.

	k	X_{el}
Salicylate	32.2	0.18
Iodide	8.7	0.27
Phenoxide	5.2	0.34
Bisulfate	4.1	0.29
Nitrate	3.8	0.38
Bromide	2.8	0.40
Nitrite	1.2	0.51
Bisulfite	1.3	0.48
Cyanide	1.6	0.47
Chloride	1.00	----
Bicarbonate	0.32	0.65
Dihydrogen Phosphate	0.25	0.68
Formate	0.22	0.70
Acetate	0.17	0.73
Aminoacetate	0.10	0.77
Hydroxide	0.09	0.77
Fluoride	0.09	0.77

X_{el} = Equivalent fraction in the resin phase.

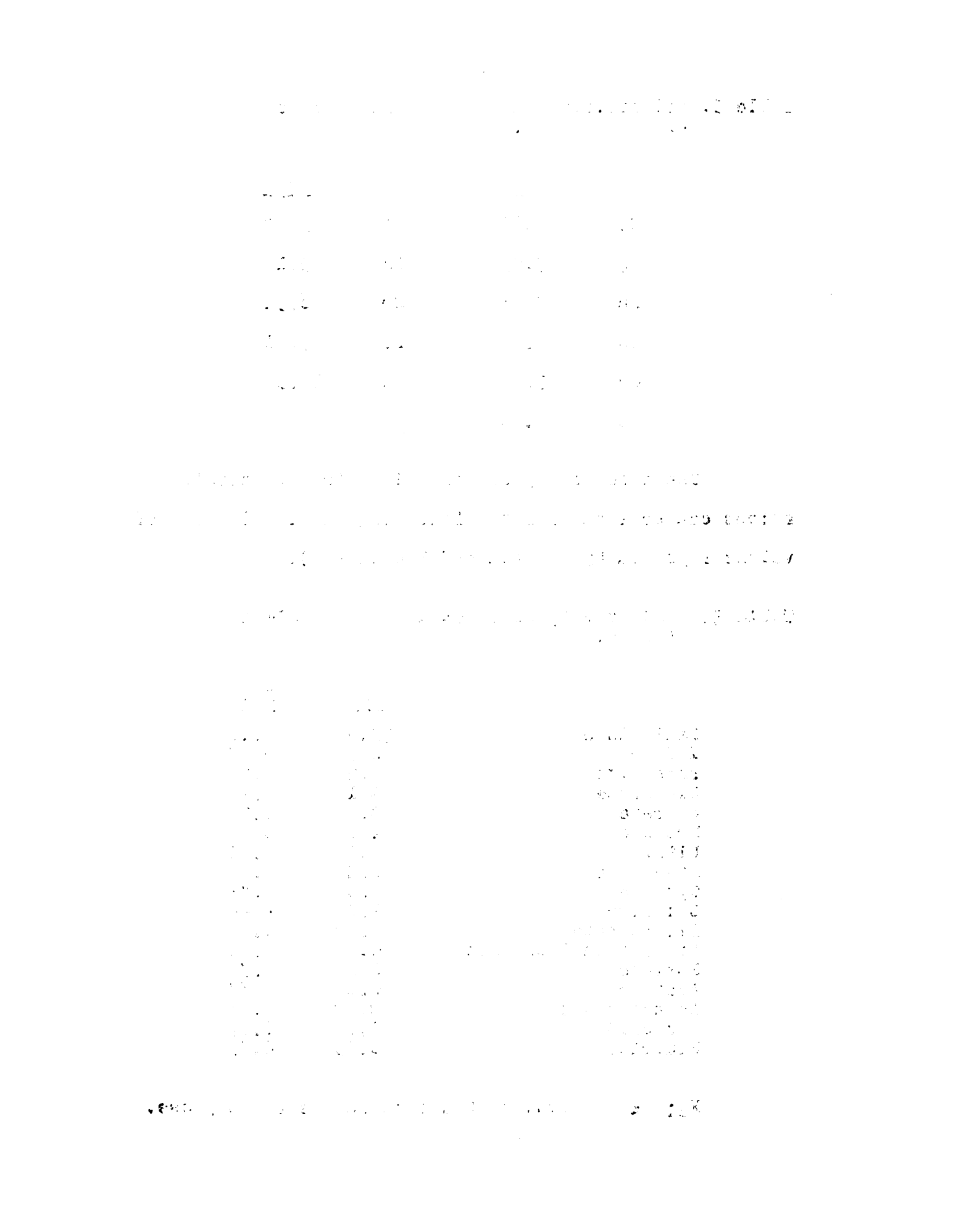


Table 3 represents the measurement of equilibrium selectivity coefficients of Dowex 1 in the chloride form. These values were obtained by mixing 5 ml. (wet volume) of resin with 50 ml. of a 0.1 N solution of the sodium salt of the anion under investigation. The value X_{Cl} represents the ion fraction of the total capacity of the resin which is present in the chloride form under equilibrium conditions. These values are reported because it has been found that the value of k is not constant over the range of ionic ratios, X_{Cl}. The value of X_{Cl} in turn relates to equilibrium conditions and is concentration dependent.

It should be noted that although the values reported are for Dowex 1 in the chloride form, the same order of selectivity would be maintained for the resin in other forms, i.e., hydroxide as used in this study. The magnitude of the values of k for Dowex 1 in the hydroxide form would have to be determined experimentally.

The effect of selectivity is greatly affected by the total ionic concentration of the solution under investigation, especially in exchanges involving multivalent ions (6). As the solution becomes stronger, the effect of selectivity becomes smaller. In the case of exchange of univalent ions for trivalent ions the selectivity coefficient is inversely proportional to the square of the total solution concentration.

The fundamental principles of column exchange

operations briefly described above for the condition of exchange of a single pair of ionic forms are greatly complicated when a solution of mixed ions (as found in environmental samples) is considered. Selke's statement (20, p. 85) that, in mixed solutions ". . . the time for appearance of the peaks [maximum concentrations] of different solutes will be proportional to the relative affinity for each solute." can be applied to the behavior of various ionic forms found in an environmental sample. From the tables of selectivity coefficients (Tables 1 and 2) it is seen, for example, that the selectivity coefficient for Dowex 50-X8 resin for cesium is 3.25 but that the coefficient for the divalent calcium ion is 5.16. From this information it can be seen that although the resin column will effectively remove both ions from a solution prior to saturation, the cesium ions sorbed by the resin may actually be displaced by calcium as saturation is approached. This displacement will cause a band of saturation for cesium ion to travel through the column ahead of the band of saturation for calcium ion. This same relationship holds true for all ion species found in the feed solution, with the result that ions for which the resin has a low affinity may be eluted into the effluent solution before actual column breakthrough capacity has been reached. It is for this reason that quantitative concentration of radionuclides can be accomplished only prior to column saturation.

UPFLOW ION EXCHANGE COLUMN

Column Preparation

The upflow column designed for concentration of environmental samples consists of a 1-1/8-inch by 3-inch polyethylene cylinder, closed at one end (LaPine Scientific Company, T42-68, No. 115). The column contains a 7 mm glass tube extending to the bottom of the column, the lower end of which is fitted with a #4 or #6 CaPlug positioned to create a void volume around the bottom of the central feed tube. This void provides for the collection of large solid particles. The rim of the CaPlug is perforated to allow the sample water to pass freely out through a layer of Pyrex glass wool (Cat. No. 3950) packed around the CaPlug.

The resin particle size chosen for application in the upflow bed investigation was 200-400 mesh for both the anion and cation resins. This corresponds to a particle size range of 0.074 to 0.038 mm.

The fine mesh resin was chosen for several of its beneficial properties.

(a) As shown by Samuelson (13, p. 106), breakthrough capacity is greatly increased as particle size is decreased.

(b) Reduction in particle size improves breakthrough curve characteristics (18, p. 106).

(c) The time for exchange equilibrium is directly

proportional to the square of the particle diameter (18, p. 93).

(d) The resin acts as a filter, holding particulate solids at the bottom of the bed.

(e) The fine mesh resin has also been used by Boni (1) to collect colloidal clay particles in river water samples which have absorbed radioactive cations.

A resin cross-linkage of 8% divinylbenzene was chosen for both anion and cation exchangers. This is a medium degree of cross-linkage and provides a stable resin which does not swell excessively when wet. The -X8 resin is more selective in its exchange reactions than resins with a lower degree of cross-linkage. Also, it is not subject to large volume changes with changes in ionic form as are lower cross-linked resins (18, p. 152). Reaction equilibrium is reached at a slower rate with the -X8 resins than with lower cross-linked resins, but this effect is minimized by the selection of the small particle 200-400 mesh resin.

The Dowex 50W resin was used in its original hydrogen form. The selectivity coefficient of Dowex 50 in the hydrogen form with 8% divinylbenzene is given in Table 1 as 1.27. This is comparable with a selectivity coefficient for calcium of 5.16 and for cesium of 3.25 (see Tables 1 and 2).

The Dowex 1 resin used was converted to the hydroxide form by passage of an excess of 10% sodium

hydroxide solution over the resin in a column operation prior to mixing the two resin types. In the hydroxide form the resin has a selectivity coefficient of 0.09 relative to chloride at 1.00 and iodide at 8.7. The selectivity coefficient of Dowex 1 in the free base (hydroxide) form is equal to that of fluoride (see Table 3).

The resin bed above the glass wool layer is placed in the form of a slury. In the case of the 200-400 mesh mixed resin used in this investigation, the resin required packing to obtain a bed of uniform density. All steps involved in the formation of the resin bed must be done in such a way as to avoid the formation of air pockets within the bed, as these tend to obstruct flow and produce a non-uniform bed.

The top of the resin bed is covered with a second layer of glass wool and the column is fitted with a rubber stopper drilled to accommodate the central feed tube and an effluent tube consisting of a bent section of 5 mm glass tubing which can be removed for column counting. The components of the upflow column and the assembled column are shown in Figure 1.

The physical characteristics and capacity of the resin bed may be varied to meet the requirements of nearly any form of sample concentration. Unless stated otherwise, all columns investigated were prepared using Dowex 50W-X8 cation exchange resin in the hydrogen form and

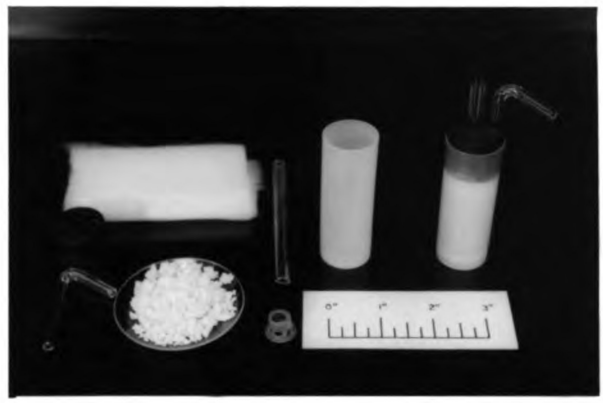


Figure 1. Upflow Ion Exchange Column and Column Components.

Figure 2. Fresh Ion Exchange Column (right) and Exhausted Column (left), showing discoloration at bottom of column due to concentration of particulate matter from 10 liters of rainwater.

Dowex 1-X3 anion exchange resin in the free base or hydroxide form.

The two resins were mixed in the ratio of 1.5:1, anion to cation (by exchange capacity). Swope (23, p. 1101), while working on the removal of mixed fission products from tap water (adjusted to a pH of 2.5 with nitric acid), has utilized mixed bed columns with a ratio of 2:1, anion to cation (by volume). The results of her investigation indicated an initial breakthrough of the anion resin. The suggestion was therefore made that a ratio of 3:1, anion to cation (by volume), be employed. In this investigation use of a ratio of 1.5:1, anion to cation (by exchange capacity), results in a ratio of approximately 2.5:1, anion to cation (by volume).

The columns were prepared using 14 grams (moist weight) of mixed resin. The compacted volume of this resin was equal to 1.07 inches^3 (0.000619 feet^3).

Column Operation

Conditions of operation of upflow columns require a balancing of factors affecting column performance. Such factors as flow rate, pH adjustment, and column dimensions must be considered and conditions chosen which produce the best over-all results.

The manufacturers' recommendations (6, p. 61) are for flow rates of from one to ten gal/min/ft^2 for normal size columns. Other investigators (23, p. 1090) and (24)

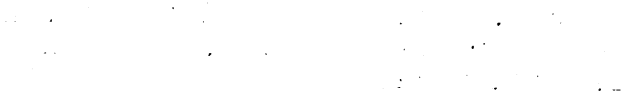
have shown that for optimum operation with mixed bed resins a flow rate on the order of 2 gal/min/ft^3 is desirable. On the basis of the manufacturers' recommendations the flow rate chosen for the column should be from 188 to 18.8 ml/min, while on the basis of Swope's investigations the selected flow rate should be 4.7 ml/min. A flow rate of approximately 10 ml/min was chosen for upflow column operation. The flow rate selected provides for the concentration of a 10 liter sample of water in under seventeen hours, as compared with a time requirement for the present evaporation system in excess of thirty hours for concentration of the same volume when multiple samples are being prepared.

The column dimensions chosen were dictated by the available counting equipment. The existing gamma spectrographic analysis equipment in use in the laboratory consists of a Nuclear Chicago, Model DS-303 Scintillation Well Detector coupled to a Nuclear Data 512 Channel Gamma Analyzer. The sodium iodide (thallium activated) crystal is three inches in diameter and has a well 1-1/8 inches in diameter by 1-3/4 inches deep.

The well dimensions severely limit the size of samples which may be counted accurately. As a result the dimensions of the column chosen are far from ideal. The length-to-diameter ratio suggested by Samuelson for column operation (18, p. 168) is between 10 and 20. The length-to-diameter ratio utilized in this investigation

Figure 3. Gamma Analysis Equipment Consisting of Nuclear Chicago, Model DS-303 Scintillation Well Detector and Nuclear Data 512 Channel Gamma Analyzer.

Figure 4. Detail of Scintillation Detector with Upflow Column in Crystal well.



is only approximately 1.6. This limitation on column depth undoubtedly has a very large effect upon column breakthrough capacity. Samuelson (18, p. 109, Fig. 5.11) shows graphically the effect of depth variation for constant resin volume.

Another important factor which must be balanced as to beneficial and detrimental effects in column operation is pH adjustment. The addition of reagents to the sample under investigation increases the total ionic concentration of the solution. If the ions added for pH adjustment have a high affinity for the resin in the column, the capacity of the column for the removal of radioactive ions will be decreased. A second consideration is that the exchange capacity of cation exchange resin decreases as the hydrogen ion content of the influent solution increases--Samuelson (18, p. 110, Fig. 5.12). Swope (23, p. 1088, Table 2) has demonstrated the effect of reduction of bed capacity at low pH but also points out that at a pH of 7.0 "The decontamination factors, . . ., are not as great as at pH 2.5, undoubtedly because most of the radioactive nuclides would be in ionic form at the lower pH, whereas some, such as zirconium, would be colloidal at pH 7.0." (23, p. 1087).

Since the purpose of sample concentration is to quantitatively determine the radionuclides present, conditions must be chosen to give the most complete removal from the sample. By pH adjustment it is therefore

necessary to sacrifice sample volume to obtain more nearly quantitative concentration.

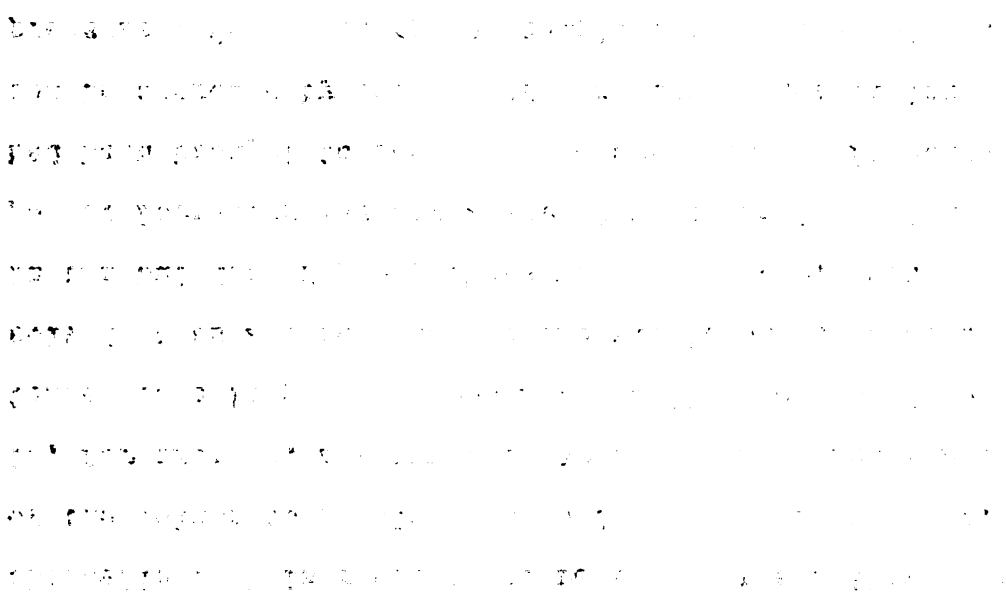
In her work on the removal of mixed fission products by means of concentration on mixed bed resins, Swope (23) has used nitric acid for pH adjustment. The nitrate anion added has a selectivity coefficient for Dowex 1 resin of 3.8, as compared with a selectivity coefficient of 0.09 for hydroxide ion (see Table 3).

Krieger, Gilchrist, and Gold (12) have reported the use of hydrofluoric acid for the concentration of Zr^{95} - Nb^{95} in the form of a fluoride complex on anion exchange resin. The addition of hydrofluoric acid for this purpose may also be utilized for the desired pH adjustment. Making rainwater solutions 0.007 M in hydrofluoric acid, as suggested by Krieger, Gilchrist, and Gold, results in a pH of approximately 3.0.

Utilization of hydrofluoric acid for pH adjustment also produces another beneficial effect. The selectivity coefficient for fluoride ion on Dowex 1 (as seen from Table 3) is 0.09, which is identical to that of hydroxide ion. In dilute solution the exhaustion of the anion resin by replacement of OH^- with F^- will be small compared with the replacement of OH^- by NO_3^- if nitric acid is used for pH adjustment.

Successful operation of the upflow column requires that no air be allowed to enter the column as it will become trapped and work up through the resin, resulting in

channeling. This requirement restricts the utilization of the column to samples low in dissolved gas content. If, for example, a rainwater sample which is below room temperature is passed through the upflow column, dissolved gases are released as the sample warms resulting in the buildup of gas pockets within the bed. Gas pocket formation was not observed with samples which had been brought to room temperature. This difficulty can be overcome by removal of dissolved gases at low pressure before passing the sample through the column.



LABORATORY INVESTIGATIONS

Effects of Solids

Krieger, Gilchrist, and Gold (12), in their investigation of the concentration of radionuclides from rainwater, separated the suspended solids from the sample by filtration prior to passing the water through the anion and cation columns. Boni (1), on the other hand, has concentrated particulate matter from his samples by means of a layer of glass wool over the resin. This second approach is more desirable for gross sample analysis since only one counting period is required.

The quantity of suspended solids present varies greatly with sample type and among individual samples of a given type. For example, a stream may show wide variations in suspended solids load from day to day as a result of recent surface runoff or stream pollution. Rainwater may be nearly free of particulate matter or it may contain a relatively large amount of solids, depending upon atmospheric conditions at the time of the rain. In periods following nuclear bomb detonations particulate fallout material may be present in the rainwater. Small radioactive particles may be adsorbed by larger nonradioactive solids, or they may be assimilated by bacteria into the structure of biological growths which in turn may be adsorbed on the surface of solids. Each of these cases demonstrates the need for inclusion of suspended

solids in a gross sample analysis.

Table 4 demonstrates the effect of filtration on a sample of aged river water containing a mixture of fission product isotopes. The water tested was Red Cedar River water which was allowed ample time for biological uptake and surface adsorption of the isotopes.

The filters used were Millipore Filters of the sizes indicated. The filter effluent was evaporated on plastic sheets which were beta-gamma counted using an end window Geiger-Muller counter. One liter of sample was passed through each filter.

Table 4. Effect of Filtration on Aged Riverwater.

Filter Size	Effluent Count Rate	Percent Reduction
0.01 μ	4.6 CPM	99.92
0.1 μ	5.9 CPM	99.90
0.45 μ	11.6 CPM	99.80
0.8 μ	14.7 CPM	99.75
1.2 μ	13.3 CPM	99.78
5.0 μ	11.2 CPM	99.82
Blank	5,966 CPM	---

$$\text{Percent Reduction} = \frac{\text{Count Rate Blank} - \text{Count Rate Sample}}{\text{Count Rate Blank}} \times 100$$

The removals obtained were essentially independent of filter size over the size range tested.

A second run was made as before using as a filter a plug of fine Pyrex glass wool. Table 5 gives the

results obtained in this test.

Table 5. Filtration of Aged Riverwater Through Glass Wool.

Filter	Effluent Count Rate	Percent Reduction
Glass Wool	128.8 CPM	98.15
Blank	6,973 CPM	---

The filtration tests indicated that filtration of certain environmental samples through a bed of glass wool resulted in substantial removals of solid particles and their associated activity.

Early Upflow Columns

Early investigations of upflow columns met with varying degrees of success in the concentration of radioactivity from rainwater. These first upflow columns were similar in design to later columns with the exception that the column itself was glass instead of polyethylene.

The rainwater used in these first tests was not fresh, but had been stored in an outside collection pan and later in the laboratory. The water used was not sufficiently uniform in composition, especially with regard to suspended solids content, to provide good comparative results among the columns tested. The early columns suffered from a lack of standardization and uniformity which was later attained when larger numbers of columns

were prepared at the same time. Despite all of these limitations the first four columns utilized for rainwater sample concentration indicated certain general trends.

The percentage removal of activity, when comparing the count rate per liter detected on the column with the count rate per liter for an identical ten-liter evaporated blank sample, ranged from a low of 38.5% to a high of 101.5%. It appeared from initial tests that under the proper conditions results comparable to those observed for evaporated samples might be obtained.

It was apparent that the removal of activity by the column was not complete. The column effluent activity, as detected by the process of evaporation and counting identical to that used for preparation of the blank sample, ranged from 20.9% to 89.9% of the activity detected for the blank. As a result, the total activity detected by the combination of column operation and effluent evaporation ranged from 69.5% to 186.3% of the activity detected from the blank.

Another characteristic of column operation observed in early investigations was that column removal efficiency decreased significantly as the sample volume increased. When an additional five liters of sample rainwater were passed through columns which had received ten liters of sample previously, the unit activity (CPM/l) detected on the columns decreased by approximately 19%. The unit activity of the final five liters of

effluent showed an increase of from 28.7% to 107.3% over the unit activity detected in the initial ten liters of effluent. The cause of this increase in effluent activity was the fact that the columns were being operated beyond their breakthrough capacity and the activity originally retained on the columns was being eluted into the effluent by nonradioactive ions with a higher affinity for the resin.

These early investigations indicated that column uniformity should be studied and steps taken to ensure uniformity of samples used for purposes of comparison. Also, in order to better evaluate column performance with respect to the evaporation method, a study should be made with regard to geometry effects and the relative efficiencies of the two methods. Finally, the advisability of proposing further investigations should be determined by conducting tests on actual rainwater samples and evaluating column performance with respect to the evaporation method. Table 6 shows the results obtained from some of the early columns tested.

Column Uniformity

The uniformity of column preparation has been investigated by conducting breakthrough studies on six sets of columns. Each column set consisted of four identical upflow columns containing 14 g. of resin

Table 6. Results of Early Column Investigations.

Condition Investigated	Column			
	A	B	C*	D
Ionic form of cation resin.	Na^+	Na^+	H^+	H^+
Ionic form of anion resin.	OH^-	OH^-	CH^-	OH^-
Feed rainwater pH.	Neutral	Neutral	Neutral	2.5
Activity, 10 l. rainwater evaporated (CPM/l).	32.42	32.42	32.42	63.15
Activity detected on column (liter 1-10) (CPM/l).	18.29	32.93	26.6	24.35
Activity detected in effluent (liter 1-10) (CPM/l).	6.66	27.53	29.18	19.6
% of blank activity detected on column.	56.4	101.5	82.0	38.5
% of blank activity detected in effluent.	20.5	84.8	89.9	31.0
Total % of blank activity detected.	76.9	186.3	171.9	69.5
Activity detected on column after 15 l. (CPM/l).	---	26.82	38.2	19.64
Activity in final 5 l. effluent (CPM/l).	---	57.10	*	25.22
% decrease in unit activity on column after passing 15 l. compared with unit activity after 10 liters.	---	18.6	---	19.4
% increase in unit activity of final 5 l. of effluent as compared with unit activity in first 10 liters.	---	107.3	---	28.7

* The results of Column C are not reliable due to ineffective transfer of solids to the column from the first ten liters of rainwater.

mixed in the ratio of 1.5:1, anion to cation by exchange capacity. The resins were in the hydroxide and hydrogen forms, respectively. The effect of pH on column capacity was studied at the same time by applying feed solutions of different pH and conductivity to each of the sets of columns.

Measurement of effluent conductivity was chosen as the criteria of column performance because it offered the advantage of being a simple test which required no time-consuming procedures, as would evaporation and activity counting. Conductivity measurement is also a test with a relatively high degree of sensitivity, especially over the range of particular interest to this investigation (the conductivity range of rainwater). Conductivity measurements, in dilute solutions, are directly related to total ionic content of the solution tested.

Test solutions were prepared using tap water diluted with distilled water to bring the conductivity of the feed solution to the desired conductivity level; pH adjustments were made with nitric acid. Conductivity and pH of feed solution and effluent were measured at one liter increments. Conductivity measurements were made using an Industrial Instruments Company "Solu Bridge", and pH measurements were made using a Beckman "Zeromatic" pH meter.

The first four sets of columns tested demonstrate

the degree of column uniformity which can be attained through careful column preparation and operation. The first set of columns received a feed solution having a natural pH of approximately 3.7. Sets two and three received feed solutions which were nearly neutral, and set four received a feed solution of approximately 3.4. Sets five and six were utilized to show the effect of disturbances within the column on uniformity.

Column 28 of set five was utilized after the central feed tube had been moved causing disturbance of the resin. Columns 32, 33, and 35 of set six received feed solution after air bubbles had been allowed to form at the bottom of the resin. In both instances channeling resulted causing early breakthrough of the columns with a resulting non-uniformity of results. Tables 7 through 12 show the results of column uniformity determinations.

It should be noted that the unit of conductivity measured for column numbers 10, 11, 12, and 13 is in micromhos/cm. The unit of conductivity measured for all other columns is in ppm NaOH. The data of column numbers 10 through 13 was obtained using a Solu Bridge, which upon subsequent calibration was found to give readings which were not a linear function of the ionic content of the solution tested. The data of this set of four columns is therefore not comparable with that of the remaining five sets of columns. The observations obtained are useful, however, for the purpose of demonstrating

Table 7. Column Breakthrough and Uniformity Determination at Low pH, Using Identical 14 g Columns. Columns #10, 11, 12, and 13.

Liter No.	Feed Solution		Effluent Solution								Effluent Average	
			Conductivity ~MHOS/CM				pH					
			Column Number				Column Number					
	Cond.	pH	10	11	12	13	10	11	12	13	Cond.	pH
1	68	3.8	0.6	0.7	0.8	0.7	6.4	6.3	6.4	6.4	0.7	6.4
2	68	3.8	0.4	0.4	0.5	0.5	6.2	6.2	6.2	6.1	0.5	6.2
3	68	3.7	0.4	0.4	0.5	0.5	6.0	6.0	5.9	5.8	0.5	5.9
4	68	3.8	0.5	0.7	0.7	0.7	6.1	5.9	5.9	5.9	0.7	6.0
5	68	3.8	0.8	1.0	0.8	1.0	5.8	5.6	5.7	5.7	0.9	5.7
6	68	3.8	1.1	1.5	1.4	1.6	5.6	5.5	5.5	5.4	1.4	5.5
7	68	3.8	1.6	2.1	2.1	2.1	5.5	5.3	5.3	5.3	2.0	5.4
8	68	3.7	4.0	3.0	4.2	3.5	5.0	5.1	5.0	5.1	4.0	5.0
9	70	3.7	4.9	4.9	4.7	4.7	4.9	4.9	4.9	4.9	4.8	4.9
10	70	3.7	4.5	4.5	4.6	4.6	4.9	5.0	5.0	4.9	4.3	5.0
11	69	3.7	3.4	3.2	3.3	3.4	5.1	5.1	5.1	5.1	3.3	5.1
12	69	3.7	4.6	4.5	4.4	4.6	4.9	4.9	4.9	4.9	4.5	4.9
13	69	3.7	4.7	4.2	4.4	4.5	4.9	4.9	5.0	4.9	4.6	4.9
14	69	3.7	5.0	4.4	4.4	5.0	4.9	4.9	4.9	4.9	4.7	4.9
15	69	3.7	4.3	3.2	3.2	4.5	4.9	5.0	5.0	4.9	3.8	5.0
16	69	3.7	5.3	4.6	5.9	7.0	4.8	4.8	4.7	4.7	5.7	4.8
17	70	3.7	6.7	7.6	11.3	12.7	4.5	4.5	4.4	4.4	9.6	4.4
18	70	3.7	16.8	18.8	24	25.8	4.3	4.2	4.2	4.1	21.4	4.2
19	70	3.7	46	45	39	40	3.9	3.9	3.9	3.9	42.5	3.9
20	71	3.6	69	67	62	49	3.6	3.7	3.7	3.8	61.8	3.7
21	71	3.6	70+	70+	70+	60	3.6	3.6	3.6	3.7	----	3.6
22	71	3.6	----	----	----	70	----	----	----	3.6	----	---

Average Feed Conductivity = 69 ~MHOS/CM

Average Feed pH = 3.7

Table 8. Column Breakthrough and Uniformity Determination at Neutral pH, Using Identical 14 g Columns. Columns #14, 15, 16, and 17.

Liter No.	Feed Solution		Effluent Solution								Effluent Average	
			Conductivity ppm NaOH				pH					
			Column Number				Column Number					
	Cond.	pH	14	15	16	17	14	15	16	17	Cond.	pH
1	19	7.2	0.3	0.2	0.2	0.2	6.0	6.4	6.2	6.5	0.2	6.3
2	19	7.3	0.5	0.2	0.4	0.2	5.6	6.3	5.7	5.8	0.3	5.9
3	19	7.3	1.3	1.1	1.1	1.0	5.2	5.0	5.0	5.0	1.1	5.0
4	19	7.4	1.8	1.5	2.0	1.5	5.8	5.6	5.5	5.4	1.7	5.6
5	19	7.6	6.9	9.8	7.4	7.4	4.1	3.9	4.0	4.0	7.9	4.0
6	19	7.1	27	30	32	38	3.7	3.6	3.4	3.4	32	3.5

Average Feed Conductivity = 19 ppm NaOH

Average Feed pH = 7.3

Table 9. Column Breakthrough and Uniformity Determination at Neutral pH, Using Identical 14 g Columns. Columns #18, 19, 20, and 21.

Liter No.	Feed Solution		Effluent Solution								Effluent Average	
			Conductivity ppm NaOH				pH					
			Column Number				Column Number					
	Cond.	pH	18	19	20	21	18	19	20	21	Cond.	pH
1	10.5	6.9	0.2	0.2	0.3	0.2	6.4	6.5	6.1	6.2	0.2	6.3
2	10.0	6.9	0.2	0.2	0.5	0.4	6.2	6.3	6.0	5.9	0.3	6.1
3	10.5	6.9	0.2	0.2	0.4	0.5	6.1	6.1	5.6	5.5	0.3	5.8
4	10.5	6.9	0.4	0.4	0.6	0.4	5.7	5.8	5.5	5.8	0.5	5.7
5	10.0	6.9	0.7	0.6	1.3	0.8	5.4	5.3	5.7	5.2	0.8	5.4
6	10.5	6.9	1.3	1.4	2.4	1.3	5.1	4.9	5.6	5.0	1.6	5.2
7	10.2	6.9	1.4	1.2	2.6	1.9	4.9	4.9	5.4	4.8	1.8	4.8
8	10.0	6.9	1.7	1.8	2.5	2.9	4.8	4.8	5.3	4.8	2.2	4.9
9	10.0	6.9	2.0	2.3	2.9	3.4	4.7	4.7	5.2	4.8	2.6	4.8
10	10.5	6.9	3.9	7.0	2.8	3.6	4.3	4.0	5.0	4.7	4.3	4.5
11	10.0	6.9	16	12.0	4.0	4.7	3.6	3.7	4.7	4.5	9.2	4.1
12	10.0	6.9	23	19	8.0	10.5	3.5	3.6	4.0	3.8	15	3.7

Average Feed Conductivity = 10.2 ppm NaOH

Average Feed pH = 6.9

Table 10. Column Breakthrough and Uniformity Determination at Low pH, Using Identical 14 g Columns. Columns #22, 23, 24, and 25.

Liter No.	Feed Solution		Effluent Solution								Effluent Average	
			Conductivity ppm NaOH				pH					
			Column Number				Column Number					
	Cond.	pH	22	23	24	25	22	23	24	25	Cond.	pH
1	30	3.4	0.2	0.4	0.1	0.1	6.3	5.7	6.4	6.6	0.2	6.2
2	28	3.4	0.2	0.8	0.5	0.1	6.0	5.2	5.3	6.0	0.4	5.6
3	27	3.4	0.9	3.1	2.3	0.4	5.1	4.4	4.5	5.4	1.7	4.8
4	28	3.4	3.5	5.0	5.7	1.5	4.3	4.2	4.1	4.8	3.9	4.4
5	26	3.4	7.8	7.5	10.0	2.8	4.0	3.9	3.8	4.4	7.0	4.0
6	28	3.4	14	14	16	9.0	3.6	3.6	3.6	3.8	13	3.6
7	27	3.3	23	21	22	27	3.4	3.5	3.4	3.2	23	3.4
8	30	3.4	30	32	31	38	3.2	3.2	3.2	3.1	33	3.2

Average Feed Conductivity = 28 ppm NaOH

Average Feed pH = 3.4

Table 11. Column Breakthrough and Uniformity Determination Showing Effect of Channeling Due to Bed Disturbance. Columns #26, 27, 28, and 29.

Liter No.	Feed Solution		Effluent Solution								Effluent Average	
			Conductivity ppm NaOH				pH					
			Column Number				Column Number				*	*
	Cond.	pH	26	27	28	29	26	27	28	29	Cond.	pH
1	17	3.5	0.2	0.2	1.4	0.2	6.1	6.2	4.9	6.1	0.2	6.1
2	16	3.6	0.2	0.2	3.5	0.2	6.1	6.2	4.3	6.0	0.2	6.1
3	16	3.6	0.3	0.2	5.0	0.2	5.8	5.9	4.2	5.9	0.2	5.9
4	16	3.6	1.4	0.4	6.8	0.3	4.9	5.4	4.0	5.7	0.7	5.3
5	16	3.5	3.0	1.4	7.1	0.4	4.4	4.9	3.9	5.7	1.6	5.0
6	16	3.6	4.7	2.0	7.3	1.0	4.1	4.7	4.0	5.1	2.6	4.5
7	15	3.6	7.0	2.9	7.5	1.9	4.0	4.4	4.0	4.7	3.9	4.4
8	16	3.6	9.7	3.7	8.2	2.6	3.8	4.3	3.9	4.5	5.3	4.2
9	16	3.6	10.2	4.0	7.6	3.5	3.7	4.2	3.9	4.3	5.9	4.1
10	16	3.5	10.5	5.1	7.7	6.1	3.8	4.2	4.0	4.0	7.2	4.0
11	16	3.6	10.0	8.3	9.0	12.0	3.8	3.9	3.9	3.7	10.1	3.8
12	18	3.6	11.5	17	11.0	21	3.6	3.5	3.7	3.3	16	3.4
13	19	3.5	14	22	12.0	22	3.6	3.4	3.8	3.4	19	3.4
14	18	3.6	14	20	12.5	23	3.6	3.4	3.8	3.4	19	3.4

Average Feed Conductivity = 16.5 ppm NaOH

Average Feed pH = 3.6

* Average values for Columns #26, 27, and 29 only. High initial results for Column #28 were the result of channeling of flow caused by movement of central feed tube during column preparation.

Table 12. Column Breakthrough and Uniformity Determination Showing Effect of Channeling Due to Air Pocket Formation. Columns #32, 33, 34, and 35.

Liter No.	Feed Solution		Effluent Solution								Effluent Average	
			Conductivity ppm NaOH				pH					
			Column Number				Column Number					
	Cond.	pH	32	33	34	35	32	33	34	35	Cond.	pH
1	12.5	3.7	0.2	0.2	0.2	0.2	6.5	6.3	6.2	6.2	0.2	6.3
2	11.0	3.8	0.2	0.2	0.2	0.2	6.3	6.2	6.1	6.1	0.2	6.2
3	11.5	3.8	0.2	0.2	0.2	0.2	6.2	6.1	6.1	5.9	0.2	6.1
4	11.0	3.8	0.2	0.2	0.2	0.4	6.2	6.0	6.1	5.4	0.2	5.9
5	12.0	3.8	0.2	0.4	0.2	0.6	6.0	5.4	5.9	5.2	0.4	5.6
6	10.5	3.8	0.2	0.9	0.2	0.8	6.1	5.0	6.0	5.0	0.5	5.4
7	12.0	3.8	0.2	1.4	0.2	1.4	5.9	4.8	5.9	4.8	0.8	5.4
8	11.5	3.8	0.4	1.9	0.2	3.2	5.5	4.6	5.8	4.4	1.4	5.1
9	11.5	3.8	0.9	2.8	0.4	4.8	5.0	4.5	5.6	4.2	1.7	4.8
10	12.0	3.7	2.4	3.2	0.4	5.0	4.5	4.3	5.4	4.1	2.8	4.6
11	11.5	3.7	3.3	3.9	0.6	6.0	4.4	4.3	5.2	4.1	3.4	4.5
12	11.0	3.8	4.8	4.3	0.9	6.7	4.3	4.3	5.0	4.1	4.2	4.4
13	12.5	3.8	5.6	5.0	1.1	7.0	4.0	4.2	4.8	4.0	4.7	4.2
14	12.0	3.8	6.5	5.5	1.5	7.4	4.1	4.2	4.8	4.0	5.2	4.3
15	12.5	3.7	7.1	5.6	2.3	8.6	4.0	4.1	4.6	4.0	5.9	4.2
16	12.5	3.8	7.8	6.0	6.1	9.1	4.0	4.1	4.1	4.0	7.2	4.0
17	12.0	3.8	8.3	6.5	10.3	10.0	4.0	4.1	3.9	3.9	8.8	3.9
18	13.0	3.8	9.0	7.5	12.0	10.0	4.0	3.9	3.7	3.9	9.6	3.9
19	12.5	3.7	8.5	9.0	14	10.0	4.0	3.9	3.7	3.9	10.4	3.9
20	12.0	3.8	9.2	10.0	14	10.0	3.9	3.9	3.6	3.9	10.8	3.8

Average Feed Conductivity = 11.8 ppm NaOH

Average Feed pH = 3.8

column uniformity within the set.

Conductivity readings for column numbers 14 through 35 were obtained using a different Solu Bridge from which conductivity readings were obtained as ppm NaOH (or mg NaOH/liter). Readings obtained from this meter were a linear function of ionic concentration of the solution tested.

The data of Tables 7 through 12 are plotted in Figures 5 through 10. The ordinate of each plot ($V \times C_i$) represents the product of the volume of feed solution passed through the column times the conductivity of the feed solution. When conductivity units expressed as ppm NaOH are used, the ordinate values represent mg NaOH applied to the column.

The abscissa of each plot represents the removal efficiency of the column, defined as $(1 - C_e/C_i) \times 100$.

C_e = Column effluent conductivity.

C_i = Column influent conductivity.

From the data obtained it is evident that columns can be prepared with a satisfactory degree of uniformity. Adequate care in preparation is required, however, to avoid disturbances within the bed which may cause channeling of fluid through the resin. Provided that proper care is taken during column preparation and operation, it is the author's conclusion that sufficiently uniform results can be obtained from upflow column operation to be satisfactory for the purpose of radionuclide concentration.

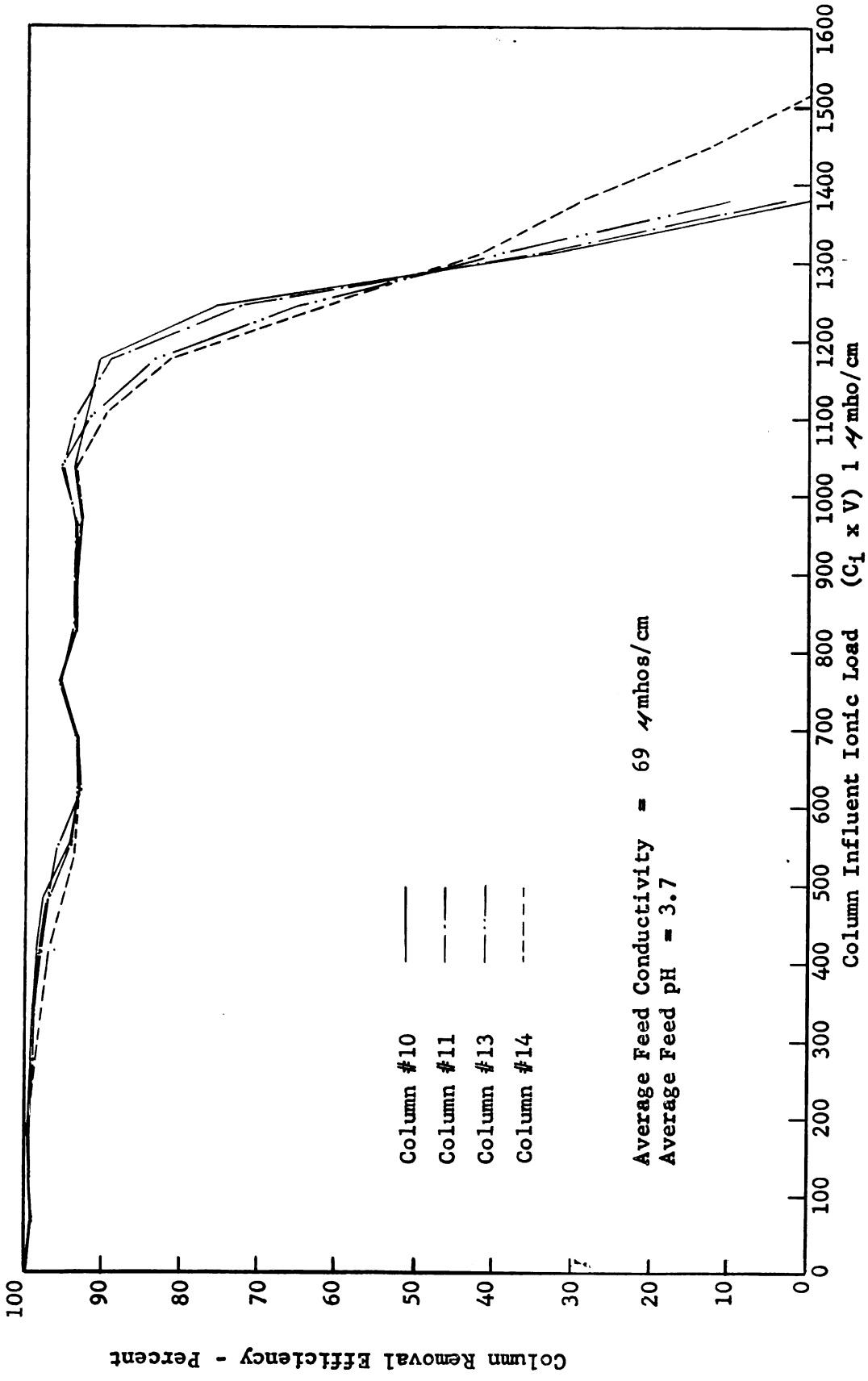


Figure 5. Uniformity Determination at Low pH, Using Identical 14 g Columns.

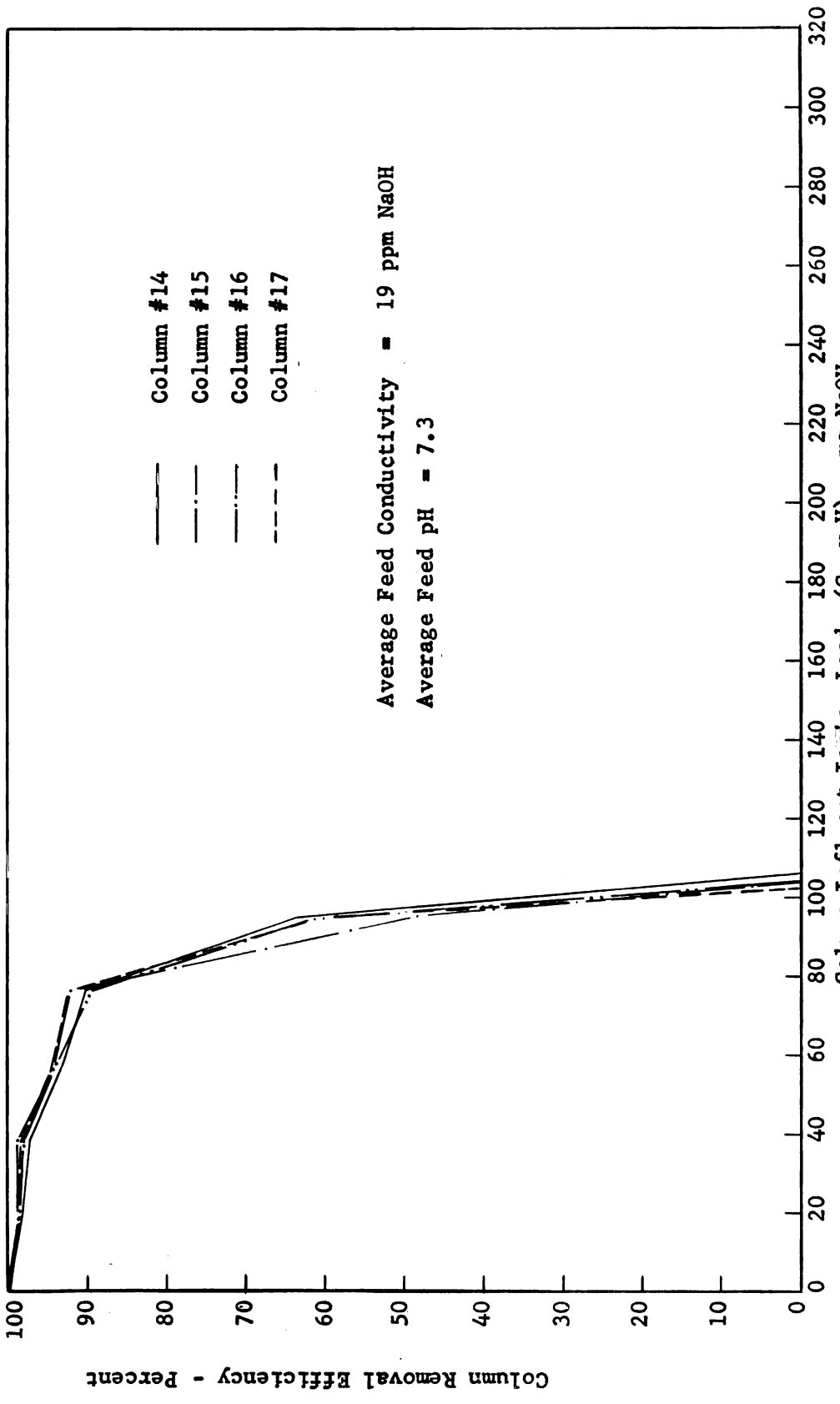


Figure 6. Uniformity Determination at Neutral pH, Using Identical 14 g Columns.

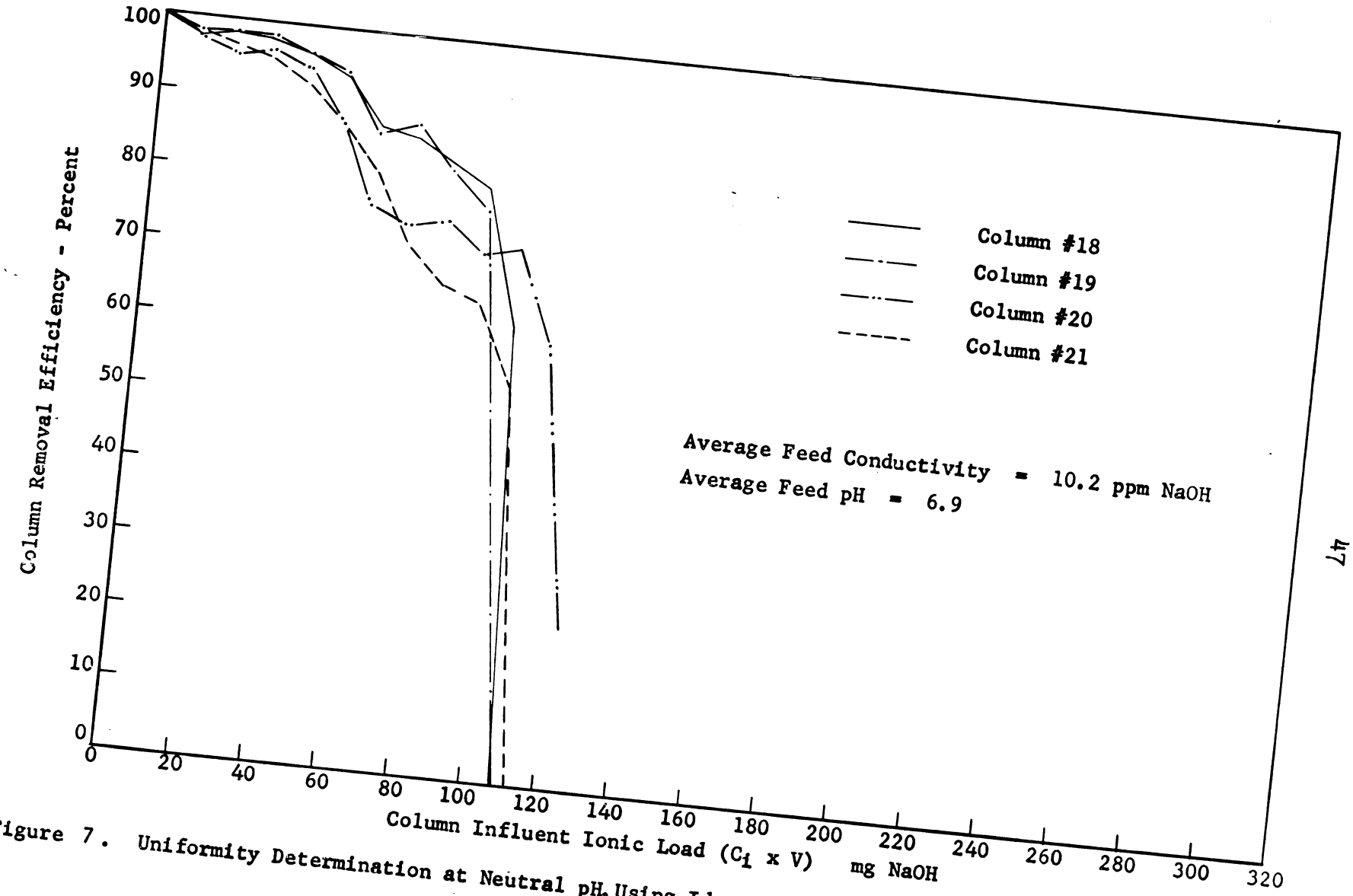


Figure 7. Uniformity Determination at Neutral pH, Using Identical 14 g Columns.

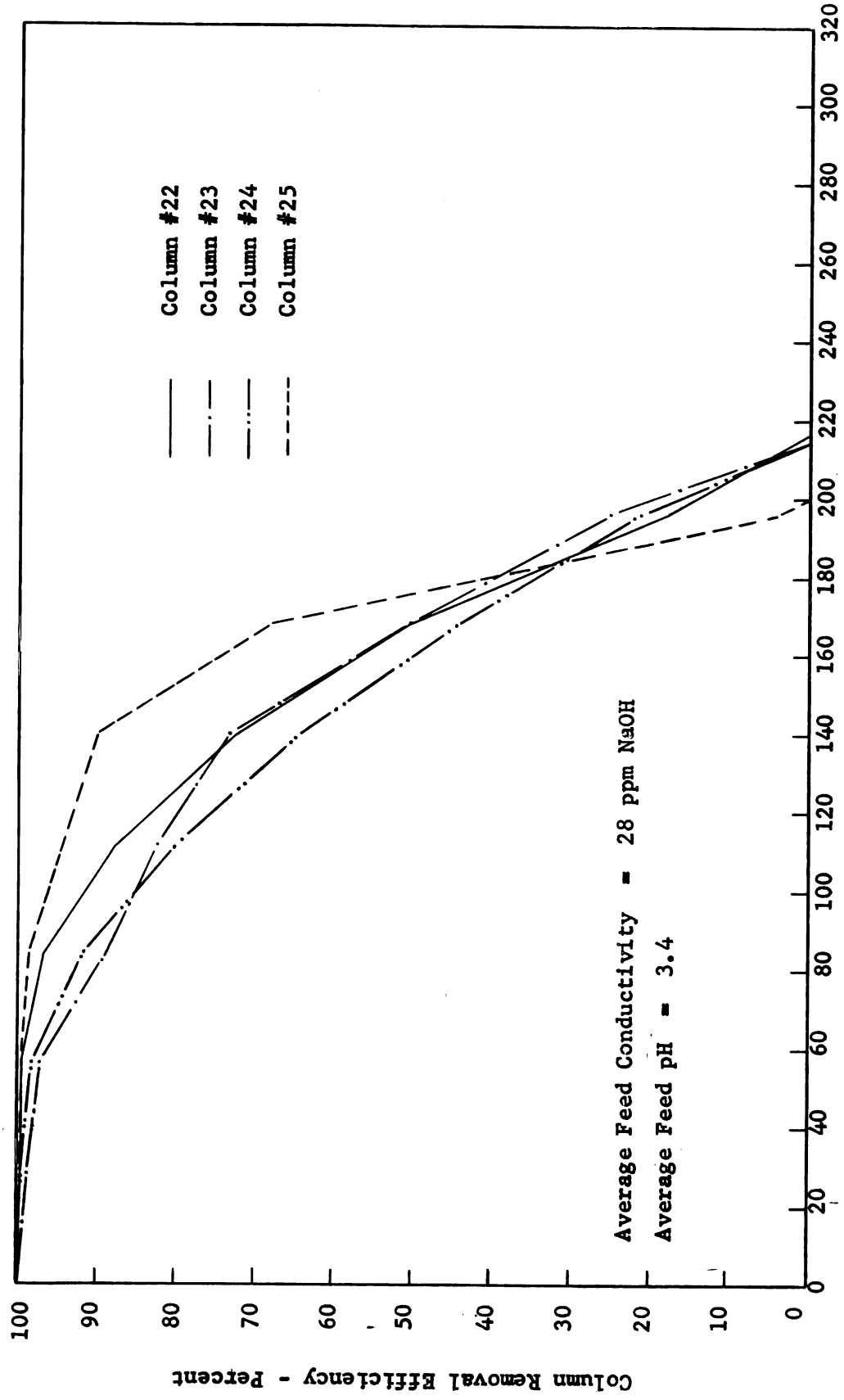


Figure 8. Uniformity Determination at Low pH, Using Identical 14 g Columns.

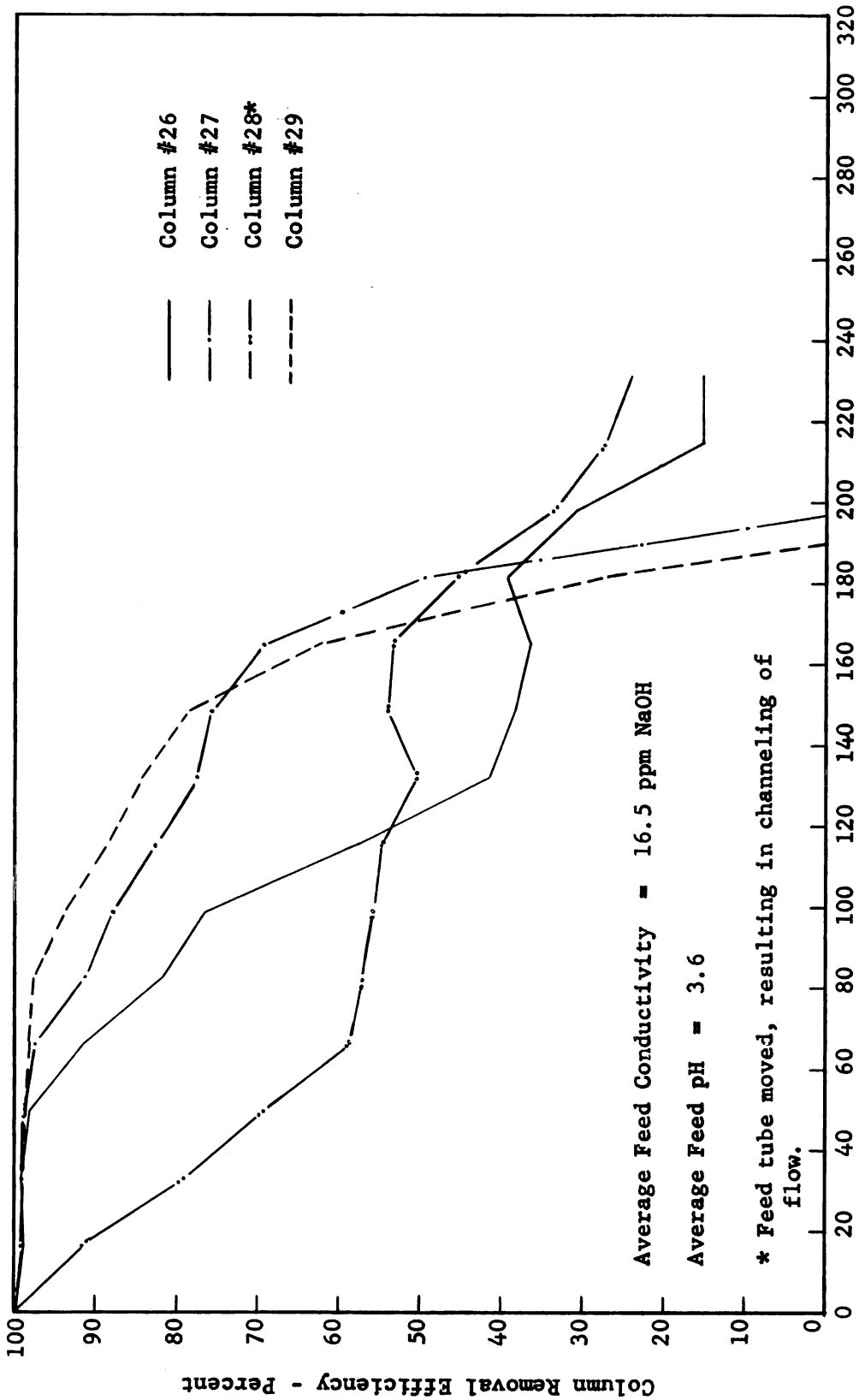


Figure 9. Uniformity Determination Showing Effect of Channeling Due to Bed Disturbance.

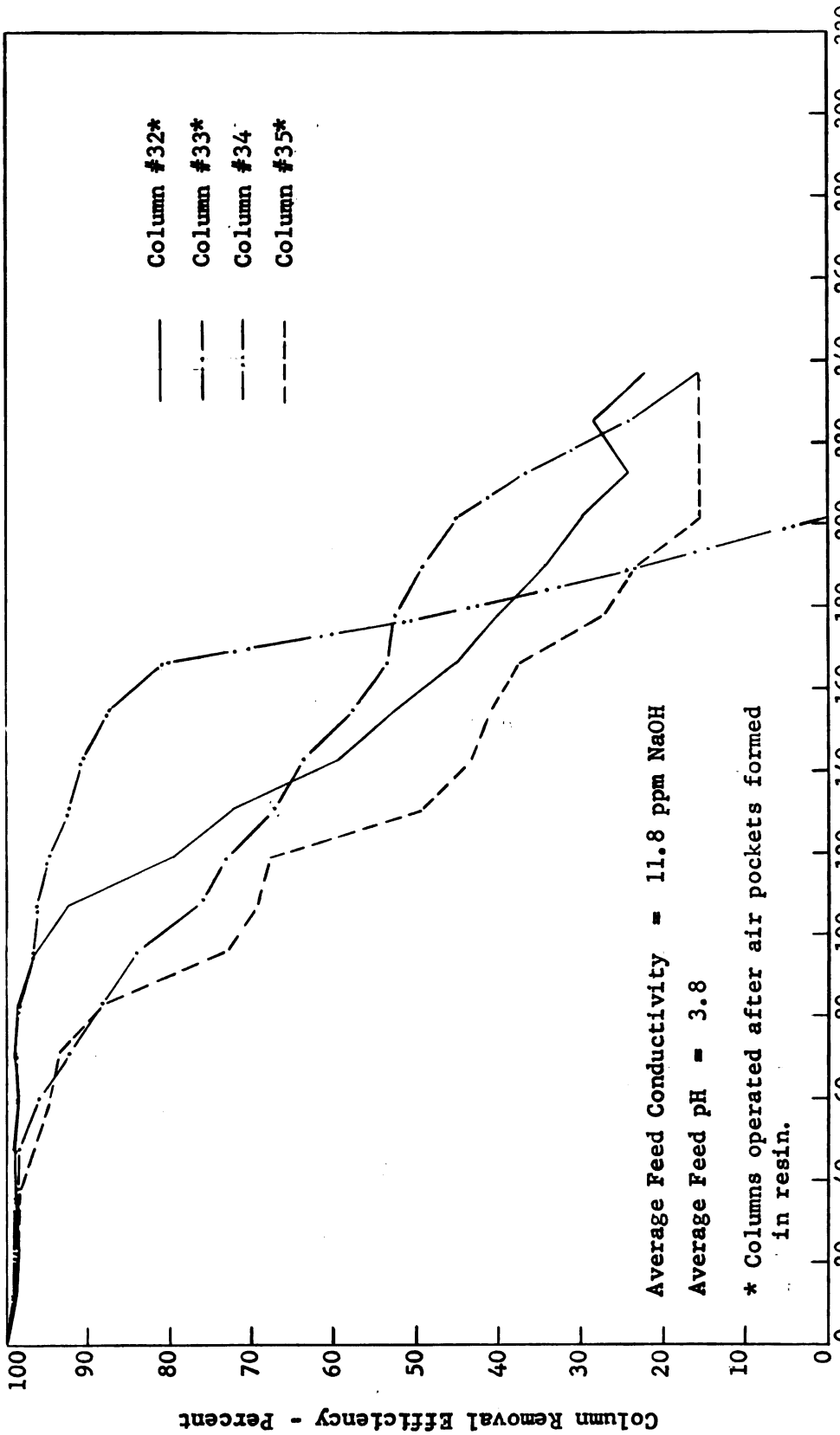


Figure 10. Uniformity Determination Showing Effect of Channeling Due to Air Pocket Formation.

Effect of pH

Figure 11 is a plot of the average values obtained from the column breakthrough studies of Tables 8 through 12. The plot represents removal efficiency vs. ionic load, $[(1 - C_e/C_i) \times 100$ vs. $V \times C_i]$ and demonstrates the effect of pH on removal efficiency. At approximately neutral pH, the total column capacity is substantially reduced as compared with removal capacity at lower pH.

It should be noted, however, that a substantial portion of the solution ionic concentration applied to the columns operated at low pH levels comes from the acid used to reduce the pH. Increased removal of radionuclides at low pH is the result of conversion of non-ionic colloids to an ionic form which is held on the resin--Swope (23, p. 1087).

Effect of Counting Geometry

The method of sample preparation presently practiced in this laboratory for gamma analysis of liquid environmental samples consists of concentration by evaporation. The samples are placed on a sheet of plastic film on a "drying table" and ultraviolet lamps are used to evaporate the sample to dryness (Figure 12). The plastic film is then trimmed, folded tightly, and placed in a plastic bottle which fits into the well of the counting crystal (Figure 13). Sample volumes up to ten liters can be placed in each section of the drying table. When

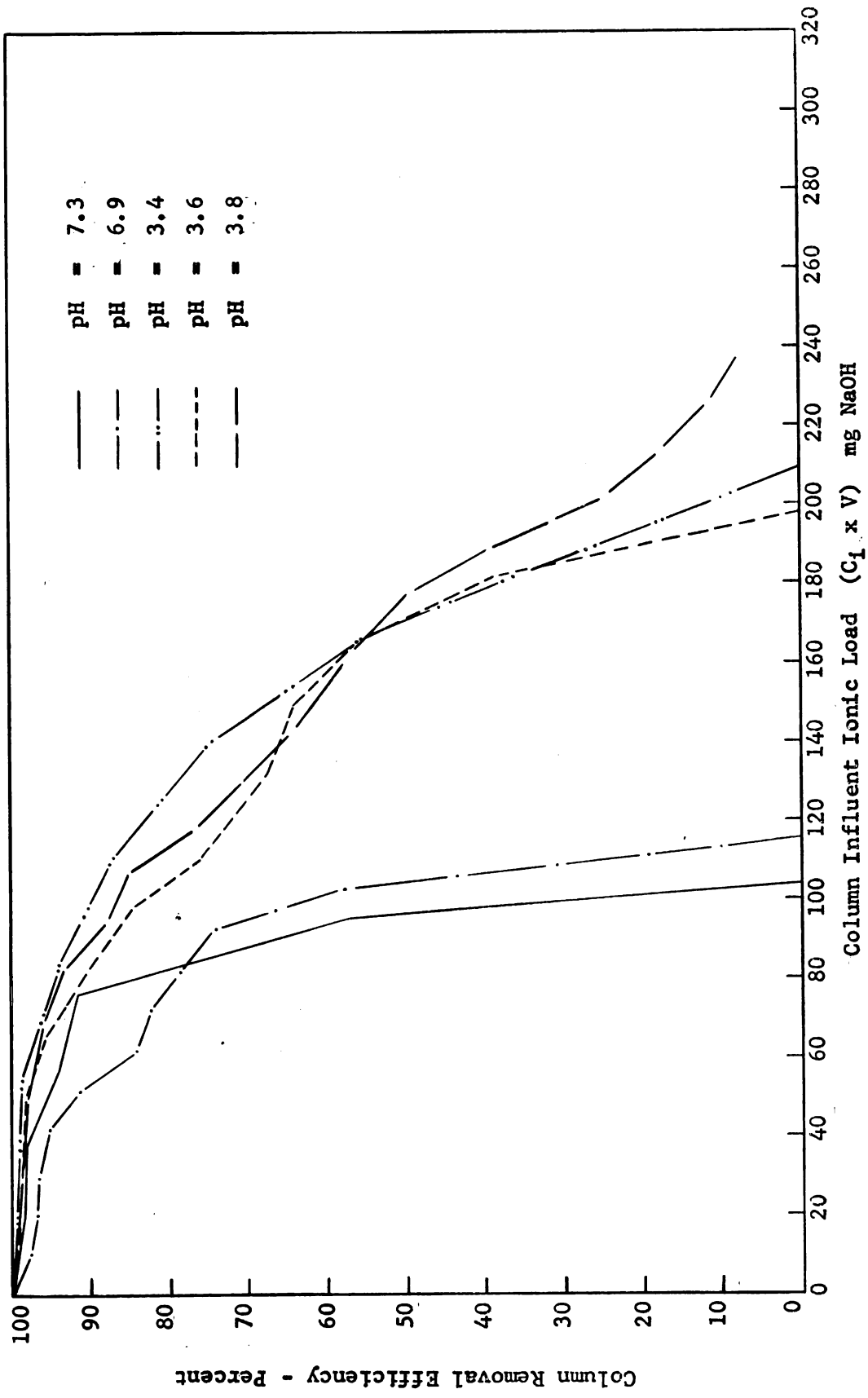


Figure 11. Effect of pH on Conductivity Breakthrough Capacity.

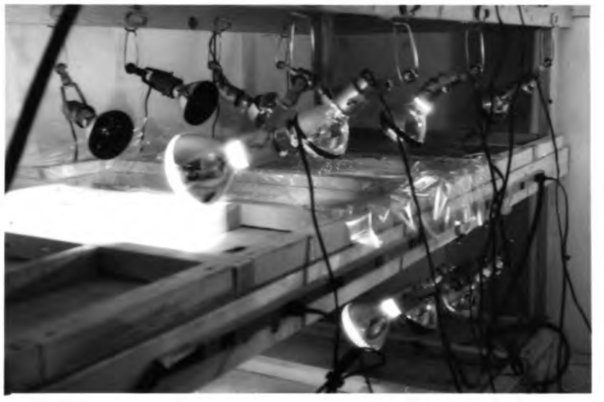


Figure 12. Evaporating Table for Drying Liquid Samples on Plastic Film.

Figure 13. Upflow Column (right) with folded plastic sheet containing 10 liter evaporated sample to be placed in 17 ml. plastic bottle for gamma analysis.

a plastic sheet capable of accommodating a ten liter sample is placed in the detector crystal the entire volume of the well is filled. This results in a geometry effect due to the poor counting conditions near the top of the crystal.

Figure 14 relates detected activity to variation of depth for a source of constant activity. Ten ml. samples of an isotope solution were diluted with distilled water to the depths indicated and the resulting count rates observed. Extrapolation of the curve to zero depth results in a theoretical count rate of approximately 640 counts per minute. This is approximately 136 percent of the count rate observed at full well depth. Self-absorption within the sample has not been considered.

Sample preparation which distributes the activity of the sample throughout the full volume of the crystal well results in this same type of geometry effect. In the design of the upflow ion exchange column this geometry effect has been minimized by concentrating high activity solid particles at the bottom of the column.

Evaluation of Sample Preparation Methods

The evaluation of upflow column performance with respect to the practice of concentration by evaporation on plastic sheets has been carried out with both natural and artificial samples. In one series of tests, ten ml. portions of a mixed isotope solution were gamma counted in the well of the scintillation detector to determine

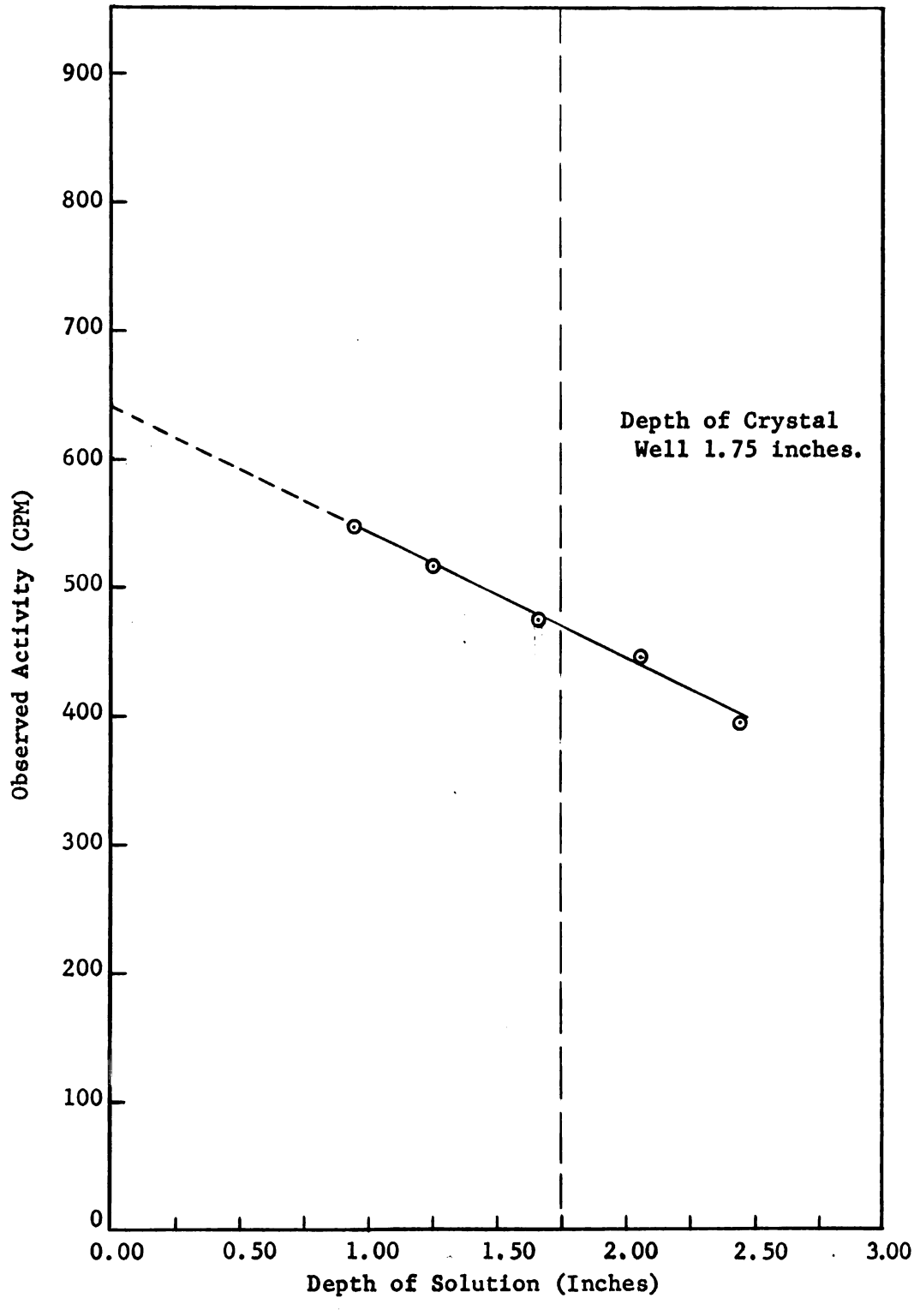


Figure 14. Variation of Count Rate With Sample Depth.

the effect of various factors on total count rate. The following is a summary of the conditions studied and the results obtained.

(A) Ten ml. of a uniform isotope solution were placed in each of three polyethylene bottles, identical to those used for upflow columns. The solution was diluted with distilled water to a depth of two inches (approximately equal to the depth of resin in prepared upflow columns). Forty-minute gamma counts of each sample were taken.

Table 13. Gamma Activity of Aqueous Isotope Solution.

Sample Number	Gamma Activity
B-1	633.9 CPM
B-2	675.7 CPM
B-3	618.7 CPM
Average	644.4 CPM

(B) Ten ml. of isotope solution were mixed with each of three one-liter volumes of tap water and passed through three upflow columns. Each column was gamma counted directly and the effluent from each column was evaporated to dryness on plastic film and gamma counted in a small 17 ml. plastic bottle. Forty-minute gamma counts were taken of each sample.

Table 14. Gamma Activity Removal From Tap Water.

Sample Number	Gamma Activity of Column	Gamma Activity of Effluent
PB-1	489.6 CPM	46.3 CPM
PB-2	540.3 CPM	8.7 CPM
PB-3	624.7 CPM	6.7 CPM
Average	551.5 CPM	20.6 CPM

(C) The test of series "B" above was rerun, substituting one liter of distilled water for the tap water in each case. All other conditions were identical.

Table 15. Gamma Activity Removal From Distilled Water.

Sample Number	Gamma Activity of Column	Gamma Activity of Effluent
PB-4	587.1 CPM	20.8 CPM
PB-5	595.8 CPM	0.4 CPM
PB-6	534.8 CPM	114.1 CPM
Average	572.6 CPM	44.8 CPM

(D) Ten ml. of isotope solution were added to each of three one-liter volumes of tap water and evaporated to dryness on plastic film. The plastic was then trimmed, folded, and placed in small (17 ml.) plastic bottles which were gamma counted directly. It should be noted that the folded plastic sheets for one-liter samples extend only 3/4 of an inch above the bottom of the crystal well. They thus provide a relatively good counting geometry. Forty-minute gamma counts of each sample were taken.

Table 16. Gamma Activity in One-Liter Evaporated Samples.

Sample Number	Gamma Activity
E1-1	873.1 CPM
E1-2	904.0 CPM
E1-3	912.4 CPM
Average	896.5 CPM

(E) Ten ml. of isotope solution were added to each of three ten-liter volumes of tap water and evaporated to dryness on plastic film. The plastic was then trimmed, folded, and placed in polyethylene containers identical to those used for column preparation. The plastic sheets extended to a height of approximately two inches (equal to the depth of resin in a prepared column). Forty-minute gamma counts of each sample were taken.

Table 17. Gamma Activity in Ten-Liter Evaporated Samples.

Sample Number	Gamma Activity
E10-1	658.7 CPM
E10-2	626.6 CPM
E10-3	647.7 CPM
Average	644.3 CPM

A comparison of these results provides a good picture of the effect of sample geometry and composition on total observed count rate for the methods of sample

preparation under investigation. For purposes of comparison it is assumed that the results of series "D" (evaporation of one liter of sample containing 10 ml. of isotope solution) are the optimum results expected. The average count rate observed for this method was 896.5 CPM.

The observed average count rate for series "A", in which the same activity was dispersed in water solution to a depth of two inches, was 644.4 CPM. The detected activity was 71.8% of the assumed optimum. This reduction in activity is in close agreement with that anticipated from the effects of counting geometry. Self-absorption within each type of sample is a factor contributing to count rate reduction; this effect has not been fully evaluated in this study.

The count rates detected in series "B" and "C", after passing one-liter portions of tap water and distilled water, respectively, through 14 g. columns, are 61.6% and 63.9% of the assumed optimum value. The observed apparent increase in effluent activity with the distilled water samples is believed to have been caused by leakage due to channeling rather than by actual column breakthrough. The fact that the average column count rate is higher for columns receiving distilled water than for those receiving tap water is attributed to the fact that the high ionic content of the tap water has caused a more complete distribution of activity throughout the depth of the column. As a result, the effect of counting

geometry has reduced the observed count rate for the tap water samples.

Series "E" is a direct evaluation of the method of evaporation of 10-liter samples. The results obtained indicate an apparent efficiency of 71.8%, which is identical to that obtained for a uniform dispersion of the activity in series "A". The close agreement of the results obtained by these two counting methods indicate that the effect of self-absorption within the plastic sheet is approximately the same as that which results from self-absorption by water.

Leakage of activity from the columns tested in series "B" and "C" only partially accounts for the decreased detection efficiency observed. The apparent effect of self-absorption is in the range of from three to six percent. Further investigation is required to fully evaluate this effect.

Column Performance with Natural Samples

After investigating column uniformity and performance characteristics using artificial samples, an evaluation of column performance was conducted using freshly collected rainwater. Two sets of four columns each were run using rainwater which had been adjusted with hydrofluoric acid to a molarity of 0.007 M. Identical ten-liter samples were passed through each column of the set and a fifth ten-liter sample was evaporated to dryness on

Table 18. Rainwater Activity Determination by Column Method. Resin Ratio 1.5:1, anion to cation by exchange capacity. Columns #37, 38, 39, and 40.

Condition Investigated	Column Number			
	37	38	39	40
Ionic form of cation resin.	H^+	H^+	H^+	H^+
Ionic form of anion resin.	OH^-	OH^-	OH^-	OH^-
Resin proportions anion to cation by exchange capacity.	1.5:1	1.5:1	1.5:1	1.5:1
Weight of resin (g).	14	14	14	14
Feed rainwater pH.	3.0	3.0	3.0	3.0
pH adjusted with HF to molarity.	0.007M	0.007M	0.007M	0.007M
Flow rate ml/min.	10	10	10	10
Activity of feed, 10 l. rainwater evaporated (CPM/l).	33.93	33.93	33.93	33.93
Activity detected on column (CPM/l).	34.28	48.50	36.43	32.26
Activity detected in effluent (CPM/l).	15.93	25.08	15.58	13.94
% of blank activity detected on column.	101.2	143.0	107.5	95.3
% of blank activity detected in effluent	47.0	73.8	45.9	41.2
Total % of blank activity detected.	148.2	216.8	153.4	136.5

Table 19. Rainwater Activity Determination by Column Method. Resin Ratio 1:1, anion to cation by exchange capacity. Columns #41, 42, 43, and 44.

Condition Investigated	Column Number			
	41	42	43	44
Ionic form of cation resin.	H^+	H^+	H^+	H^+
Ionic form of anion resin.	OH^-	OH^-	OH^-	OH^-
Resin proportions anion to cation by exchange capacity.	1:1	1:1	1:1	1:1
Weight of resin (g).	14	14	14	14
Feed rainwater pH.	2.9	2.9	2.9	2.9
pH adjusted with HF to molarity.	0.007M	0.007M	0.007M	0.007M
Flow rate ml/min.	10	10	10	10
Activity of feed, 10 l. rainwater evaporated (CPM/l).	13.40	13.40	13.40	13.40
Activity detected on column (CPM/l).	11.17	11.98	11.74	12.28
Activity detected in effluent (CPM/l).	13.83	12.49	10.38	9.38
% of blank activity detected on column.	83.3	89.4	87.7	91.6
% of blank activity detected in effluent.	103.1	93.1	77.4	70.0
Total % of blank activity detected.	186.4	181.5	165.1	161.6

plastic film. Tables 18 and 19 show the results of this series of tests. Resin proportions were adjusted in an attempt to determine if column performance could be improved by using a larger percentage of cation resin. The average results for the four columns of each set were:

Table 20. Average Rainwater Removal. Resin Ratio 1.5:1, anion to cation by exchange capacity, Columns #37, 38, 39, and 40.

Activity of 10 liter blank	33.93 CPM/l
Activity detected on column	37.87 CPM/l
Activity detected in effluent	17.63 CPM/l

Table 21. Average Rainwater Removal. Resin Ratio 1:1, anion to cation by exchange capacity, Columns #41, 42, 43, and 44.

Activity of 10 liter blank	13.40 CPM/l
Activity detected on column	11.80 CPM/l
Activity detected in effluent	11.52 CPM/l

The activity detected on columns #37 through 40 was 109% of the activity detected in the evaporated blank. These columns contained an anion to cation resin ratio of 1.5:1 by exchange capacity. Columns #41 through 44 contained an anion to cation resin ratio of 1:1. The activity detected on these columns was only 88% of that detected in the evaporated blank. These results seem to confirm the observation of Swope (23) that higher removal efficiencies are obtained with anion to cation resin

ratios greater than 1:1.

The results obtained from this series of tests are similar in one respect to the results of the early column tests using rainwater, in that the sum of the activity detected on the column and in the evaporated effluent is greater than that detected in the evaporated blank. The sum of the activity detected on the column and in the effluent ranged from 136.5% to 216.8% of that detected in the blank. This effect is undoubtedly the result of a variation in counting efficiency for the two methods.

Although adequate data is not available for an exact efficiency determination for each method, certain observations can be made which will help explain this apparent increase in activity. First, it is evident that the column is not capable of quantitatively concentrating the activity from ten liters of rainwater. This is apparent from the fact that there is activity present in the effluent. The activity passing through the column is ionic in form rather than particulate, since the combination of glass wool and resin bed form an effective filter. It is believed that the activity passed into the effluent is the result of column breakthrough in which ions of low affinity for the resin are passed into the effluent first. A reduction in sample volume should result in quantitative removal.

A second factor which helps to explain the

apparent increase in activity observed is that the resin column is very efficient for the concentration of particulate matter at the bottom of the column. The high activity associated with the solids from rainwater samples is therefore concentrated by the upflow column in the position of optimum counting geometry in the bottom of the crystal well. Figure 14 indicates a linear relationship between count rate and depth of sample for samples of constant activity over the range of depths investigated (0.94 to 2.44 inches). This straight line relationship has been extrapolated to zero depth resulting in a predicted minimum theoretical count rate equal to 136% of that detected at full crystal well depth. For crystal wells in which depth is large compared with well radius, however, the activity detected would be expected to increase at an increasing rate as the sample depth is reduced. As a result, when high activity solid particles are retained very near the bottom of the column, the activity detected may be high enough to result in the apparent increases in sample count rates experienced.

The ionic activity retained on the column and that eluted into the effluent and detected by counting the plastic sheet is dispersed throughout the volume of the crystal well and therefore is affected by both geometry and self-absorption effects.

DISCUSSION

The study of factors influencing the development of a system for the quantitative concentration of radionuclides from liquid environmental samples for direct gamma analysis using the counting equipment available has accomplished the basic works for achieving its objective. The upflow column developed provides for the concentration of all particulate matter present in the sample and the major portion of all ionic forms up to column breakthrough. Upflow column design minimizes the effects of counting geometry in the crystal well of gamma scintillation equipment by concentrating sample activity at or near the bottom of the column where optimum counting is achieved. Filtration of solid materials is effectively achieved without the buildup of a mat of solids over the resin surface which obstructs flow (as has been experienced with downflow columns). Upflow columns can be fabricated to meet the requirements set by available counting equipment from inexpensive, readily available materials. Column preparation is simple and uniform columns can be prepared easily.

The size limitations imposed by the available crystal well have limited the size of column suited for direct counting to such an extent that the resin capacity is exceeded when ten-liter rainwater samples are passed through the column. Limited experimental results indicate

that a sample size of from five to seven liters of rainwater should not exceed the capacity of the 14 g. columns tested. Additional investigation is required to determine more precisely the maximum sample size applicable. The author feels that the column size limitation is the major factor restricting utilization of the upflow column for concentration and direct gamma analysis. The method can be utilized successfully with large volume samples if a large volume crystal well is available to accommodate the column size required.

When such equipment is not available, the practice of sample evaporation on plastic film with subsequent direct counting of the plastic sheet may be utilized to advantage. The evaporation method may also be utilized for comparison of results obtained from upflow column operation.

Each method offers certain advantages over the other. The upflow column offers savings in time of sample preparation and space requirements as compared to the evaporation method. Sample handling during preparation is not required with upflow columns as it is in the trimming and folding of plastic sheets following evaporation. The sample container is completely closed during column operation, while the evaporation process requires that the sample be exposed to the atmosphere and activity may be lost or gained in the form of dust.

The concentration of solids at the bottom of the

upflow column may result in an apparent high count rate from this form of activity, but if column capacity is not exceeded and well volume is sufficient to provide reasonable counting geometry for the entire depth of resin this effect should be minimized. In this respect the evaporation method provides the advantage of a completely uniform sample in which particulate and ionic activities are uniformly dispersed. The resulting count rate is therefore affected only by geometry and self-absorption.

Several of the results obtained in the evaluation of column performance with regard to the evaporation method showed activity variations in excess of those predicted by statistical variations due to natural isotope decay. The sample activity and counting period were chosen in such a way as to produce an expected variation in count rate of less than one percent from identical ten ml. isotope solution samples. In spite of this fact, activity variations for identical conditions showed an average variation of approximately ten percent among the samples tested. While other factors (such as gamma analyzer instability resulting from temperature variations within the equipment and fatigue effects) may have contributed to activity variations in the samples counted, the major cause of such variations is believed to have resulted from a lack of uniformity of sample. Examination of the stock isotope mixture from which the ten ml. portions were taken disclosed the presence of a form of

biological growth. The dispersion of this growth was not homogeneous and therefore uniform sample preparation was not possible. Although the samples prepared lacked the degree of uniformity desired, interpretation of the results obtained is still useful in evaluating the methods under investigation.

The statistical error to be expected with five-liter rainwater samples having a unit activity of 25 CPM/l and allowing a forty-minute counting period with 325 CPM background is approximately 3.5%. Statistical reliability will be increased using larger sample volumes or longer counting periods. Reliability will also be increased if sample activity is higher than 25 CPM/l, but at this time this appears to be about the level of activity present in rainwater samples.

Consideration has been given to several factors relating to the design and operation of the upflow column. The resin ionic forms utilized were chosen based upon the high affinity of Dowex 50W and Dowex 1 resins in the hydrogen and hydroxide forms for all of the ionic forms normally found in environmental samples containing mixed fission products. A flow rate of approximately ten ml. per minute was selected with consideration for both ion exchange reaction time requirements and sample processing time. These two factors have been balanced in an effort to obtain satisfactory exchange reactions within a reasonable processing time.

Adjustment of sample pH levels to approximately 3.0 has been carried out using hydrofluoric acid. The lowering of pH has been shown by others to produce more complete removal of radionuclides from aqueous samples. The use of hydrofluoric acid for pH adjustment serves two additional purposes. It forms an anionic complex with zirconium which can be concentrated on anion exchange resin. Due to the low selectivity coefficient of Dowex 1 in the hydroxide form for the fluoride anion, pH adjustment using hydrofluoric acid reduces the amount of exchange capacity taken up by nonradioactive anions associated with other acids utilized for pH reduction. Further investigation of this second effect is required to fully evaluate the increase in capacity obtained.

The anion to cation resin ratio chosen for mixed bed operation has been based upon similar investigations by Swope (23) in which she proposes the use of an anion to cation resin ratio of as much as 3:1 (by volume). The author has utilized an anion to cation resin ratio of approximately 2.5:1 (by volume) or 1.5:1 (by exchange capacity). It is felt that basing the resin ratio on exchange capacity rather than volume is more meaningful in respect to the reactions taking place, and it is a term which can be readily translated from one resin type to another.

The use of an anion to cation resin ratio greater than 1:1 is opposed to the logical expectation that since

most radioactive ions are cations a larger proportion of cation resin should be utilized. This was apparently the reasoning of Boni (1), but Swope (23) has shown improved removal (while sacrificing sample size) using a high anion to cation ratio in a mixed bed.

Elutriation of activity from the upflow columns for the purposes of radiochemical separation or further analysis has not been attempted, but such a process should be no more complicated than the reverse flow elutriation of normal downflow columns. A slightly higher percentage of the particulate matter from the sample may be retained on the column due to deeper bed penetration, but all ionic activity should be readily displaced from the column simply by reversing the direction of flow in the elutriation step.

CONCLUSIONS

The evaluation of the upflow ion exchange column developed in this study has led to the following conclusions:

1. Upflow columns can be prepared with sufficient uniformity to be satisfactory for radionuclide concentration provided that proper care is taken during column preparation and operation.

2. Solid particles from environmental samples are concentrated at the bottom of the resin column where counting conditions are optimum.

3. Limited results have shown that an anion to cation resin ratio of 1.5:1 (by exchange capacity) produces more complete removal of activity from rainwater at low pH than does a resin ratio of 1:1.

4. The 14 g. resin columns studied did not have sufficient exchange capacity to quantitatively concentrate the activity from 10-liter samples of rainwater.

5. Due to the limitations imposed by available crystal well dimensions, the 14 g. upflow columns investigated would not contain sufficient resin to be satisfactory for concentration of stream water samples.

6. The method of evaporation employed offers the advantage of producing a uniform sample. The contribution of particulate and ionic activities to the total observed activity is a direct function of the quantity of the two

forms present.

7. Sample evaporation on plastic sheets can be utilized for any type of liquid environmental sample.

8. The evaporation method may be utilized as the method of sample preparation for direct analysis when column capacity would be exceeded by the sample volume required for statistical reliability.

FUTURE STUDIES

Both methods of sample preparation studied require further investigation. The following studies should be undertaken:

1. Upflow column breakthrough capacity for rainwater samples should be determined.

2. The effect on total column capacity when hydrofluoric acid is used for pH adjustment, as opposed to the use of nitric acid, should be evaluated.

3. The optimum anion to cation resin ratio for removal of radionuclides from environmental samples should be determined.

4. Methods should be developed for the utilization of samples prepared for gamma analysis for subsequent beta analysis using liquid scintillation spectrographic methods. Resin samples could be treated in several ways:

   A. Activity held on the column could be elutriated from the column in a reverse flow process.

   B. The resin could be wet or dry ashed prior to beta sample preparation.

5. The evaporation method of sample preparation should be evaluated with respect to sample uniformity and counting efficiency.

6. Self-absorption of both the ion exchange resin and plastic sheet utilized for evaporation should be determined.

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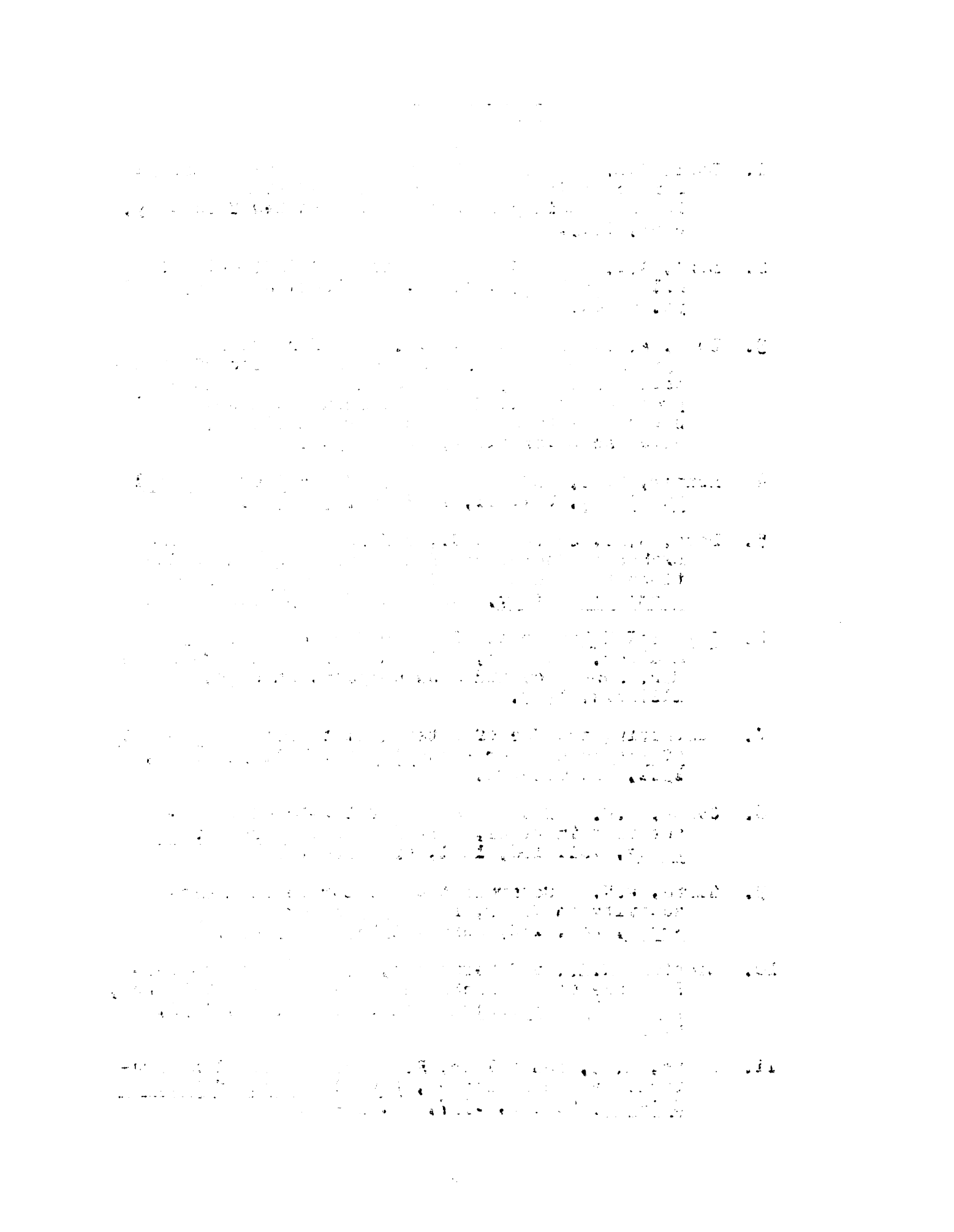

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