DETERMINATION OF LOW-LEVEL RADIOACTIVITY IN WATER

by

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Submitted by

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SUMMARY STATEMENT

A review of the literature pertinent to this research has been made, with emphasis placed on ion exchange and its application to the field of radioactivity.

To aid in the analysis of experimental data, studies on planchet preparation and reproducibility of counts were conducted. The results of these studies are indicative of the planning required for statistical accuracy.

A method which will eliminate the need of transporting large volumes of water from the field to the laboratory for evaporation and radioassay has been investigated. This method employs the concentration of radionuclides from water by ion exchange resins.

Radionuclides must be removed from the resin for counting since ion exchange resins can not be counted directly. The usual technique, elution, is not considered practical for removing the radionuclides adsorbed on the resin for determining gross alpha, beta and gamma activity.

Two techniques for ashing ion exchange resins have been extensively explored, wet ashing and dry ashing. At present, the dry ashing technique seems to be the better choice.

Since the radioactivity in natural water is distributed between filterable and non-filterable matter, preliminary investigations into the separation of filterable and non-filterable matter by the use of membrane filter media are under way.

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A. STATEMENT AND PURPOSE OF RESEARCH

1. The Problem

Extensive research has been conducted on the determination of low concentrations of radionuclides in water. Investigations continue for an accurate method of analysis to detect activity in water near background level and to follow any increase from contamination. It is also highly desirable that this method will distinguish between filterable and non-filterable forms of radioactivity. Determinations of this type are essential in every area of potential radioactive contamination and for the proper evaluation of data collected after contamination may have occurred. Therefore, an urgent need exists for a reliable, reproducible and rapid method for the detection of gross activity of the order of 10^{-8} μc/ml in water supplies.

The limitations of presently available equipment make it impossible to detect low-level radioactivity in water without first concentrating the radioactive substances. The required concentration of activity must be sufficiently high to achieve a significant count in a reasonable length of time. Concentration may be accomplished by either chemical or physical techniques. Generally, evaporation has been employed for the concentration of radionuclides from a given volume of water. Other methods, including distillation and solvent-extraction techniques, also have been employed for this purpose. The method of concentration by ion exchange lends itself to the analysis of a large number of radionuclides from water samples. It shows promise to be more rapid than many radiochemical separation techniques now used for specific radionuclides. This method is especially attractive for the determination of gross activity and suitable for mass sampling.

As a result of these and similar investigations, it is expected that additional information on the distribution of radioactivity between filterable and non-filterable matter will be obtained and that a contribution toward increasing the knowledge of the mechanism of ion exchange uptake will result. Based on such information, a simple and reliable method for rapid radioassays would be of immediate and general application in this field.

2. Purpose of the Study

The purpose of these investigations is to develop a rapid and reproducible method for determining the gross alpha, beta and gamma radioactivity in water. At present no commercially available instrument is capable of measuring an activity approaching 10^{-8} μc/ml in water. Therefore, some method of concentration is required. The usual method is evaporation, but it is subject to a number of limitations, including loss of short-lived isotopes that may die out during the period required for sample preparation. It is impractical to count 0.22 disintegration per minute for water containing radioactivity of 10^{-7} uc/ml with an instrument registering a background rate of 10 to 20 counts per minute. If a liter of water containing 10^{-7} μc/ml of activity is concentrated by evaporation and deposited in a thin layer on a planchet, it becomes possible to concentrate an activity of 220 d.p.m. Because of self-adsorption due to dissolved solids and geometry of the instrument, however, only a portion of these disintegrations may be registered as counts. Consequently, it is necessary to develop methods of radioassay to determine the gross alpha, beta and gamma activities in water at levels as low as 10^{-8} μc/ml, or 10 μμc/l. Measurements of activities of this low order of magnitude, or even lower, are needed to determine the background radioactivity in natural waters and to detect increases in activity before they reach levels which interfere with the use of the water.

Specifically, the purpose of this research program is to develop a suitable technique for the separate determination of filterable and non-filterable radioactivity. It has been proposed to concentrate the non-filterable activity by membrane filter media and the filterable activity by ion exchange resins. The objective of this method is to permit detection of gross alpha, beta and gamma activities of the order of 10^{-8} μc/ml. A later phase of this program consists of studies of improved methods for specific isotope identification. From these investigations the following results are expected:

(1) A rapid and reliable method for the analysis of gross low-level activity in water of the order of 10^{-8} μc/ml;

(2) An accurate and simple technique for the separate determination of filterable and non-filterable activities; and

(3) A portable apparatus for the separation of filterable and non-filterable activities and for their concentration. As a result of the basic studies, this apparatus will be designed to yield reproducible results and will eliminate the need for transporting large volumes of water from the field into the laboratory.

B. RELATION TO THE PRESENT STATE OF KNOWLEDGE IN THE FIELD

The literature is replete with many studies devoted to the determination of specific radionuclides in water. Much of this work has been performed and reported during the past decade. Although considerable information has become available on methods of radioanalysis for many important nuclides, many of these methods apply primarily to activities several magnitudes greater than the maximum permissible levels, as recommended by the National Committee on Radiation Protection and published in National Bureau of Standards Handbooks 52[a], 61[b] and 69[c]. During the past several years techniques for radionuclide identification have become increasingly refined with the advent of radiation energy spectroscopy. Multi-channel spectrum analyzers are available for the detection of radionuclides in low concentrations and with activities approaching background levels.

Concentration of radionuclides by ion exchange resins has been studied extensively. The investigations by Bunney, et al. (1) and Freiling, et al. (2) have been devoted largely to the adsorption of mixed fission products and the rare earths on Dowex 2. Others interested in the concentration

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[a] National Committee on Radiation Protection, "Maximum Permissible Amounts of Radioisotopes in the Human Body and Maximum Permissible Concentrations in Air and Water", Nat. Bur. Stand., Handbook 52, U.S. Govt. Printing Office, Washington, D. C. (1953)

[b] National Committee on Radiation Protection, "Regulation of Radiation Exposure by Legislative Means", Nat. Bur. Stand., Handbook 61, U.S. Govt. Printing Office, Washington, D.C. (Dec. 1955)

[c] National Committee on Radiation Protection, "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure", Nat. Bur. Stand., Handbook 69, U.S. Govt. Printing Office, Washington, D. C. (1959)

of specific radionuclides include Bryant, et al. (3) who concentrated Strontium-90 on a modified Dowex 50 X4 cation exchange resin; Strelow (4) who studied the quantitative adsorption of thorium on Dowex 50 cation exchange resin; Karttunen and Evans (5) studied the separation of rhodium on Dowex 50W-X8 cation exchange resin; Maeck and Rein (6), using the same resin, separated radioiodine from mixed fission products to obtain an overall recovery of 97.1 per cent, Khopkar and De (7) studied the behavior of uranium on Amberlite IR-120 and Wish (8) separated tellurium from uranium by Dowex 2 anion exchange resins.

The results of several adsorption studies to determine the behavior of radionuclides on various ion exchange materials and measurements of specific distribution coefficients between resin and influent have been cited in the literature. Among these, investigations on the behavior of radionuclides on ion exchange media were reported by several groups (3, 4, 5, 7) and information on the behavior and distribution coefficients were reported by others (1, 2, 8).

The gamma ray spectrometric technique has been discussed by Hagee, et al. (9); DeLange (10) applied it to leached uranium-thorium ore analysis, while Kahn and Reynolds (11) discussed four methods of concentrating low levels of activity in water in preparation for gamma ray spectrometric analysis. Transport of radioactivity as related to exchange phenomena and aquatic biota have been reported by Barker (12).

Below is a list of the cited literature, including pertinent information:

(1) Bunney, L. R., Ballou, N. E., Pascual, J. and Foti, S., "Quantitative Radiochemical Analysis by Ion Exchange. Anion Exchange Behavior of Several Metal Ions in Hydrochloric, Nitric and Sulfuric Acid Solutions." Anal. Chem., 31, 324-326 (March, 1959).

The authors adsorbed americium, cerium (iii), molybdenum, protactinium, niobium, ruthenium, strontium, thorium, uranium (vi), yttrium, and zirconium on the anion exchange resin Dowex 2 from solutions of hydrochloric, nitric, and sulfuric acids (0.1N - conc.) and measured their distribution coefficients. Data to calculate the distribution coefficients was determined with a Beckman DU spectrophotometer, Fischer photometer, well-type scintillation counter, and by alpha and beta proportional counting. Distribution coefficients, K_d, for the elements studied ranged from a high value of 10,000 to a low value of 0.1. K_d is defined as the ratio of the activity per gram of resin to the activity per milliliter of solution applied to the resin.

(2) Freiling, E. C., Pascual, J. and Delucchi, A. A., "Quantitative Radiochemical Analysis by Ion Exchange. Anion Exchange Equilibrations in Phosphoric Acid Solutions." Anal. Chem., 31, 330-331 (March 1959)

Dowex 2 anion exchange resin in the phosphate form was equilibrated with cesium, strontium, cerium (iii), zirconium (iv), tellurium (iv), cerium (iv), neptunium (iv), niobium (v), molybdenum (vi), and uranium (vi) in various strengths of phosphoric acid solutions and their distribution coefficients were calculated. At low phosphoric acid concentrations cesium and tellurium (iv) are not adsorbed, strontium, cerium (iii) and cerium (iv) are weakly adsorbed and the remaining elements are strongly adsorbed.

(3) Bryant, E.A., Sattizahn, J. E. and Warren, B., "Strontium-90 by an Ion Exchange Method", Anal. Chem., 31, 334-337 (March 1959)

A method for the determination of strontium in a sample which contains up to 0.1 gram of iron or uranium is described. The authors state that the radiochemical yield is greater than 97 per cent. Strontium is adsorbed on a modified Dowex 50 X-4 cation exchange resin and, after a growth period, the daughter Yttrium-90 is eluted and adsorbed on another column of the same cation exchange resin and eluted with α-hydroxyisobutyric acid. Counting was accomplished with a methane gas flow proportional counter.

(4) Strelow, F. W. E., "Separation of Thorium from Rare Earths, Zirconium, and other Elements by Cation Exchange Chromatography", Anal. Chem., 31, 1201-1203 (July 1959)

The semiquantitative affinities of 23 cations for AG 50 resins in hydrochloric acids were investigated and thorium was found to be quantitatively adsorbed on Dowex 50 cation exchange resin. Elution curves were prepared for those cations which exhibited a high affinity for AG 50 resins. These curves were presented for cerium and thorium.

(5) Karttunen, J. O., and Evans, N. B., "Cation Exchange Separation and Spectrophotometric Determination of Microgram Amounts of Rhodium in Uranium-Base Fissium Alloys", Anal. Chem., 32, 917-920 (July 1960)

A nitric acid solution of fissium alloy from which uranium has been extracted, containing uranium, molybdenum, ruthenium, palladium and zirconium is fumed with perchloric acid. The resulting solution is passed through Dowex 50 W-X8 cation exchange resin. Rhodium is selectively eluted with 0.3 M hydrochloric acid and measured spectrophotometrically with tin (ii) chloride.

(6) Maeck, W. J. and Rein, J. E., "Determination of Fission Product Iodine. Cation Exchange Purification and Heterogeneous Isotopic Exchange", Anal. Chem., 32, 1079-1083 (August 1960)

Radioiodine in fission product mixtures is separated from the other activities by cation exchange. Radioiodine passes through the cation exchange column and then undergoes heterogeneous isotopic exchange with preformed silver iodide. Over-all recovery of I-131 is 97.1 per cent.

(7) Khopkar, S. M. and De, A. K., "Cation-Exchange Behavior of Uranium (VI) on Amberlite IR-120, Separation from Mixtures", Analytica Chimica Acta, 22, 153-158 (1960)

Studies on the quantitative adsorbtion and elution of milligram amounts of uranium (vi) with the cation exchange resin Amberlite IR-120 are reported. The separation of uranium from thorium, zirconium, cerium (iii), copper and nickel was also investigated. Uranium was determined by extraction with 8-quinolinol-chloroform and measured spectrophotometrically at 430 mμ with a Hilger Quartz spectrophotometer.

(8) Wish, L., "Quantitative Radiochemical Analysis by Ion Exchange. Uranium and Tellurium", Anal. Chem., 32, 920-922 (July 1960)

A scheme for separating tellurium from uranium is described. Tellurium is eluted from Dowex 2 anion exchange resin with less than 1N phosphoric acid. Quantitative yields and purities greater than 99 per cent were claimed for the separation and distribution coefficients measured.

(9) Hagee, G. R., Goldin, A. S. and Straub, C. P., "Use of the Gamma Spectrometer in the Identification of Radionuclides in Water", Journal, American Water Works Association, 50, 621-627 (May 1958)

The basis of gamma spectrometry and its application to the radiochemical assay of water are discussed. Typical spectra for rainwater, milk and sludge from an old cistern are presented. The authors point out the advantages as well as the disadvantages of single and multiple-channel gamma ray spectrum analyzers for the identification of radionuclides in water.

(10) DeLange, P. W., "Analysis of Naturally Leached Uranium-Thorium Ore Samples. Application of Pure Gamma Spectrometry", Anal. Chem., 32, 1013-1017 (July 1960)

Applications of presently available radiometric procedures to the analysis of naturally leached ores are discussed along with possible errors in radiometric analysis and a statistical treatment of the data. Gamma ray spectrometry was applied for the analysis of leached uranium-thorium ore samples and the results compared with other radiometric, chemical and mass spectrometric methods.

(11) Kahn, B. and Reynolds, S. A. "Determination of Radionuclides in Low Concentrations in Water", Journal, American Water Works Association, 50, 613-620 (May 1958)

The authors describe a gamma spectrometric technique as well as four volume reduction methods for the determination of radionuclides in low concentrations in water. The four concentration methods are precipitation, ion exchange, distillation and extraction. A brief discussion of the sensitivity of gamma ray spectrometry is included.

(12) Barker, F. B., "Factors Affecting the Transport of Radioactivity by Water", Journal, American Water Works Association, 50, 603-612 (May 1958)

The author discusses the factors which affect the transport of radioactivity in surface and ground water including the concentration of activity by aquatic biota and the ion exchange capacities of several clays for radiostrontium and radiocesium.

C. RESULTS OF EXPERIMENTAL WORK

1. Radionuclide Concentration by Ion Exchange Resins

It has been established rather conclusively that radionuclides are removed from solution by ion exchange resins, although little work has been reported on the removal of very low-level mixtures of radionuclides in water.

Most of the naturally occurring radionuclides are fairly well adsorbed by ion exchange media. Almost all of these radionuclides or their complexes are tri- or tetra valent ions. Many of the cations have small ionic radii and are considerably hydrated. For further discussion see Appendix A, "An Outline of Theories Related to Ion Exchange". Uranium complexes particularly well, forming a number of anionic complexes with nitrates, sulfates, chlorides, carbonates, etc.

The only naturally occurring radionuclides likely to be present in water in measurable amounts are Uranium-238, Thorium-232, and Radium-226 and their disintegration products. These radionuclides are found to be adsorbed quite well by ion exchange resins and both uranium and thorium are quantitatively adsorbed.

Some of the factors governing the exchange of ions are: (i) ionic radius, (ii) activity of the ion, (iii) valence state, (iv) hydration of both the resin and the ion, (v) diffusion rate through the resin, (vi) flow rate through the column, and (vii) temperature, as further discussed in Appendix A.

All of these factors have to be taken into consideration in selecting the resin(s) which will best concentrate a nuclide, or a group of nuclides, from a water sample. If the resin is very highly cross linked, diffusion of the exchanging ions will be hampered, if not completely stopped. If the mesh size of the resin is too small, the flow rate will be affected adversely. Rate of flow and degree of cross linkage also influence the speed of equilibrium. The capacity for exchange and stability of the resins used are also important in determining the most suitable resin(s).

From results obtained thus far, it appears that resins of medium cross linkage, high exchange capacity, high stability, and 40-60 mesh size for optimum flow rate, will best concentrate radionuclides. Good results have been obtained with a polystyrene, sulfonated cation exchanger in the hydrogen form, and a highly basic quaternary amine polystyrene anion exchanger in the hydroxyl form.

Preliminary investigations have been performed with mixed resins because radionuclides exist as both cationic and anionic complexes. According to Swope (1) and others, a bed of mixed cation and anion exchange resins will concentrate radionuclides more efficiently from a given sample of water than will monobeds containing either anion or cation exchangers.

2. Reproducibility of Sample Preparation and Accuracy of Counting

An important part of any report is an indication of the reliability of the results. Also, as an integral part of the planning of any experiment it is necessary to establish the degree of reliability expected for the results. Besides the usual errors arising from common laboratory manipulations, there are errors characteristic of radioactivity measurements. The latter may arise from the following sources: (i) random emission of radiation from a source, (ii) detection of the nuclear radiation, and (iii) technique of radiation measurement. Radiation intensity variations resulting from interaction of the radiation with matter before reaching the detector may be listed as follows:

(i) Adsorption of alpha, beta and gamma rays, the latter with the production of secondary radiation;

(ii) Self-absorption of radiation;

(iii) Scattering and backscattering of radiation.

A given experimental result will have an over-all observed uncertainty resulting from one or more of these factors.

The various errors enumerated above could be classified as either (i) determinate errors, or (ii) indeterminate errors. The determinate error can be minimized by applying known correction or calibration factors. After allowance is made for all determinate errors, the values obtained from a set of supposedly identical data will still show some variation. Indeterminate errors are minimized by refining experimental technique. When they are treated in accordance with probability considerations, it is possible to express an experimental result with an error for which a probability of occurrence may be assigned. It may be pointed out that even the correction or calibration factors applied to minimize determinate errors are subject to inherent indeterminate errors.

In planning the organized collection of laboratory data on studies for the determination of low-level radioactivity in water, and the analysis of the significance of this data, it was necessary to evaluate these variables: (i) the reproducibility of activity determinations from a single source of radiation, (ii) the difference between the activity from two similarly prepared sources of radiation over a period of time, and (iii) the reproducibility of sample preparation as determined from a number of samples, prepared and counted on the same day.

To examine the reproducibility of alpha and beta activity determinations from one sample of mixed fission products (10 λ of M.F.P.), the sample was counted for one hour each day over a period of 17 days. The variations of the net counting rates are presented in Figure 1. It shows that the arithmetic mean for the alpha activity is 22.3 c.p.m., which is the best estimate of the true value if only indeterminate errors are assumed to be present. The set of measured values show the usual scatter. For the given set of measurements there is a probability of 68.3 per cent that a single value will not show a deviation from the mean by more than 9.1 c.p.m. Similarly, 68.3 per cent of the time, counts ranging between 13.2 and 31.4 c.p.m. are expected due to chance factors alone.

For the given set of beta measurements the mean value is 1544 c.p.m. as shown in Figure 1. The value of the standard deviation is 60.5 c.p.m. which means that 68.3% of the time, counts ranging between 1484 and 1605 c.p.m. are expected due to chance factors alone.

These results showed that the counting procedure was not under control at the time these data were obtained.

In the course of these studies it is necessary to determine the difference due to indeterminate errors between similarly prepared planchets. To examine whether there is any significance between the means, a hypothesis was set up that planchets prepared similarly would yield no significant difference in activities. As shown in Table I, t values were determined separately from the calculated alpha and beta net counting rates. Using Student's t distribution, probabilities of 40.7 per cent and less than one per cent, respectively, were found. These results signify that one could expect as great, or greater, difference between the alpha activities

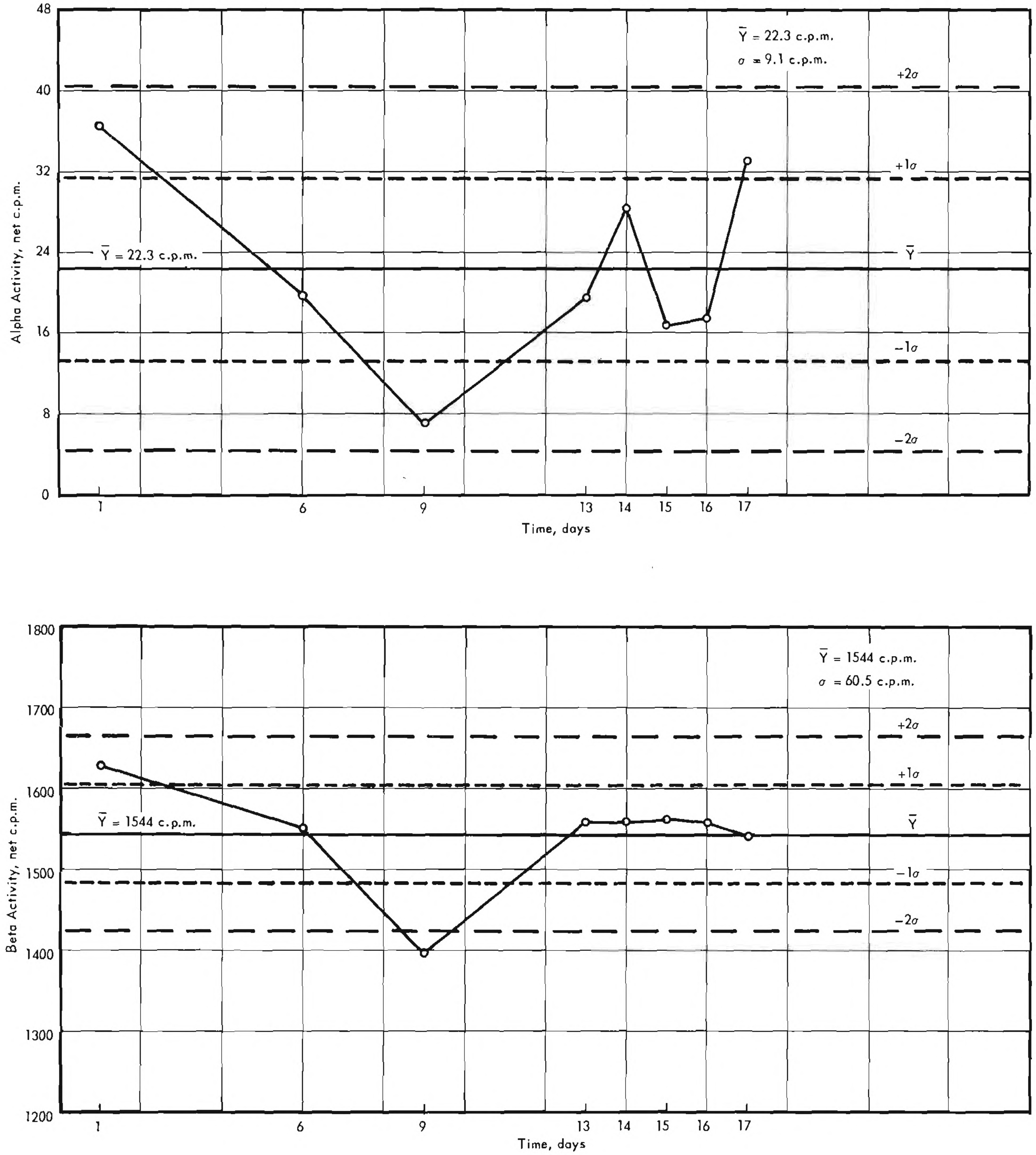

Figure 1. Variation of Alpha and Beta Counting Rates of Mixed Fission Product Sample with Time.

TABLE I

t Test for Difference Between Activity from Mixed Fission Products Deposited on Planchets(*)

α-activity (c.p.m.)		β-activity (c.p.m.)	
Planchet A	Planchet B	Planchet A	Planchet B
36.8	36.4	1626	1100
19.8	18.7	1550	1146
7.0	10.7	1397	1089
19.4	21.8	1559	1126
28.3	21.6	1558	1000
16.9	14.9	1562	916
17.3	12.8	1559	1119

Note: (*) 10 λ MFP deposited on each planchet from a stock solution of 10 λ MFP/100 ml.

Results from Statistical Analysis

Standard Error of $\bar{d}_\alpha$:

$$\sigma_{\bar{d}} = \frac{\sigma_{\bar{d}}}{\sqrt{n}} = 1.38$$

$$t = \frac{(\bar{d} - \bar{d}')}{\sigma_{\bar{d}}} = 0.89$$

$P_\alpha = 0.407$

Standard Error of $\bar{d}_\beta$:

$$\sigma_{\bar{d}} = \frac{\sigma_{\bar{d}}}{\sqrt{n}} = 42.1$$

$$t = \frac{(\bar{d} - \bar{d}')}{\sigma_{\bar{d}}} = 11.3$$

$P_\beta < 0.001$

41% of the time due to chance factors alone. In the case of the beta activities the hypothesis was rejected because differences as great, or greater, than the average difference between the activities on the planchets are expected due to chance alone less than 1% of the time.

On the basis of these statistical results, the experiments which followed had to be planned with improved sample preparation methods.

To study the reproducibility of sample preparation, two milliliters of a solution of uranyl acetate(*) were deposited on each of thirteen 2-in. diam. stainless steel planchets and both alpha and beta activities determined. The results are presented in Table II. From the results of statistical analyses, also shown in Table II, it may be observed that for the given set of alpha activity measurements the chance of obtaining a deviation of a single value from the mean of 324 c.p.m. by an amount less than or equal to 71.1 c.p.m. is 68.3 per cent. Similarly, for beta activity measurements, the chance of observing a deviation of a single value from the mean of 1305 c.p.m. by an amount less than or equal to 206 c.p.m. is 68.3 per cent, assuming the data to be normally distributed. To examine the latter assumption of normality, σ/A.D. was applied to test the data and the results are shown in Table II. As a further evaluation of the experimental data, the measures of skewness (α_3) and kurtosis (α_4) are also presented in Table II. The results indicate that the alpha activity data is moderately left skewed ($\alpha_3 = +0.57$) and that the distribution is platykurtotic ($\alpha_4 = 1.7$). The beta activity data is moderately right skewed ($\alpha_3 = -0.50$) and also platykurtotic ($\alpha_4 = 2.2$).

(*) 0.5 gm $UO_2\ (C_2H_3O_2)_2 \cdot 2H_2O$ in 100 mls.

TABLE II

Reproducibility Study of Sample Preparation

Planchet Number	α-activity (c.p.m.)	β-activity (c.p.m.)	Total α + β activity expressed as: α-activity (%)	β-activity (%)
1	406	1485	21.5	78.5
2	373	1235	23.2	76.8
3	449	1579	22.2	77.9
4	249	1277	16.3	83.7
5	312	1312	19.2	80.8
6	288	1437	16.7	83.3
7	310	1421	17.9	82.1
8	386	1570	19.8	80.3
9	421	976	30.1	69.9
10	245	1412	14.8	85.2
11	281	1246	18.4	81.6
12	230	1118	17.0	83.0
13	264	904	22.6	77.4

Results of Statistical Analysis

Arithmetic Mean, $\bar{X}$	324	1305
Standard Deviation, σ	71.1	206
Test for Normality, $\frac{\sigma}{A.D.}$	1.12	1.24
Skewness, α_3	+0.57	-0.50
Kurtosis, α_4	1.7	2.2

It appears from these results that considerable variation exists in the preparation of samples, although the indeterminate errors of radioactivity measurements are a part of the variance of this data. Further improvements of the reproducibility of sample preparation and the accuracy of counting are necessary and statistical methods of analysis will follow the principles outlined by Jarrett (2), the Radiological Health Handbook (3), other publications prepared by the R. A. Taft Sanitary Engineering Center (4, 5) and other reference texts.

3. Wet Ashing Method

A method for wet ashing ion exchange resins has been investigated, using a mixture of concentrated perchloric, nitric and sulfuric acids. This method does not require any highly specialized equipment. The prime requisite is the availability of a well ventilated fume hood.

During the ashing procedure, a part of the sulfuric acid is decomposed into sulfur trioxide and water, the sulfur trioxide being driven off with heat. After ashing is completed the substances adsorbed on the resin are contained in a small volume of concentrated sulfuric acid.

(a) Wet Ashing Procedure:

After the sample has been run through the column, the resin is removed from its container and placed in an evaporating dish for drying. When dry, the resin is transferred to a one liter erlenmeyer flask. Three ml of concentrated perchloric acid for each gram of dry resin, plus 10 ml excess perchloric acid, are added. A volume equal to that of the perchloric acid, consisting of two-thirds volume concentrated nitric acid and one-third volume concentrated sulfuric acid is added. Finally, a catalytic amount (approx. 3 ml) of saturated vanadium pentoxide solution in concentrated ammonium hydroxide is added. The flask is placed on a suitable heating apparatus (either an electric Kjeldahl heater or a good hotplate) and heated gently. Electric heating is necessary to obtain even heat distribution. The reaction must be carried out in a fume hood because the fumes are irritating and corrosive. The reaction is accompanied by a vigorous production of foam which may be controlled by alternately cooling and heating the mixture or use of Dow-Corning Antifoam A. The latter leaves a residue, however. Completion of the reaction is indicated by the vigorous evolution of perchloric acid fumes and chlorine.

The wet combustion reaction takes from two to three hours for completion depending on the amount of resin used, varying from 15 to 25 grams.

The same radionuclide solution was applied to pairs of mixed ion exchange resins. After collection of the radioactivity on the beds, the resins were subjected to the wet ashing method. A solution of uranyl acetate (0.237 gm/100 ml) was applied to each of a pair of mixed bed resins and a solution of mixed fission products (10 λ/100 ml) was run through each of another pair of mixed bed resins. Values of the activities of the ashed resins, presented in Table III, show good agreement between corresponding α and $\alpha + \beta$ activities, associated respectively with each pair of ashed resins, regardless of whether uranyl acetate or mixed fission products were applied to the column. Additional studies are necessary to further evaluate the reproducibility of the wet ashing method.

4. Dry Ashing Method

A method of dry ashing ion exchange resins is also under investigation. Several variations of this technique have been employed beyond the direct dry ashing method. These variations included dry ashing with the following oxidizing agents: (1) magnesium nitrate, (2) ammonium nitrate, and

TABLE III

Results of the Wet Ashing Method

Retention Efficiencies of the Ion Exchange Column(a)

Conc. of Influent Solution	Flow Rate (ml/min)	Activity(b) of Influent (c.p.m.)(c)	Activity of Effluent (c.p.m.)	Activity of Ashed Resin (c.p.m.)	Leakage Ratio = Activity Effluent / Activity Influent (%)
A. Uranyl Acetate (gm/100 ml)					
0.237	0.5	Not counted	0	84,943 $\alpha+\beta$ 6,210 α (d)	0
0.237	0.5	Not counted	0	101,368 $\alpha+\beta$ 11,093 α (e)	0
B. Mixed Fission Products (λ/100 ml)					
10	0.5	760 $\alpha+\beta$ 0.6 α	0	4,456 $\alpha+\beta$ 27.7 α (f)	0
10	0.5	760 $\alpha+\beta$ 0.6 α	0	4,290 $\alpha+\beta$ 21 α (f)	0

(a) Mixture of Permutit S-1 and Q resins

(b) Uncorrected for self-adsorption

(c) All c.p.m. values are net counting rates

(d) Assay of ashed resin on a single planchet

(e) Assay of ashed resin on two planchets and counts totalized

(f) It is recognized that the measured activity of the ashed resin exceeds the activity applied. This enigma has been observed in every case when the activity from M.F.P. in the ashed resin was determined. Some of this activity may be caused by the absorption of gamma rays with the production of secondary radiation and/or chemical reaction with the resin during the ashing procedure creating a more complex decay scheme.

(3) pretreatment with hydrogen peroxide. However, the direct dry ashing method proved to be the most feasible. This method is easy to perform and requires only two basic items of equipment, porcelain evaporating dishes and a muffle furnace. The dry ashing method requires less manipulation and supervision than the wet ashing method.

(a) Dry Ashing Procedure:

After the influent solution has been run through the ion exchange column, the resin is transferred quantitatively to a porcelain evaporating dish for drying.

The initial step is to dry the resin under an infrared heat lamp or in a 103°C oven. It is quite important that the resin be dried thoroughly before placing it into the muffle furnace to prevent the resin from expanding explosively with a "popcorn" effect. After the resin is thoroughly dry, it is placed in a cold muffle furnace. The furnace should be brought up to a maximum temperature of 350-400°C. The resin is left in the furnace for about five hours, or overnight, if convenient. The remaining ash contains the substances which were adsorbed on the resin. The ash may be dissolved with 6 M nitric acid and quantitatively transferred to a stainless steel planchet for drying and counting. Several adaptations of the method of final sample preparation have been used and their evaluation toward an improved procedure continues.

To evaluate the dry ashing method, the same radionuclide solutions (uranyl acetate and mixed fission products), resins and experimental procedures were used as for the evaluation of the wet ashing method. The activities of the dry ashed resins, presented in Table IV, show excellent agreement between corresponding $\alpha+\beta$ activities for each pair of ashed resins and fair agreement between the associated alpha activities. This agreement holds true

TABLE IV

Results of the Dry Ashing Method

Retention Efficiencies of the Ion Exchange Column(a)

Conc. of Influent Solution	Flow Rate (ml/min)	Activity(b) of Influent (c.p.m.)(c)	Activity of Effluent (c.p.m.)	Activity of Ashed Resin (c.p.m.)	Leakage Ratio = $\frac{\text{Activity Effluent}}{\text{Activity Influent}}$ (%)
A. Uranyl Acetate (gm/100 ml)					
0.05	3.5	39,329 $\alpha+\beta$ 10,495 α	0	33,424 $\alpha+\beta$ 9,771 α	0
0.05	8.0	39,329 $\alpha+\beta$ 10,495 α	0	32,358 $\alpha+\beta$ 6,520 α	0
B. Mixed Fission Products (λ/100 ml)					
10	8.0	760 $\alpha+\beta$ 0.6 α	0	1,019 $\alpha+\beta$ 4.8 α (d)	0
10	12.0	760 $\alpha+\beta$ 0.6 α	0	1,000 $\alpha+\beta$ 2.6 α (d)	0

(a) Mixture of Permutit S-1 and Q resins

(b) Uncorrected for self-adsorption

(c) All c.p.m. values are net counting rates

(d) It is recognized that the measured activity of the ashed resin exceeds the activity applied. This enigma has been observed in every case when the activity from M.F.P. in the ashed resin was determined. Some of this activity may be caused by the absorption of gamma rays with the production of secondary radiation and/or chemical reaction with the resin during the ashing procedure creating a more complex decay scheme.

for both groups of radionuclides. Further studies are required to ascertain the reproducibility of the dry ashing method.

5. Comparison of Wet and Dry Ashing Methods

Both of the ashing procedures described are useful depending on several variables, such as: (i) the quantity of resin required for radionuclide concentration, (ii) the reproducibility based on the number of liquid transfers and volatility of the nuclides present in the sample, (iii) the equipment and temperature available for ashing, (iv) the amount of supervision necessary, and (v) the time required for the reaction to go to completion. As both of these methods are further investigated there may be other pertinent considerations favoring one method.

According to the results obtained to date, the advantages of the wet ashing procedure are as follows:

(1) This procedure is particularly applicable to small quantities of resin, up to a quantity of 25 grams.

(2) Wet ashing may be carried out in a liquid medium and at a lower temperature than dry ashing.

(3) The wet ashing procedure is slightly faster than the dry ashing procedure.

The wet ashing technique has the disadvantage that it is limited to a resin quantity of approximately 25 grams. When the mass of resin exceeds this amount, problems of foaming and reaction vessel size are created.

The dry ashing procedure has a number of advantages over the wet ashing technique, which are as follows:

(1) Dry ashing is less subject to error than wet ashing because fewer liquid transfers are involved.

(2) Less equipment is required than for wet ashing.

(3) Little direct supervision is necessary. Several samples may be placed into the muffle furnace and left unattended until ashing is complete.

(4) Dry ashing is particularly useful when relatively non-volatile, heavy metals are adsorbed on the resin.

The dry ashing procedure requires a slightly greater period for completion which is a disadvantage as compared to the wet ashing method.

6. Separation of Filterable and Non-Filterable Matter

Radionuclides in very low concentrations, as when the activity approaches 10^{-8} μc/ml, may convert from ions to colloids. As colloids these radionuclides may be classed along with the colloids causing turbidity (clay, silt, finely divided organic matter, microscopic organisms) and other suspended solids. The size zone of at least one dimension of the dispersed material ranges from approximately 5 mμ to 500 mμ. Colloids may be retained on membrane filter media. These filters are available from one commercial source (6) with pore sizes from 10 mμ to 5 μ.

Millipore membrane filters, type HA (hydrosol assay), 47 mm diam. with a pore size of 0.45 ± 0.2 μ (450 mμ), readily available, were used for a preliminary study on the retention of activity by a membrane filter. The results, as shown in Table V, point out that up to three per cent of the $\alpha+\beta$ activity was retained by the filter when relatively high uranyl acetate concentrations were employed.

The alpha plus beta activity retained on the filter was found to be lower from water samples containing 1,805 p.p.m. of added solids. The lower values are probably due to the larger self-adsorption factor caused by the portion of the solids which were also retained on the filter. There

TABLE

Retention of Non-Filterable Matter on Millipore Filter, Type HA, 047 mm

Concentration of Uranyl Acetate[1]			Activity of Solution Applied to Filter (cpm)	Activity of Filter (cpm)	Activity Retained on Filter (%)	Remarks
(gm/ml)	Molar Concentration (x 10^{-3})	Parts per Million				
0.01/100	2.357	100	8,155 $\alpha+\beta$	145 $\alpha+\beta$	1.78	
			2,288 α	1.4 α	0.06	
0.01/200	1.178	50	8,155 $\alpha+\beta$	310 $\alpha+\beta$	3.80	
			2,288 α	3.1 α	0.14	
0.01/300	0.7856	33	8,155 $\alpha+\beta$	226 $\alpha+\beta$	2.76	
			2,288 α	1.4 α	0.06	
0.01/200	2.357	50	8,155 $\alpha+\beta$	67 $\alpha+\beta$	0.82	Water containing 1805 ppm total solids[2], excl. of UAc
			2,288 α	1.4 α	0.06	
0.1/200	11.78	500	50,802 $\alpha+\beta$	1,657 $\alpha+\beta$	3.26	
			18,324 α	27.1 α	0.15	
0.1/200	11.78	500	50,802 $\alpha+\beta$	502 $\alpha+\beta$	0.99	Water containing 1805 ppm total solids[2], excl. of UAc
			18,324 α	20.2 α	0.15	

[1] Uranyl Acetate = $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$

[2] Water containing 1805 ppm of total solids is composed of:

KCl	1.945 meq.
$FeCl_3 \cdot 6H_2O$	0.688 meq.
$CaCl_2$	1.442 meq.
$MgCl_2 \cdot 6H_2O$	0.728 meq.

Note: A flow rate of 50 ml/min was used in all cases.

appears to be no difference between alpha activities retained on the filter with and without the added 1,805 p.p.m. solids. This phenomenon can not be explained by self-adsorption. However, the alpha activity was so small that no meaningful comparisons can be made.

As pointed out by Barker (7) a portion of the total gross activity of natural water is contained in the suspended solids. A membrane filter serves the purpose of separating filterable and non-filterable matter from a water sample for a more detailed analysis of gross activity.

7. Elution

Although elution is a well established analytical procedure for removing adsorbed ions from ion exchange resins, it is not considered applicable in these studies for several reasons:

1. Elution generally requires large volumes of an elutriant which must be reduced first by evaporation before transfer to a 2-in. diam. planchet for drying and counting can be accomplished. Elution involves liquid transfers which tend to produce errors of manipulation.

2. It is probable that a single elutriant would not suffice. Assuming that the use of one elutriant were possible, it would still require its use at different concentrations and pH values. To assist in the selection of the type and concentration of elutriant, a qualitative analysis of the water sample is needed.

3. A time consuming separation of a mixed bed ion exchanger into its components is necessary before elution can be accomplished satisfactorily for determining gross alpha, beta and gamma activity.

D. FUTURE PLAN

On the basis of previous studies on the adsorption of radionuclides in water, the investigations will be intensified with natural and artificial radionuclides to determine the optimum conditions for concentrating them. Much work remains to be done to evaluate the best resin(s) for the different radionuclides and for mixtures of radionuclides. The determination of an optimum resin will be based on theoretical and practical considerations, such as: flow rate, solids concentration, mesh size, degree of cross linkage, and stability; whereas flow rate, solids concentration and pore size will be determining factors in the ultimate choice of a suitable membrane filter.

Investigations with natural and simulated stream and lake waters will be carried out to determine the amount of resin required to concentrate sufficient radioactivity for counting and to study interference by any minerals in the water.

A portable field apparatus, as shown in Figure 2, has been designed to separate filterable from non-filterable matter and pass the filtrate onto the ion exchange column. The non-filterable matter will be retained by a membrane filter. As illustrated in Figure 2, a plastic squeeze bottle is mounted above the millipore filter to provide the required pressure for filtration and to standardize the amount of water run through the resin.

Additional research is required to improve and refine both wet and dry ashing methods and to compare them for final choice of method.

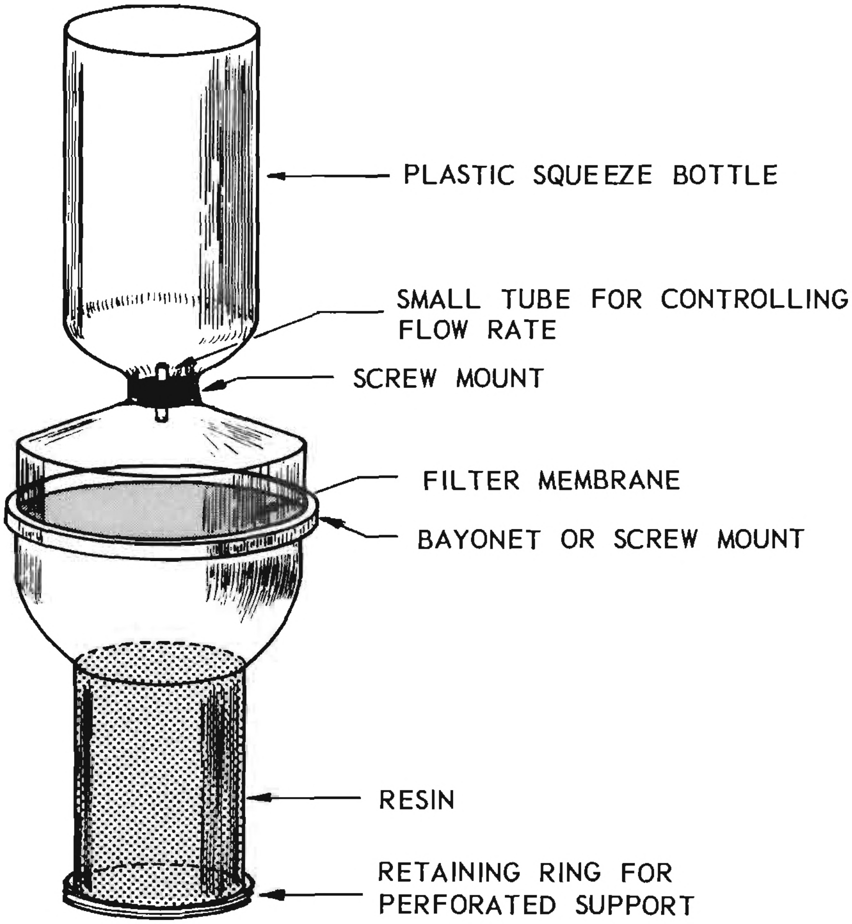

Figure 2. Portable Equipment for the Separation and Concentration of Low-Level Radioactivity in Water.

APPENDIX A

An Outline of Theories Related to Ion Exchange

Three theories are generally advanced to explain the mechanism of ion exchange: (i) the Crystal Lattice theory, (ii) the Double Layer theory and (iii) the Donnan Membrane theory. Each of these theories is outlined briefly below.

Crystal Lattice Theory

When placed in a highly polar medium, crystals composed of ionic solids may exhibit the exchange of ions at the surface of the crystal lattice. When an ionic solid is placed in a highly polar medium the net attractive forces binding the ion to the crystal are decreased. How readily these surface ions are replaced by other ions depends on several factors: (i) the nature of the forces binding the ion to the crystal, (ii) concentration of the exchanging ion, (iii) charge of the exchanging ions, (iv) sizes of the two ions, (v) accessibility of lattice ions, and (vi) solubility effects. The density of the ionic solid has much to do with exchangeability. Porous minerals such as the zeolites exhibit ion exchange with no prior subdivision. More dense substances require varying amounts of grinding before they will act as ion exchangers (8, 9).

Double Layer Theory

The Double Layer theory was first proposed by Helmholtz to explain the electrokinetic properties of colloids. Many attempts have been made to relate the Double Layer theory to certain ion exchange phenomena.

The Double Layer theory proposes an inner fixed layer and an outer diffuse layer of charges. The charged layers are due to adsorbed ions, there being no sharp boundary between the ions in the two layers. These adsorbed ions may be quite different from the ions in the inner portion of the colloid. Since the ions of the diffuse outer layer extend into the external liquid medium any change in the pH, or ionic concentration of the external liquid medium, will upset the equilibrium and a new equilibrium will be established. Therefore, the ionic concentration of the diffuse outer layer of the colloid may be constantly changing.

Conversely, in the crystal lattice system a number of exchange sites are available which must be satisfied, regardless of pH or concentration (8, 10).

Donnan Membrane Theory

The Donnan Membrane theory considers the unequal distribution of ions on two sides of a semipermeable membrane. One side contains an electrolyte, one ion of which is nonduffisible.

An exchange of ions must take place until the concentration ratios are equal on both sides of the membrane. The Donnan theory explains (i) the inability of free electrolytes to enter the resin phase of resins having a high exchange capacity, (ii) the effect of valency, (iii) the effects of solution volume and electrolyte concentration, and (iv) the effect of the fixed ion concentration of the resin phase. In applying the Donnan theory to ion exchange, the colloidal micelle to which is attached the exchangeable ion, is considered as the nondiffusible ion (resin particle) and the interface between the solid and liquid phases may be considered as the membrane. The Donnan Membrane theory does not conflict with either the Double Layer or the Crystal Lattice theories, but offers a more quantitative understanding of the phenomena of ion exchanges occurring in natural exchangers, such as the zeolites and the synthetic resins (8, 10).

Regardless of whether one approaches ion exchange from the standpoint of the Crystal Lattice theory, the Double Layer theory, or the Donnan Membrane theory, the laws of electroneutrality apply. The differences between the theories presented are only in the origin and position of the exchange site, but help to predict the behavior of a particular isotope on a particular type of resin.

Affinity and Selectivity

Ion exchange resins exhibit varying degrees of affinity and selectivity for different ions. Ion exchange is controlled by electrostatic forces and governed by the laws of electroneutrality.

The affinity of an ion exchange resin for a given ion is determined by the charge and the ionic radius of the exchanging ion.

The ionic hydration theory assumes that all ions in aqueous solution are hydrated and that the degree of hydration increases with increasing charge and decreasing crystallographic radius. The affinity for exchange increases as the degree of hydration increases. Since the ability of an ion to hydrate depends on the intensity of the charge on its surface, the degree of hydration of an ion is proportional to its valence and inversely proportional to its ionic radius (8, 9, 11).

At low concentrations (aq) and ordinary temperatures, exchange increases with increasing valency and increasing atomic number (at constant valence) of the exchanging ion.

Summary

The mechanism of ion exchange characteristic of modern synthetic ion exchange resins, particularly the resins which are copolymers composed of polymerized styrene and cross linked with divinyl benzene, probably combines part of all three theories discussed.

The polymer structure of an ion exchange resin is analogous to the structure of an ionic crystal. Therefore, pore size and rate of diffusion through the lattice to an exchange site are important in ion exchange resins.

The surface of the discrete particles of an ion exchange resin may be like that of a colloidal particle in which the surface of the colloid follows the same pattern as the crystal lattice of the parent ion.

The Donnan Membrane theory serves to explain the principle and mechanism of ion exclusion.

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G. LIST OF PUBLICATIONS

This grant was initiated on December 1, 1959. Therefore, no publications have as yet resulted from the work described in this progress report or from this grant.

H. STAFF

The following professional personnel have been employed on this project since December 1, 1959:

W. N. Grune	Principal Investigator	Dec. 1, 1959 to present	20% time
R. C. Peek, Jr.	Graduate Research Asst.	Dec. 1, 1959 to June 1, 1960	37.5% time
V. Florence	Research Assistant	Feb. 1, 1960 to present	70% time
E. E. Ozburn	Research Assistant	Dec. 1, 1960 to present	40% time
J. H. Mehaffey, Jr.	Research Assistant	Dec. 1, 1959 to present	12.5% time
J. E. Munzer(*)	Sr. Sanitary Engineer	Dec. 1, 1959 to present	5% time

Note: (*) Mr. Munzer is a Regular Corps officer of the U. S. Public Health Service. He is, therefore, not employed on this project but has continued his interest in this project for his Ph. D. thesis.

FINAL REPORT

RESEARCH GRANT RG-6837

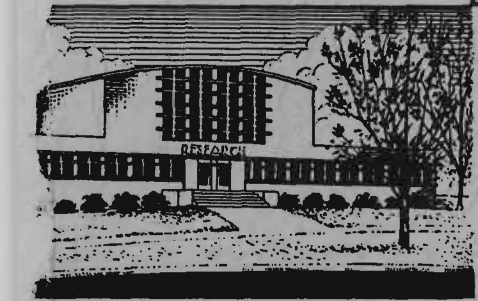
DETERMINATION OF LOW-LEVEL RADIOACTIVITY IN WATER

by

WERNER N. GRUNE
Professor of Sanitary Engineering
and
ROSS B. HUGHES, Research Assistant
GEORGE W. GIBSON, Graduate Research Assistant

Covering the Period
1 December 1959 to 31 May 1962

Performed for
NATIONAL INSTITUTES OF HEALTH
PUBLIC HEALTH SERVICE
DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
Washington 25, D.C.



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FINAL REPORT

RESEARCH GRANT RG-6837

DETERMINATION OF LOW-LEVEL RADIOACTIVITY IN WATER

By

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Project B-206

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PUBLIC HEALTH SERVICE
DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
Washington 25, D.C.

ABSTRACT

A review of the literature pertinent to this research has been made, with emphasis placed on ion exchange and its application to the field of radioactivity.

To aid in the analysis of experimental data, studies on planchet preparation and reproducibility of counts were conducted. The results of these studies are indicative of the planning required for statistical accuracy.

A method which will eliminate the need of transporting large volumes of water from the field to the laboratory for evaporation and radioassay has been investigated. This method employs the concentration of radionulcides from water by ion exchange resins to permit the detection of gross activity in water of the order of 10^{-8} μc/ml.

Radionuclides must be removed from the resin for counting since ion exchange resins can not be counted directly. The ususal technique, elution, is not considered practical for removing the radionuclides adsorbed on the resin for determining gross alpha, beta and gamma activity.

Two techniques for ashing ion exchange resins have been extensively explored, wet ashing and dry ashing. The dry ashing technique has been chosen as a better method.

Since the radioactivity in natural water is distributed between filterable and non-filterable matter, preliminary investigations into the separation of filterable and non-filterable matter by the use of membrane filter media have been conducted.

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A. STATEMENT AND PURPOSE OF RESEARCH

1. The Problem

Extensive research on the determination of low concentrations of radionuclides in water has been conducted. Investigations continue for an accurate method of analysis to detect activity in water near background level and to follow any increase from contamination. It is highly desirable that this method will distinguish between filterable and non-filterable forms of radioactivity. Determinations of this type are essential in every area of potential radioactive contamination and for the proper evaluation of data collected after contamination may have occurred. Therefore, an urgent need exists for a reliable, reproducible, and rapid method for the detection of gross activity of the order of 10^{-8} $\mu c/ml$ in water supplies.

The limitations of presently available equipment make it impossible to detect low-level radioactivity in water without first concentrating the radioactive substances. The concentration of activity must be sufficiently high to achieve a significant count in a reasonable length of time. Concentration may be accomplished by either chemical or physical techniques. Evaporation has been the most common method employed for the concentration of radionuclides from a given volume of water. Other methods, including precipitation, electrolysis, distillation, and solvent-extraction techniques, also have been employed for this purpose. The method of concentration by ion exchange lends itself to the analysis of a large number of radionuclides from water samples. It may prove to be more rapid than other radiochemical separation techniques now used for specific radionuclides. This method is especially attractive for the determination of gross activity and is suitable for mass sampling.

As a result of this and similar investigations, it is expected that additional information on the distribution of radioactivity between filterable and non-filterable matter will be obtained and that a contribution toward increasing the knowledge of the mechanism of ion exchange uptake will result. Based on such information, a simple and reliable method for rapid radioassays would find immediate and general application in this field.

2. Purpose of the Study

The purpose of this investigation is to develop a rapid and reproducible method for determining the gross alpha, beta, and gamma radioactivity in water. The basic problem of measuring an activity approaching 10^{-8} μc/ml in water samples is the concentration of the radionuclides. The most common method is evaporation which is subject to a number of limitations, including loss of short-lived isotopes that may die out during the period required for sample preparation. It is impractical to count 0.22 disintegration per minute for water containing radioactivity of 10^{-7} μc/ml with an instrument registering a background rate of 10 to 20 counts per minute. If a liter of water containing 10^{-7} μc/ml of activity is concentrated by evaporation and deposited in a thin layer on a planchet, it has an activity of 220 d.p.m. Because of self-absorption due to dissolved solids and geometry of the instrument only a portion of these disintegrations may be registered as counts. This makes it necessary to develop a method of radioassay to determine the gross alpha, beta and gamma activities in water at levels as low as 10^{-8} μc/ml, or 10 μμc/l. Measurements of activities in this low order of magnitude, or even lower, are needed to determine the background radioactivity in natural waters and to detect increases in activity before they reach levels which interfere with its use.

Specifically, the purpose of this research program is to develop a suitable technique for the separate determination of filterable and non-filterable radioactivity. It is proposed to concentrate the non-filterable activity by ion exchange resins. The objective of this method is to permit detection of gross alpha, beta and gamma activities of the order of 10^{-8} μc/ml. A later phase of this program consists of studies of improved methods for specific isotope identification.

B. RELATION TO THE PRESENT STATE OF KNOWLEDGE IN THE FIELD

The literature is replete with many studies devoted to the determination of specific radionuclides in water. Much of this work has been performed and reported during the past decade. Considerable information has become available on methods of radioanalysis for many important nuclides. Many of these methods apply primarily to activities several magnitudes greater than the maximum permissible levels, as recommended by the National Committee on Radiation Protection and published in National Bureau of Standards Handbooks 52(1), 61(2), and 69(3). During the past several years techniques for radionuclide identification have become increasingly refined with the advent of radiation energy spectroscopy. Multi-channel spectrum analyzers are available for the detection of radionuclides in low concentrations and with activities approaching background levels.

Concentration of radionuclides by ion exchange resins has been studied extensively. The investigations by Bunney, et al.(4)(16) and Freiling, et al.(5)(16) have been devoted largely to the adsorption of mixed fission products and the rare earths on Dowex 2 and Dowex 50. Others interested in the concentration of specific radionuclides include Bryant, et al.(6) who concentrated Strontium-90 on a modified Dowex 50-X4 cation exchange resin; Strelow (7) who studied the quantitative adsorption of thorium on Dowex 50 cation exchange resin; Karttunen and Evans(8) studied the separation of rhodium on Dowex 50W-X8 cation exchange resin; Maeck and Rein(9), using the same resin, separated radioiodine from mixed fission products to obtain an overall recovery of 97.1 per cent; Khopkar and De(10) studied the behavior of uranium on Amberlite IR-120 and Wish(11) separated tellurium from uranium by Dowex 2 anion exchange resins.

The results of several adsorption studies to determine the behavior of radionuclides on various ion exchange materials and measurements of specific distribution coefficients have been cited in the literature. Among these, investigations on the behavior of radionuclides on ion exchange media were reported by several groups(6)(7)(8)(10) and information on the behavior and distribution coefficients were reported by others(4)(5)(11).

The gamma ray spectrometric technique has been discussed by Hagee, et al.(12). DeLange(13) applied it to leached uranium-thorium ore analysis, while Kahn and Reynolds(14) discussed four methods of concentrating low levels of activity in water in preparation for gamma ray spectrometric analysis. Transport of radioactivity as related to exchange phenomena and aquatic biota have been reported by Barker(15).

Below is a discussion of the cited literature, the numbers referring to articles in the list of references.

Bunney, et al.(4) adsorbed americium, cerium (iii), molybdenum, protactinium, niobium, ruthenium, strontium, thorium, uranium (vi), yttrium, and zirconium on the anion exchange resin Dowex 2 from solutions of hydrochloric, nitric, and sulfuric acids (0.1N - conc.) and measured their distribution coefficients. Data to calculate the distribution coefficients was determined with a Beckman DU spectrophotometer, Fischer photometer, well-type scintillation counter, and by alpha and beta proportional counting. Distribution coefficients, K_d, for the elements studied ranged from a high value of 10,000 to a low value of 0.1. K_d is defined as the ratio of the activity per gram of resin to the activity per milliliter of solution adsorbed by the resin at equilibrium.

Freiling, et al.(5) equilibrated Dowex 2 anion exchange resin in the phosphate form with cesium, strontium, cerium (iii), zirconium (iv), tellurium (iv), cerium (iv), neptunium (iv), niobium (v), molybdenum (vi), and uranium (vi) in various strengths of phosphoric acid solutions and calculated their distribution coefficients. At low phosphoric acid concentrations cesium and tellurium (iv) are not adsorbed, strontium, cerium (iii) and cerium (iv) are weakly adsorbed and the remaining elements are strongly adsorbed.

A method for the determination of strontium in a sample which contains up to 0.1 gram of iron or uranium is described by Bryant, et al.(6). The authors state that the radiochemical yield is greater than 97 per cent. Strontium is adsorbed on a modified Dowex 50-X4 cation exchange resin and, after a growth period, the daughter Yttrium-90 is eluted and adsorbed on another column of the same cation exchange resin and eluted with α-hydroxyisobutyric acid. Counting was accomplished with a methane gas flow proportional counter.

The semiquantitative affinities of 23 cations for AG 50 resins in hydrochloric acids were investigated by Strelow(7) and thorium was found to be quantitatively adsorbed on Dowex 50 cation exchange resin. Elution curves were prepared for those cations which exhibited a high affinity for AG 50 resins. These curves were presented for cerium and thorium.

A nitric acid solution of fissium alloy containing uranium, molybdenum, ruthenium, palladium and zirconium from which uranium has been extracted, is fumed with perchloric acid by Karttunen and Evans(8).

The resulting solution is passed through Dowex 50W-X8 cation exchange resin. Rhodium is selectively eluted with 0.3 M hydrochloric acid and measured spectrophotometrically with tin chloride.

Maeck and Rein(9) separated radioiodine in fission product mixtures from the other activities by cation exchange. Radioiodine passes through the cation exchange column and then undergoes heterogeneous isotopic exchange with preformed silver iodide. Over-all recovery of I-131 is 97.1 per cent.

Studies on the quantitative adsorption and elution of milligram amounts of uranium (vi) with the cation exchange resin Amberlite IR-120 are reported by Khopkar and De(10). The separation of uranium from thorium, zirconium, cerium (iii), copper and nickel was also investigated. Uranium was determined by extraction with 8-quinolinol-chloroform and measured spectrophotometrically at 430 mμ with a Hilger Quartz spectrophotometer.

A scheme for separating tellurium from uranium is described by Wish(11). Tellurium is eluted from Dowex 2 anion exchange resin with less than 1N phosphoric acid. Quantitative yields and purities greater than 99 per cent were claimed for the separation and distribution coefficients measured.

The basis of gamma spectrometry and its application to the radiochemical assay of water are discussed by Hagee, et al.(12). Typical spectra for rainwater, milk and sludge from an old cistern are presented. The authors point out the advantages as well as the disadvantages of single and multiple-channel gamma ray spectrum analyzers for the identification of radionuclides in water.

Applications of presently available radiometric procedures to the analysis of naturally leached ores are discussed by DeLange(13) along with possible errors in radiometric analysis and a statistical treatment of the data. Gamma ray spectrometry was applied for the analysis of leached uranium-thorium ore samples and the results compared with other radiometric, chemical and mass spectrometric methods.

Kahn and Reynolds(14) describe a gamma spectrometric technique as well as four volume reduction methods for the determination of radionuclides in low concentrations in water. The four concentration methods are precipitation, ion exchange, distillation and extraction. A brief discussion of the sensitivity of gamma ray spectrometry is included.

Barker(15) discusses the factors which affect the transport of radioactivity in surface and ground water including the concentration of activity by aquatic biota and the ion exchange capacities of several clays for radiostrontium and radiocesium.

Freiling and Bunney(16) present a method of separation of the activities known to be found in uranium fission (i.e., Y, La, Ce, Pr, Nd, Pm, Sm and Eu), together with Gd and Tb using 250-500 mesh Dowex-50 cation exchange resin in the ammonium form and lactic acid eluants of various strengths at a pH of 3 and a temperature of 87°.

The separation of uranium from the ions interfering with its analysis is accomplished by Fisher and Kunin(17) by the adsorption of the uranium VI sulfate complex on a quaternary ammonium anion exchange resin. Uranium is eluted for analysis by dilute perchloric acid. A table of interfering anions is presented.

Setter, et al.(18) discuss the filter and evaporation method for determining nonvolatile radioactive contamination in water. Levels as low as 10 μμc per liter (beta) and 2 μμc per liter (alpha) are detectable. Sample preparation and counting techniques are discussed.

Tompkins, et al.(19), by the process of elution from ion-exchange columns with complex-forming reagents, separate trace amounts to macroscopic amounts of cationic species from fission product radioisotopes, including individual rare earths. The application of the results to the problem of curie-level fission product separation is shown and the necessary development steps required for the quantitative separation of large masses of rare earth elements are outlined. Elution with various solutions of citrate separates the various adsorbed elements.

C. RESULTS OF EXPERIMENTAL WORK

1. Separation of Filterable and Non-Filterable Matter

Radionuclides in very low concentrations, as when the activity approaches 10^{-8} μc/ml, may convert from ions to colloids. As colloids these radionuclides may be classed along with the colloids causing turbidity (clay, silt, finely divided organic matter, microscopic organisms) and other suspended solids. The size zone of at least one dimension of the dispersed material ranges from approximately 5 mμ to 500 mμ. Colloids may be retained on membrane filter media. These filters are available from one commercial source(20) with pore sizes from 10 mμ to 5 μ.

A portable field apparatus, as shown in Figure 1, has been designed to separate filterable from non-filterable matter and pass the filtrate onto the ion exchange column. The non-filterable matter will be retained by a membrane filter. As illustrated in Figure 1, a provision for a vacuum line is made to supply the required pressure drop for the filtration.

Millipore membrane filters, type HA (hydrosol assay), 47 mm diam. with a pore size of 0.45 ± 0.2 μ (450 mμ), were used for a preliminary study on the retention of activity by a membrane filter. The results, as shown in Table I, point out that up to three per cent of the $\alpha+\beta$ activity was retained by the filter when relatively high uranyl acetate concentrations were employed.

The alpha plus beta activity retained on the filter was found to be lower from water samples containing 1,805 p.p.m. of added solids. The lower values are probably due to the larger self-adsorption factor

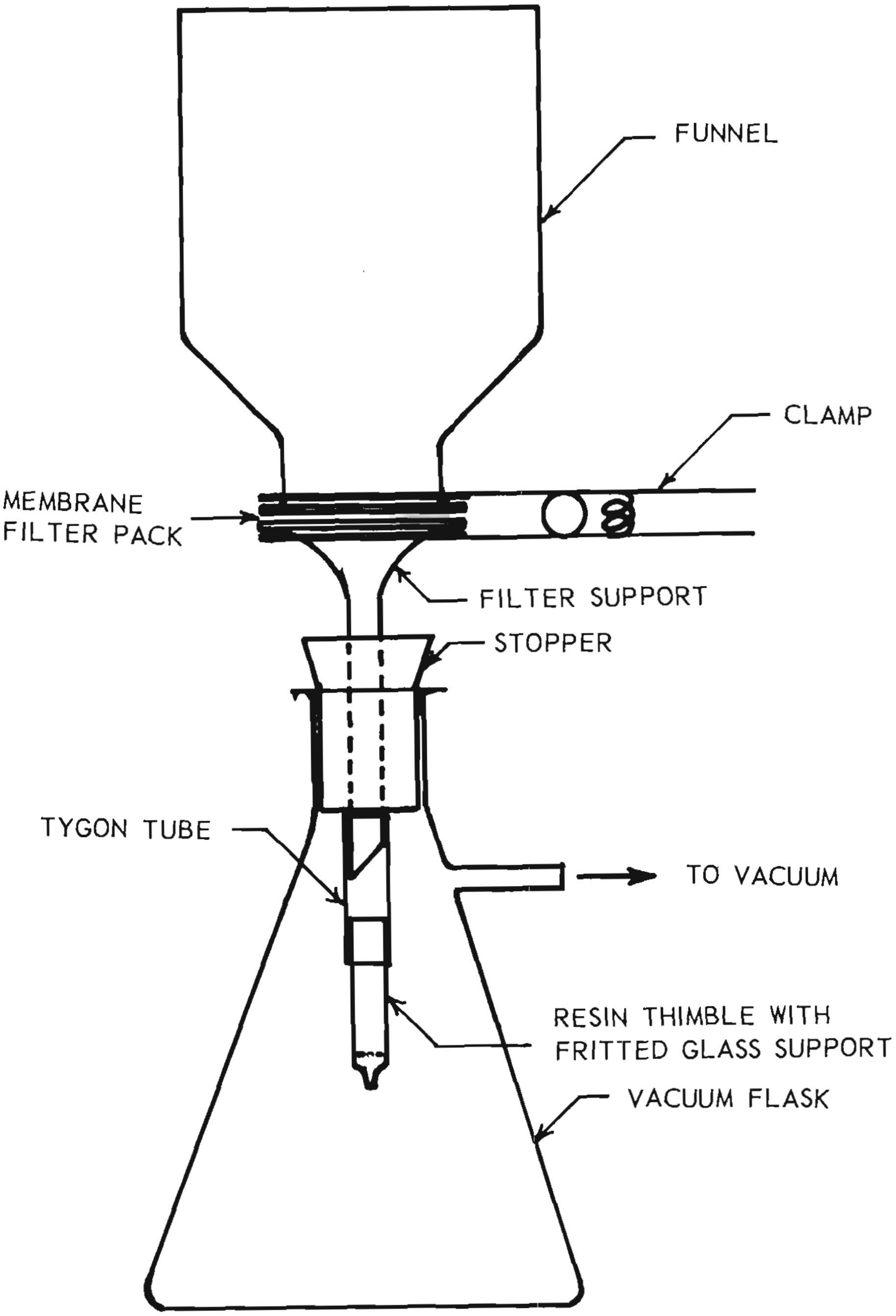

Figure 1. Apparatus for Separation and Concentration of Radioactivity in Water.

TABLE I

Retention of Non-Filterable Matter on Millipore Filter, Type HA, 047 mm

Concentration of Uranyl Acetate(a)			Activity of Solution Applied to Filter (cpm)	Activity of Filter (cpm)	Activity Retained on Filter (%)	Remarks
(gm/ml)	Molar Concentration (x 10^{-3})	Parts per Million				
0.01/100	2.357	100	8,155 $\alpha+\beta$	145 $\alpha+\beta$	1.78	
			2,288 α	1.4 α	0.06	
0.01/200	1.178	50	8,155 $\alpha+\beta$	310 $\alpha+\beta$	3.80	
			2,288 α	3.1 α	0.14	
0.01/300	0.7856	33	8,155 $\alpha+\beta$	226 $\alpha+\beta$	2.76	
			2,288 α	1.4 α	0.06	
0.01/200	2.357	50	8,155 $\alpha+\beta$	67 $\alpha+\beta$	0.82	Water containing 1805 ppm total solids(b) excl. of UAc
			2,288 α	1.4 α	0.06	
0.1/200	11.78	500	50,802 $\alpha+\beta$	1,657 $\alpha+\beta$	3.26	
			18,324 α	27.1 α	0.15	
0.1/200	11.78	500	50,802 $\alpha+\beta$	502 $\alpha+\beta$	0.99	Water containing 1805 ppm total solids(b) excl. of UAc
			18,324 α	20.2 α	0.15	

(a) Uranyl Acetate = $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$

(b) Water containing 1805 ppm of total solids is composed of:

KCl	1.945 meq.
$FeCl_3 \cdot 6H_2O$	0.688 meq.
$CaCl_2$	1.442 meq.
$MgCl_2 \cdot 6H_2O$	0.728 meq.

Note: A flow rate of 50 ml/min was used in all cases.

caused by the portion of the solids which were also retained on the filter. There appears to be no difference between alpha activities retained on the filter with and without the added 1,805 p.p.m. solids. This phenomenon can not be explained by self-adsorption. However, the alpha activity was so small that no meaningful comparisons can be made.

As pointed out by Barker(15), a portion of the total gross activity of natural water is contained in the suspended solids. A membrane filter serves the purpose of separating filterable and non-filterable matter from a water sample for a more detailed analysis of gross activity.

The results obtained from experiments using flocculating agents to facilitate the filtration of filterable and non-filterable components of a water sample are shown in Table II. This table shows that the fastest and most complete flocculation was obtained with the use of acetic acid or calcium chloride and heating up to the boiling point. The concentration of these two agents apparently is not critical as is evidenced by the identical results obtained in these runs.

TABLE II

Results of Flocculation Experiments

Volume of Sample	Type of Sample	Flocculant	Time Allowed for Settling	Results
250 ml	muddy[(a)] creek water	Heat to boiling point for 1, 5 and 10 min.	16 hrs.	Incomplete flocculation
250 ml	muddy creek water	Boil for 1 to 5 minutes	16 hrs.	Incomplete flocculation
250 ml	muddy creek water	5 ml conc. HCl	4 hrs.	Incomplete flocculation
250 ml	muddy creek water	5 ml conc. HNO_3	4 hrs.	Incomplete flocculation
250 ml	muddy creek water	5 ml conc. H_2SO_4	4 hrs.	Incomplete flocculation
250 ml	muddy creek water	5 ml conc. oxalic acid	4 hrs.	Incomplete flocculation
250 ml	muddy creek water	5 ml conc. acetic acid	2 hrs.	Complete flocculation
250 ml	Kaolinite 1000 ppm	5 ml conc. acetic acid, heat to boiling point	1 hr.	Complete flocculation
250 ml	Bentonite 1000 ppm	5 ml conc. acetic acid, heat to boiling point	2 hrs.	Complete flocculation
250 ml	muddy creek water	5 ml conc. acetic acid, heat to boiling point	1 hr.	Complete flocculation
250 ml	muddy creek water	1 gm $CaCl_2$ heat to boiling point	1 hr.	Complete flocculation
250 ml	Kaolinite 1000 ppm	1 gm $CaCl_2$ heat to boiling point	1 hr.	Complete flocculation
250 ml	Bentonite 1000 ppm	1 gm $CaCl_2$ heat to boiling point	1 hr.	Complete flocculation
250 ml	muddy creek water	Conc. NH_4OH 1, 5, 10, 15 and 20 ml	16 hrs.	No flocculation
250 ml	muddy creek water	Conc. NH_4OH 0.1 and 0.5 ml	16 hrs.	No flocculation
500 ml	muddy creek water	Separan NP 10[(b)] 1, 2.5, 5, 7.5, 10, 15, 20 and 25 ml of 0.05% soln. and 10 ml of 1.0% soln.	16 hrs.	Incomplete flocculation
500 ml	muddy creek water	Separan NP20[(b)] 1, 2.5, 5, 7.5, 10, 15, 20 and 25 ml of 0.05% soln. and 10 ml of 1.0% soln.	16 hrs.	Incomplete flocculation

Table continues on next page

TABLE II

Results of Flocculation Experiments
Continued

Volume of Sample	Type of Sample	Flocculant	Time Allowed for Settling	Results
500 ml	muddy creek water	Separan AP 30 (b) 1, 2.5, 5, 7.5, 10, 15, 20 and 25 ml of 0.05% soln. and 10 ml of 1.02 soln.	16 hrs.	Incomplete flocculation
500 ml	muddy creek	egg albumin soln. (c) 5, 10, 20, 30, 40 and 50 ml of prepared soln.	24 hrs.	No flocculation
100 ml	muddy creek water	1.0 ml Edistin soln. (d) pH adjusted from 6.68 of original water sample to 1.90, 2.50, 3.00, 3.49, 4.00, 4.51, 5.00, 5.48 and slightly basic in 10 samples	24 hrs.	No flocculation

(a) Creek water from Douglas County, Georgia, 7.2 miles east of the Carrol County line on Highway 166. These water samples contained suspended red clays and had a turbidity of 250.

(b) Separan NP 10, NP 20, AP 30, are trade names for synthetic flocculants manufactured by Dow Chemical Company, Abbott Road Building, Midland, Michigan. Separan NP 10 and NP 20 are non-ionic water soluble polyacrylamide flocculating agents and Separan AP 30 is a synthetic, high molecular weight, anonic polymer effective in neutral and basic solutions.

(c) This egg albumin solution was prepared by extracting the albumin from one medium size egg and diluting to two liters with distilled water.

(d) Edistin is a protein of the globulin class which is extracted from hemp seed.

2. Radionuclide Concentration by Ion Exchange Resins

It has been established rather conclusively that radionuclides are removed from solution by ion exchange resins, although little work has been reported on the removal of very low-level mixtures of radionuclides in water.

Most of the naturally occurring radionuclides are fairly well adsorbed by ion exchange media. Almost all of these radionuclides or their complexes are tri- or tetra valent ions. Many of the cations have small ionic radii and are considerably hydrated. Uranium complexes particularly form a number of anionic complexes with nitrates, sulfates, chlorides, carbonates, etc.

The only naturally occurring radionuclides likely to be present in water in measurable amounts are Uranium-238, Thorium-232, and Radium-226 and their disintegration products. These radionuclides are found to be adsorbed quite well by ion exchange resins and both uranium and thorium are quantitatively adsorbed.

Some of the factors governing the exchange of ions are: (i) ionic radius, (ii) activity of the ion, (iii) valence state, (iv) hydration of both the resin and the ion, (v) diffusion rate through the resin, (vi) flow rate through the column, and (vii) temperature.

All of these factors have to be taken into consideration in selecting the resin(s) which will best concentrate a nuclide, or a group of nuclides, from a water sample. If the resin is very highly cross linked, diffusion of the exchanging ions will be hampered, if not completely stopped. If the mesh size of the resin is too small, the flow rate will be affected adversely. Rate of flow and degree of cross linkage also influence the speed of equilibrium. The capacity for exchange and stability of the resins used are also important in determining the most suitable resin(s).

From the results obtained it appears that resins of medium cross linkage, high exchange capacity, high stability, and 40-60 mesh size for optimum flow rate, will best concentrate radionuclides. Good results have been obtained with a polystyrene, sulfonated cation exchanger in the hydrogen form, and a highly basic quaternary amine polystyrene anion exchanger in the hydroxyl form.

Investigations have been performed with mixed resins because radionuclides exist as both cationic and anionic complexes. According to Swope (21) and others, a bed of mixed cation and anion exchange resins will concentrate radionuclides more efficiently from a given sample of water than will monobeds containing either anion or cation exchangers.

3. Wet Ashing Method

A method for wet ashing ion exchange resins has been investigated, using a mixture of concentrated perchloric, nitric and sulfuric acids. This method does not require any highly specialized equipment. The prime requisite is the availability of a well ventilated fume hood.

During the ashing procedure, a part of the sulfuric acid is decomposed into sulfur trioxide and water, the sulfur trioxide being driven off with heat. After ashing is completed the substances adsorbed on the resin are contained in a small volume of concentrated sulfuric acid.

(a) Wet Ashing Procedure:

After the sample has been run through the column, the resin is removed from its container and placed in an evaporating dish for drying. When dry, the resin is transferred to a one liter erlenmeyer flask. Three ml of concentrated perchloric acid for each gram of dry resin, plus 10 ml excess perchloric acid, are added. A volume equal to that of the perchloric acid, consisting of two-thirds volume concentrated nitric acid and one-third volume concentrated sulfuric acid is added. Finally, a catalytic amount (approximately 3 ml) of saturated vanadium pentoxide solution in concentrated ammonium hydroxide is added. The flask is placed on a suitable heating apparatus (either an electric Kjeldahl heater or a good hotplate) and heated gently. Electric heating is necessary to obtain even heat distribution. The reaction must be carried out in a fume hood because the fumes are irritating and corrosive. The reaction is accompanied by a vigorous production of foam which may be controlled by alternately cooling and heating the mixture or use of Dow-Corning Antifoam A. The latter leaves a residue, however. Completion of the reaction is indicated by the vigorous evolution of perchloric acid fumes and chlorine.

The wet combustion reaction takes from two to three hours for completion depending on the amount of resin used, varying from 15 to 25 grams.

The same radionuclide solution was applied to pairs of mixed ion exchange resins. After collection of the radioactivity on the beds, the resins were subjected to the wet ashing method. A solution of uranyl acetate (0.237 gm/100 ml) was applied to each of a pair of mixed bed resins and a solution of mixed fission products (10 λ/100 ml) was run through each of another pair of mixed bed resins. Values of the activities of the ashed resins, presented in Table III, show good agreement between corresponding α and $\alpha + \beta$ activities, associated respectively with each pair of ashed resins, regardless of whether uranyl acetate or mixed fission products were applied to the column.

TABLE III

Results of the Wet Ashing Method

Retention Efficiencies of the Ion Exchange Column(a)

Conc. of Influent Solution	Flow Rate (ml/min)	Activity(b) of Influent (cpm)(c)	Activity of Effluent (cpm)	Activity of Ashed Resin (cpm)	Leakage Ratio = $\frac{\text{Activity Effluent}}{\text{Activity Influent}}$ (%)
A. Uranyl Acetate (gm/100 ml)					
0.237	0.5	Not counted	0	84,943 $\alpha+\beta$) 6,210 α) (d)	0
0.237	0.5	Not counted	0	101,368 $\alpha+\beta$) 11,093 α) (e)	0
0.1	3.5	39,329 $\alpha+\beta$ 10,492 α	0	7,378 $\alpha+\beta$ 630 α	0
0.1	8.0	50,802 $\alpha+\beta$ 18,324 α	0	4,482 $\alpha+\beta$ 416 α	0
0.1	12.0	50,802 $\alpha+\beta$ 18,324 α	0	28,150 $\alpha+\beta$ 4,824 α	0
B. Mixed Fission Products (λ/100 ml)					
10	3.5	760 $\alpha+\beta$ 0.6 α	0	409 $\alpha+\beta$ 1.0 α	0
10	8.0	760 $\alpha+\beta$ 0.6 α	0	368 $\alpha+\beta$ 0.6 α	0

(a) Mixture of Permutit S-1 and Q resins

(b) Uncorrected for self-adsorption

(c) All cpm values are net counting rates

(d) Assay of ashed resin on a single planchet

(e) Assay of ashed resin on two planchets and counts totalized

4. Dry Ashing Method

A method of dry ashing ion exchange resins has been investigated. Several variations of this technique have been employed beyond the direct dry ashing method. These variations included dry ashing with the following oxidizing agents: (1) magnesium nitrate, (2) ammonium nitrate, and (3) pretreatment with hydrogen peroxide. However, the direct dry ashing method proved to be the most feasible. This method is easy to perform and requires only two basic items of equipment, porcelain evaporating dishes and a muffle furnace. For resin samples less than 15 ml the ashing may be accomplished directly in a 2 in x 5/16 in planchet. The dry ashing method requires less manipulation and supervision than the wet ashing method.

(a) Dry Ashing Procedure:

After the influent solution has been run through the ion exchange column, the resin is transferred quantitatively to a porcelain evaporating dish for drying.

The initial step is to dry the resin under an infrared heat lamp or in a 103°C oven. It is quite important that the resin be dried thoroughly before placing it into the muffle furnace to prevent the resin from expanding explosively with a "popcorn" effect. After the resin is thoroughly dry, it is placed in a cold muffle furnace. The furnace should be brought up to a maximum temperature of 350-400°C. The resin is left in the furnace for about five hours, or overnight if convenient. The remaining ash contains the substances which were adsorbed on the resin. The ash may be dissolved with 6 M nitric acid and quantitatively transferred to a stainless steel planchet for drying and counting. Several adaptations of the method of final sample preparation have been used and the most successful for the 15 ml resin samples employed is to dry ash directly on a 2-inch planchet.

To evaluate the dry ashing method, the same radionuclide solutions (uranyl acetate and mixed fission products), resins and experimental procedures were used as for the evaluation of the wet ashing method. The activities of the dry ashed resins, presented in Table IV, show excellent agreement between corresponding $\alpha + \beta$ activities for each pair of ashed resins and fair agreement between the associated alpha activities. This agreement holds true for both groups of radionuclides.

A typical sample of results of the dry ashing technique can be seen in Figure 2. Each planchet in the top row contains a 15 ml sample of backwashed and drained Permutit Q and S-1 resins in the sodium and chloride form, respectively, mixed in a ratio of Q to S-1 = 0.9 by volume. The samples were dried at 110°C overnight and then ashed overnight at 600°C. In the bottom row, the planchets on the left and right contain 15 ml of Dowex 50W-X8 in the hydrogen and radium forms, respectively, dried and ashed as above. After ashing, the sample on the left was treated with a solution of Lucite in acetone in order to fix the residue on the planchet and prevent sample loss. Ther center planchet in the lower row is a wet ashed sample of Permutit Q and S-1. The texture of this sample appears satisfactory, however, the total wet ashing procedure for this sample took 10 hours to complete.

TABLE IV

Results of the Dry Ashing Method

Retention Efficiencies of the Ion Exchange Column(a)

Conc. of Influent Solution	Flow Rate (ml/min)	Activity(b) of Influent (cpm)(c)	Activity of Effluent (cpm)	Activity of Ashed Resin (cpm)	Leakage Ratio = $\frac{\text{Activity Effluent}}{\text{Activity Influent}}$ (%)
A. Uranyl Acetate (gm/100 ml)					
0.05	3.5	39,329 α+β 10,495 α	0	33,424 α+β 9,771 α	0
0.05	8.0	39,329 α+β 10,495 α	0	32,358 α+β 6,520 α	0
0.1	12.0	50,502 α+β 18,324 α	0	18,748 α+β 2,928 α	0
B. Mixed Fission Products (λ/100 ml)					
10	8.0	760 α+β 0.6 α	0	1,019 α+β) (d) 4.8 α)	0
10	12.0	760 α+β 0.6 α	0	1,000 α+β) (d) 2.6 α)	0
10	3.5	760 α+β 0.6 α	0	616 α+β 2.3 α	0
10	12.0	760 α+β 0.6 α	0	824 α+β) (d) 3.0 α)	0

(a) Mixture of Permutit S-1 and Q resins

(b) Uncorrected for self-adsorption

(c) All cpm values are net counting rates

(d) It is recognized that the measured activity of the ashed resin exceeds the activity applied. This enigma has been observed in many cases when the activity from M.F.P. in the ashed resin was determined. Some of this activity may be caused by the absorption of gamma rays with the production of secondary radiation and/or chemical reaction with the resin during the ashing procedure creating a more complex decay scheme.

TOP ROW PLANCHETS

Each of the four samples contains a 15 ml sample of dry ashed Permutit Q and S-1 resin mixture in the sodium and chloride forms, respectively. Samples were dried at 110°C, then ashed at 600°C.

BOTTOM ROW PLANCHETS (from left to right)

(1) Sample of Dowex 50W-X8 in the hydrogen form, dry ashed and fixed with Lucite and acetone solution; (2) Sample of wet ashed Permutit Q and S-1 mixture; (3) Sample of Dowex 50W-X8 in the sodium form, dry ashed without any further treatment.

Figure 2. Typical Samples of Wet and Dry Ashed Resins.

5. Elution

Although elution is a well established analytical procedure for removing adsorbed ions from ion exchange resins, it is not considered applicable in these studies for several reasons:

1. Elution generally requires large volumes of an elutriant which must be reduced first by evaporation before transfer to a 2-inch diameter planchet for drying and counting. Elution involves liquid transfers which tend to produce errors of manipulation.

2. It is probable that a single elutriant would not suffice. Assuming that the use of one elutriant were possible, it would still require its use at different concentrations and pH values. To assist in the selection of the type and concentration of elutriant, a qualitative analysis of the water sample is needed.

3. A time consuming separation of a mixed bed ion exchanger into its components is necessary before elution can be accomplished satisfactorily for determining gross alpha, beta and gamma activity.

Table V summarizes the information obtained from a thorough library study. Based on the available information, the feasibility of using an elution technique for the removal of adsorbed radionuclides on ion exchange resins was eliminated as practical for a rapid radioassay technique.

TABLE V

Literature Survey on Elution from Ion Exchange Resins

Element and State	Type Ion Exchange Resin	Eluant	Remarks	Reference
Rb, Cs, Sr, Ba, Y, As(V), Rh (III), Ag(I), Br^- rare earths and most of the fission products	Strong anion	Conc. HCl and then 0.5 M HCl	Conc. HCl and then dilute HCl to remove all of this group. No single elution will do.	(22)
U(VI)	Strong anion	H_2SO_4 hot 1-2M	Not eluted with HCl from 0-9M* - conc. Not eluted with HNO_3 from 1M -8M - conc. * Peak adsorption	(22)
Zn(IV), Nb(V)	Strong anion	HF-HCl mixture	Not removed with dilute HCl	(22)
Mo(VI), Tc(VII)	Strong anion	HF-HCl mixture	Not removed with conc. HCl	(22)
Ru(IV), Rh(IV), Pd(II), Pd(IV)	Strong anion	Displacement with Zn(II) or Cd(II) complexes for Pd(II), 4M HCl for Rh(IV) and Pd(IV); Ru(IV) is unknown	Pd(II) is <u>very</u> strongly adsorbed	(22)
Ag	Strong anion	Conc. HCl	Ag absorbed at low M HCl only	(22)
Zn, Cd(II)	Strong anion	Very dilute HCl or H_2O	Adsorbed from 0.1 - 2.0M HCl solution	(22)
Ge(IV), Sn(II), Sn(IV)	Strong anion	HF-HCl mixture, or oxalate solutions	Not eluted with HCl	(22)
As(III), Sb(III), Sb(V)	Strong anion	HF-HCl mixture, or oxalate solutions	Not eluted with HCl, HF-HCl mixture must be correct conc.	(22)
U(VI) in sulfate complex	Strong anion, Amberlite XE-117 in sulfate form	1M $HClO_4$	Sulfate complex form not necessary for successful application of $HClO_4$ eluant	(17)

Table V continued on next page

TABLE V

Literature Survey on Elution from Ion Exchange Resins
Continued

Element and State	Type Ion Exchange Resin	Eluant	Remarks	Reference
Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Td, (from U fission)	Cation, Dowex 50, 250-500 mesh, NH_3 form	1M lactic acid, various dilutions of 1M for separations	Citric acid has also been used	(16)
Ti	Strongly basic anion	8M HCl	These elements were left on the resin after elutriation with 2.5% HF and are successively eluted in the order listed. The eluate of the 2.5% HF contains Ce, Al, Mn, Ni, Cr, Co and Fe, which passed through a second strongly basic anion exchange column	(23)
W		10% HF+60% HCl		
Mo		20% HF+25% HCl		
Nb		14% NH_4Cl+4% HF		
Ta		14% NH_4Cl plus 4% NH_4F		
Al, Mn, Ni, Cr	Strongly basic anion	9 M HCl	These were elutriated from the first column with 2.5% HF and taken up on a second column and elutriated	(23)
Co		4 M HCl		
Fe		0.5 M HCl		
Zn, Cb, Y, Ce, Sr, Ba, Nd, Eu, Pn, La	Amberlite IR-1 (or) IR-100, 40-60 mesh H^+ form	5% citric acid adjusted to pH of 5 with NH_4OH	Various pH ranges used for separation of individual ions but the most difficult removed with 5% citric acid. Adsorbed from 0.01 - 0.01N acid solution	(19)
U	Amberlite XE-117, Type 2 or Dowex 2 (sulfate form) anion	1M $HClO_4$ (hot) or HCl	Adsorbed from solution containing 10 ml 6% sulfurious acid in 100 ml, pH controlled between 1.0 and 1.5 with H_2SO_4	(24)
Al, Ni, Ti, Co	Dowex 1-X8 200-400 mesh, Cl form, strong basic anion	7 M HCl followed by 5 M HCl	All adsorbed from 7 M HCl solution	(25)
Cu		3 M HCl		
Fe		0.5 M HCl		
Pb	Amberlite IRA-400 anion	0.01 N HCl	Adsorbed from N HCl	(29)

Table V continued on next page

TABLE V

Literature Survey on Elution from Ion Exchange Resins.
Continued

Element and State	Type Ion Exchange Resin	Eluant	Remarks	Reference
Zn	Dowex 2	12 N HCl + 0.4 N HF	Used very small columns (0.2 cm diam.)and results are said not to directly apply to larger columns by other authors	(27)
U, Mo		4 N HCl + 0.4 N HF		
Np		7 N HCl + 0.10 N HF		
Nb		6 N HCl + 0.10 N HF		
Rare earths and Zr	Dowex 50 cation	Conc. HCl	Thorium strongly adsorbed and not eluted with conc. HCl from Dowex 50. The resin is oven ashed at 1250° C to determine Th gravametrically	(7)
U(VI)	Amberlite IR-120 and Dowex A-1, cation	0.5 M oxalic acid	This article shows greater than 100% recovery in U elutions (by weights)	(10)
Rare earths		5 N HCl		
Se (IV), Te (IV), Br^-, I^-	strong anion	CH_3OH for Se(IV), NO_3^- solns. for Br^- and I^-, oxalate solutions for Te(VI)	Not eluted with 8M-conc. for Br^- and I^-.	(22)

6. Comparison of Wet and Dry Ashing Methods

Both of the ashing procedures described are useful depending on several variables, such as: (i) the quantity of resin required for radionuclide concentration, (ii) the reproducibility based on the number of liquid transfers and volatility of the nuclides present in the sample, (iii) the equipment and temperature available for ashing, (iv) the amount of supervision necessary, and (v) the time required for the reaction to go to completion.

According to the results obtained,the advantages of the wet ashing procedure are as follows:

(1) This procedure is particularly applicable to small quantities of resin, up to a quantity of 25 grams.

(2) Wet ashing may be carried out in a liquid medium and at a lower temperature than dry ashing.

(3) The wet ashing procedure is slightly faster than the dry ashing procedure.

The wet ashing technique has the disadvantage that it is limited to a resin quantity of approximately 25 grams. This method also requires constant attention during its initial digestion stages. When the mass of resin exceeds 25 grams, problems of foaming and reaction vessel size are created.

The dry ashing procedure has a number of advantages over the wet ashing technique, which are as follows:

(1) Dry ashing is less subject to error than wet ashing because fewer liquid transfers are involved.

(2) Less equipment is required than for wet ashing.

(3) Little direct supervision is necessary. Several samples may be placed into the muffle furnace and left unattended until ashing is complete.

(4) Dry ashing is particularly useful when relatively non-volatile, heavy metals are adsorbed on the resin.

The dry ashing procedure requires a slightly greater period for completion which is a disadvantage as compared to the wet ashing method.

7. Reproducibility of Sample Preparation and Accuracy of Counting

An important part of any report is an indication of the reliability of the results. Also, as an integral part of the planning of any experiment it is necessary to establish the degree of reliability expected for the results. Besides the usual errors arising from common laboratory manipulations, there are errors characteristic of radioactivity measurements. The latter may arise from the following sources: (i) random emission of radiation from a source, (ii) detection of the nuclear radiation, and (iii) technique of radiation measurement. Radiation intensity variations resulting from interaction of the radiation with matter before reaching the detector may be listed as follows:

(i) Absorption of alpha, beta and gamma rays, the latter with the production of secondary radiation;

(ii) Self-adsorption of radiation;

(iii) Scattering and backscattering of radiation.

A given experimental result will have an overall observed uncertainty resulting from one or more of these factors.

The various errors enumerated above could be classified as either (i) determinate errors, or (ii) indeterminate errors. The determinate error can be minimized by applying known correction or calibration factors.

After allowance is made for all determinate errors, the values obtained from a set of supposedly identical data will still show some variation. Indeterminate errors are minimized by refining experimental technique. When they are treated in accordance with probability considerations, it is possible to express an experimental result with an error for which a probability of occurrence may be assigned. It may be pointed out that even the correction or calibration factors applied to minimize determinate errors are subject to inherent indeterminate errors.

In planning the organized collection of laboratory data on studies for the determination of low-level radioactivity in water, and the analysis of the significance of this data, it was necessary to evaluate these variables: (i) the reproducibility of activity determinations from a single source of radiation, (ii) the difference between the activity from two similarly prepared sources of radiation over a period of time, and (iii) the reproducibility of sample preparation as determined from a number of samples, prepared and counted on the same day.

To examine the reproducibility of alpha and beta activity determinations from one sample of mixed fission products (10 λ of M.F.P.), the sample was counted for one hour each day over a period of 17 days. The variations of the net counting rates are presented in Figure 3. It shows that the arithmetic mean for the alpha activity is 22.3 cpm, which is the best estimate of the true value of only indeterminate errors are assumed to be present. The set of measured values show the usual scatter. For the given set of measurements there is a probability of 68.3 per cent that a single value will not show a deviation from the mean by more than 9.1 cpm. Similarly, 68.3 per cent of the time, counts ranging between 13.2 and 31.4 cpm are expected due to chance factors alone.

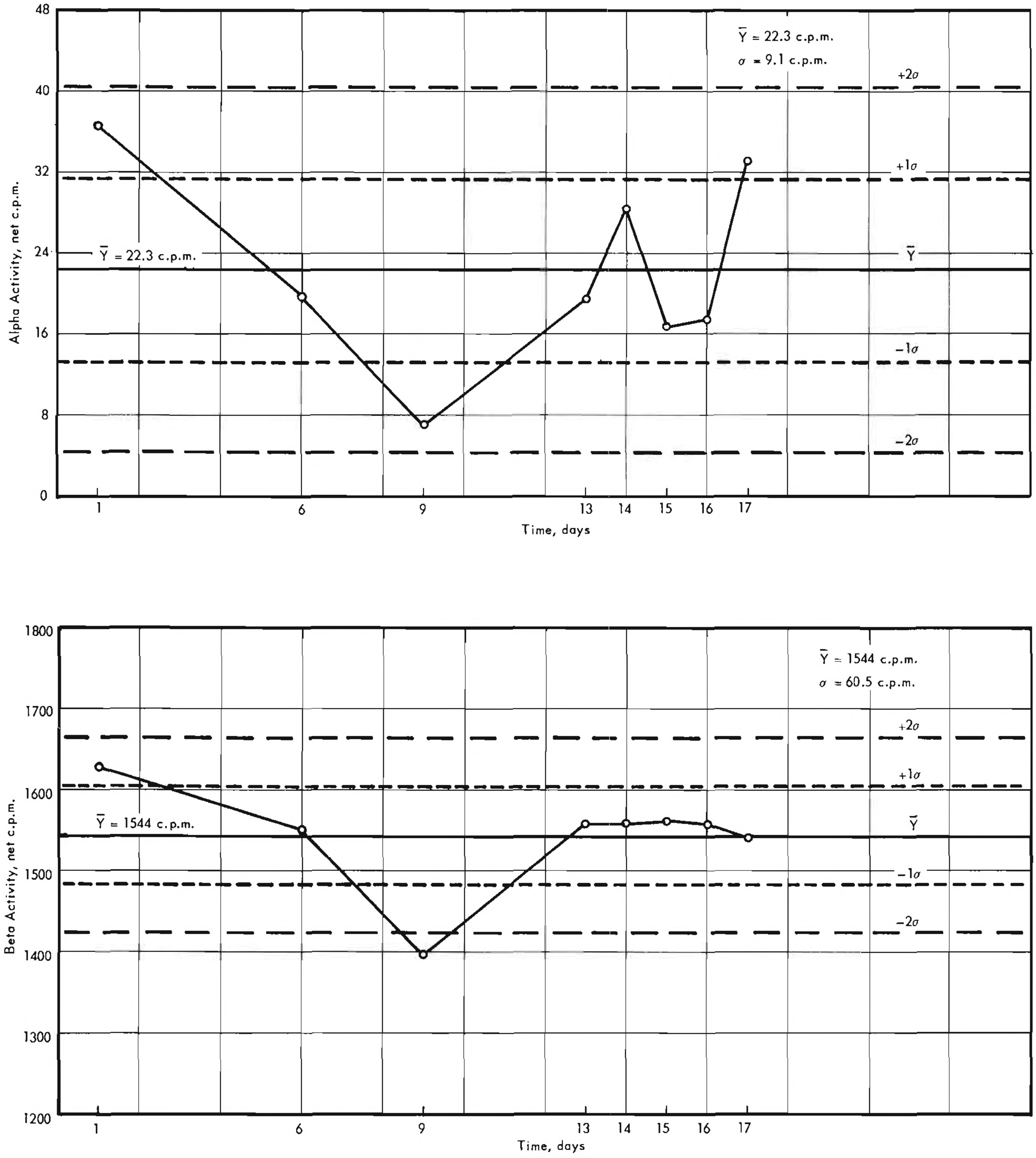

Figure 3. Variation of Alpha and Beta Counting Rates of Mixed Fission Product Sample with Time.

For the given set of beta measurements the mean value is 1544 cpm as shown in Figure 3. The value of the standard deviation is 60.5 cpm which means that 68.3 per cent of the time, counts ranging between 1484 and 1605 cpm are expected due to chance factors alone.

In the course of these studies it was necessary to determine the difference due to indeterminate errors between similarly prepared planchets. To examine whether there is any significance between the means, a hypothesis was set up that planchets prepared similarly would yield no significant difference in activities. As shown in Table VI, t values were determined separately from the calculated alpha and beta net counting rates. Using Student's t distribution, probabilities of 40.7 per cent and less than one per cent, respectively were found. These results signify that one could expect as great, or greater, difference between the alpha activities 41 per cent of the time due to chance factors alone. In the case of the beta activities the hypothesis was rejected because differences as great, or greater, than the average difference between the activities on the planchets are expected due to chance alone less than one per cent of the time.

On the basis of these statistical results, the experiments which followed had to be planned with improved sample preparation methods.

To study the reproducibility of sample preparation, two milliliters of a solution of uranyl acetate(*) were deposited on each of thirteen 2-inch diam. stainless steel planchets and both alpha and beta activities determined. The results are presented in Table VII. From the results of statistical analysis, also shown in Table VII, it may be observed that for the given set of alpha activity measurements the chance of obtaining a

---

(*) 0.5 gm $UO_2 (C_2H_3O_2)_2 \cdot 2 H_2O$ in 100 mls.

TABLE VI

t Test for Difference Between Activity from Mixed Fission Products Deposited on Planchets(*)

α-activity (cpm)		β-activity (cpm)	
Planchet A	Planchet B	Planchet A	Planchet B
36.8	36.4	1626	1100
19.8	18.7	1550	1146
7.0	10.7	1397	1089
19.4	21.8	1559	1126
28.3	21.6	1558	1000
16.9	14.9	1562	916
17.3	12.8	1559	1119

Note (*) 10 λ MFP deposited on each planchet from a stock solution of 10 λ MFP/100 ml.

Results from Statistical Analysis

Standard Error of $\bar{d}_\alpha$:

$$\sigma_{\bar{d}} = \frac{\sigma_{\bar{d}}}{\sqrt{n}} = 1.38$$

$$t = \frac{(\bar{d} - \bar{d}')}{\sigma_{\bar{d}}} = 0.89$$

$P_\alpha = 0.407$

Standard Error of $\bar{d}_\beta$:

$$\sigma_{\bar{d}} = \frac{\sigma_{\bar{d}}}{\sqrt{n}} = 42.1$$

$$t = \frac{(\bar{d} - \bar{d}')}{\sigma_{\bar{d}}} = 11.3$$

$P_\beta < 0.001$

TABLE VII

Reproducibility Study of Sample Preparation

Planchet Number	α-activity (cpm)	β-activity (cpm)	Total $\alpha + \beta$ activity expressed as: α-activity (%)	β-activity (%)
1	406	1485	21.5	78.5
2	373	1235	23.2	76.8
3	449	1579	22.2	77.9
4	249	1277	16.3	83.7
5	312	1312	19.2	80.8
6	288	1437	16.7	83.3
7	310	1421	17.9	82.1
8	386	1570	19.8	80.3
9	421	976	30.1	69.9
10	245	1412	14.8	85.2
11	281	1246	18.4	81.6
12	230	1118	17.0	83.0
13	264	904	22.6	77.4

Results of Statistical Analysis

Arithmetic Mean, $\overline{X}$	324	1305
Standard Deviation, σ	71.1	206
Test for Normality, $\frac{\sigma}{A.D.}$	1.12	1.24
Skewness, α_3	+0.57	-0.50
Kurtosis, α_4	1.7	2.2

deviation of a single value from the mean of 324 c.p.m. by an amount less than or equal to 71.1 c.p.m. is 68.3 per cent. Similarly, for beta activity measurements, the chance of observing a deviation of a single value from the mean of 1305 c.p.m. by an amount less than or equal to 206 c.p.m. is 68.3 per cent, assuming the data to be normally distributed. To examine the latter assumption of normality, σ/A.D. was applied to test the data and the results are shown in Table VII. As a further evaluation of the experimental data, the measures of skewness (α_3) and kurtosis (α_4) are also presented in Table VII. The results indicate that the alpha activity data is moderately left skewed ($\alpha_3 = +0.57$) and that the distribution is platykurtotic ($\alpha_4 = 1.7$). The beta activity data is moderately right skewed ($\alpha_3 = -0.50$) and also platykurtotic ($\alpha_4 = 2.2$).

It appears from these results that considerable variation exists in the preparation of samples, although the indeterminate errors of radioactivity measurements are a part of the variance of this data. Further improvements of the reproducibility of sample preparation and the accuracy of counting are necessary. Statistical methods of analysis should follow the principles outlined by Jarrett(28), the Radiological Health Handbook(29), publications prepared by the R.A. Taft Sanitary Engineering Center(30)(31), and other reference texts.

D. CONCLUSIONS

1. High concentrations of suspended solids in water samples tend to clog millipore membrane filters and retard or prevent passage of the filtrate. The use of filter packs with larger pore size millipore membranes on top, followed by successively smaller pore size membranes permit filtration to proceed at much faster rates. Water samples with very high concentrations (above 500 ppm) of suspended solids can not be filtered in a reasonable length of time even with a filter pack. However, these samples are readily flocculated with acetic acid after which filtration can be readily accomplished.

2. The filterable portion of a sample (that portion which is retained on the filter pack) should be placed on a planchet and the filter paper dissolved and burned off with acetone or ethyl alcohol. Subsequently, addition of a few drops of Lucite in acetone fixes the sample on the planchet and it is ready for radioanalysis. Up to three per cent of the combined alpha and beta activity was retained by type HA millipore membrane filters when relatively high concentrations of uranyl acetate solutions were applied. With higher concentrations of solids, the activity retained on the membrane decreased due to increased self-absorption.

3. The non-filterable portion of the sample (that portion passing through the filter membrane) is adsorbed on a mixed bed of ion exchange resin in which the resins have been converted to the H^+ and OH^- form. The maximum flow rate of the sample through the resin should not exceed a value which would give less contact time than 30 minutes.

4. The wet ashing procedure on polystyrene based ion exchange resins is time consuming and requires considerable experimental skill. The oxidation of the styrene polymer proceeds with the formation of large amounts of foam which usually cannot be controlled without the addition of anti-foaming agents. These anti-foaming agents leave residues which interfere with counting of the

sample. Transfers from the wet ashing digester to planchets are difficult to accomplish quantitatively and time consuming. The wet ash method of reducing polystyrene based ion exchange resins does not appear to be satisfactory.

5. Polystyrene based ion exchange resins may be dry ashed by first drying the resin at 103°C, followed by firing in a muffle furnace at 600°C for five hours. The residues remaining are greater than desirable from the standpoint of self-absorption and the solids are distributed on the planchet in a random density pattern. The dry ash method can be accomplished with almost no attention during ashing and can usually be ashed directly in a 2-inch x 5/16-inch planchet, thus requiring no transfers. Further work is needed to perfect the sample preparation technique and improve reproducibility.

6. Elution is not considered to be feasible toward the solution of a rapid radioassay method because (a) relatively large volumes of elutriant must be evaporated, (b) proper elutriant selection is dependent on the qualitative analysis of each individual water sample, and (c) a mixed bed resin can not be satisfactorily eluted unless it is first separated into its components.

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F. PUBLICATIONS

Thus far, the following publication has resulted from this study:

Grune, W.N., "Determination of Low-Level Radioactivity in Water", Water and Sewage Works, 108, 472 (1961)

G. STAFF

The following professional personnel have been employed on this project since December 1, 1959:

W.N. Grune	Principal Investigator	Dec 1, 1959 to May 31, 1962	20% time
R.C. Peek, Jr.	Graduate Research Asst.	Dec 1, 1959 to Jun 1, 1960	37.5% time
J.H. Mehaffey, Jr.	Research Assistant	Dec 1, 1959 to May 31, 1962	12.5% time
J.E. Munzer(*)	Sr. Sanitary Engineer	Dec 1, 1959 to May 31, 1962	5% time
V. Florence	Research Assistant	Feb 1, 1960 to Aug 31, 1961	70% time
E.E. Ozburn	Research Assistant	Dec 1, 1960 to Aug 31, 1961	40% time
G.W. Gibson, Jr.	Graduate Research Asst.	Sep 1, 1961 to May 31, 1962	40% time
R.B. Hughes	Research Assistant	Mar 1, 1962 to May 31, 1962	90% time

(*) Mr. Munzer is a Regular Corps officer of the U.S. Public Health Service. He was not employed on this project but will use a part of this project for his Ph.D. thesis.