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THE RADIOACTIVE DETERMINATION
OF URANIUM IN SEA WATER.

In Partial Fulfillment
For The Master's Degree
In Chemical Oceanography

by

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To Whom It May Concern:

This is to certify that the thesis entitled
"The Radioactive Determination of Uranium in Sea Water"
by Mr. Robert Wong measures up to the required standards
of the Master's thesis in this Department.

Yours truly,

-ew

THE RADIOACTIVE DETERMINATION
OF URANIUM IN SEA WATER.

ABSTRACT.

The determination of small amounts of uranium of the order of parts per hundred million has usually been carried out by indirect radioactive measurements. Such measurements cannot be employed except when the radio-elements are known to be in equilibrium. The separation of the uranium and its isotopes in such small amounts, is accomplished with the use of an ion-exchanger and separated in a radioactively pure state with the use of co-precipitators. the iron (and aluminum) being added. The alpha-particle activity of the uranium is determined as a measure of its concentration. The method is tested by two control tests. A variance of 3.0% for these tests substantiates the validity of the method but the efficiency of the extraction was approximately 50%.

INTRODUCTION

It is presumed that the ocean came into being as soon as the Earth cooled below the condensation point of water, and since that time it has been receiving substances leached and eroded from the continents. Some of these substances have made the journey from the continent to the ocean and back again several times and may continue to do so. However, in the case of the radioactive substances which cease to exist after a time, a limit to this phenomena exists. The non-radioactive sediments may come and go, but all the radioactive elements, whether of long or short life, cannot exist eternally but are transitory. It is then also true that uranium cannot exist forever.

The determination of minute traces of uranium which are present in nearly all materials has received scant attention especially when one considers the quantity of data available concerning the radium content of all types of matter. In a few radioactive problems the uranium is present in sufficient amount for determination by standard chemical procedure. In the majority of radioactive problems, particularly those of interest to the geophysicist, such as the determination of geologic time and the production of radioactive heat, equilibrium in uranium-238, uranium-235, and thorium series has been established. Equilibrium in the uranium-238 series is established in less than 10^6 years;

geologically a very short period of time. The other two series attain equilibrium in much less than 10^6 years. If the uranium-238 series is in equilibrium, the measurement of radon is equivalent to a determination of the uranium or of any member of its series. An extremely small amount of the gaseous radon, the disintegration product of radium, can be easily separated from the other members of the series and measured by its ionizing effect.

PREVIOUS WORK

Hitherto no standard analytical method for measuring uranium with the necessary degree of sensibility has been known, electrometric methods failing in the case of extremely minute amounts of uranium owing to its very weak activity. A determination suggested by Joly (1), using a colorimetric method proposed by Walker (2), was undertaken 40 years ago. The quantity of uranium expected from the radium content amounted to over one milligram in the 8 grams of sample but the actual weight of uranium actually present was .6 milligrams. However, he asserts that about one half of the uranium present might have been lost in the chemical operation.

In 1930 Herculano de Carvalho (3) measured the amount of uranium in the water from some springs in Portugal using the colorimetric method with ferrous cyanide and found quantities of about 10^{-6} grams per litre. Where large samples of water are available and the solid content is low, the

uranium can be considerably concentrated by evaporation into a small fraction of its original volume before the other substances dissolved in the water begin to crystallize. In sea-water, however, which holds between 30 and 40 grams of dissolved salts per litre, the problem of finding the minute amount of uranium is therefore much more difficult.

Hernegger (4), has developed an optical method of determining uranium by comparing the fluorescence in ultra-violet light of fused sodium fluoride beads, to which known and unknown amounts of uranium have been added. He used a glass spectrograph of very high light-gathering power and by photographing the characteristic band-spectra due to uranium fluorescence and comparing the intensities with those found with the controls of known uranium content. The method is claimed to easily detect uranium in as small amounts as 10^{-10} grams. In collaboration with Karlik (5), measurements of the uranium content of ocean water of Norway wherein the uranium was concentrated from samples of one liter or more, gave consistent results averaging 1.5×10^{-6} gram uranium per liter.

PRESENT WORK

The sea water samples as obtained were filtered through glass-wool filters to eliminate any solid matter which would adversely influence the efficiency of the exchange resin. The seawater sample as obtained was slightly alkaline and hence to prevent colloidal hydroxides from passing through the exchange column unchanged, the pH was

adjusted to 4 by the addition of purified HCl.

Each seawater or control sample was then pumped through the ion exchange column containing IR-120 in the sodium form and U-238, U234, U235 and other divalent or higher valence ions were concentrated on the resin. The uranium was then eluted along with other ions such as Fe and Ag, etc, which form complex ions with NaCN. The complex was then decomposed by evaporating with concentrated H_2SO_4 . Purified $FeCl_3$ and $AlCl_3$ was then added to the solution and the boiling solution was precipitated with concentrated NH_4OH . By this precipitation, the uranium was also precipitated if in macro-amounts or co-precipitated if in micro-amounts. This precipitate was then treated with adaptations from the procedure given by Urry (6) for the determination of small amounts of uranium.

In this procedure, U-238 and its isotopes U-235 and U-234 are separated from all the other radio-elements by the use of co-precipitators. The sequence of co-precipitation is such that all the reagents need only be free of uranium, thorium, ionium, and actinium. The iron and aluminum in the solution are used as the carrier agents in the final precipitation of the uranium. The concentration by these carriers is the important principle of the method because the radioactive measurement of the uranium requires a "thin layer" of less than a certain thickness and consequently of less than a given mass for a given area. For very low uranium concentrations it is possible to separate the iron

plus aluminum from the uranium and to return only a small portion of the former as co-precipitations, which results in a much higher concentration factor.

The final precipitate of the oxides of iron, aluminum and uranium is dried, ignited, and weighed. The precipitate is ground and sprinkled on an adhesive surface to form a thin layer and the rate of emission of the α -particles from the uranium is determined photographically. The rate of emission is a direct measure of the number of atoms of uranium present in the thin layer.

PRINCIPLE OF ION-EXCHANGE

Our use of an ion exchange resin in the initial separation of uranium from sea water warrants a brief but necessary discussion due to the difficulties arising from the nature of our exhaust solution, sea water.

To illustrate the reactions of ion exchange resins, it is necessary only to substitute a large, insoluble, synthetic molecule in place of one of the ions in equations that illustrate ordinary double decomposition. The result depicts a type of reaction that will trade ions. The ion exchange resins are actually large, insoluble acids and bases. If the resin is a cation exchanger, it will possess reactive acid groups as part of the resin molecule. In any case other cations can replace the hydrogen of these acid groups to produce insoluble "resin salts". As a solution containing cations is passed through a column containing large

numbers of cation exchange resin particles, hydrogen ions are released from the resin's acid groups, and metallic ions are absorbed. As a result, the cation resin bed becomes enriched with metallic ions. If it is not necessary to separate the sodium ions from a solutions as in our case, the cation exchanger is used in the sodium form, that is, the resin is first treated with a solution of sodium chloride to replace all of the hydrogen ions on the resin with sodium ions. Then, when the solutions passes over the active exchange centers, sodium replaces the other metallic ions in solution. Therefore, ion exchange resins form compounds with definite compositions which enter into chemical reactions as do other compounds. The reactions are double replacement or metathesis reactions and, at equilibrium, are governed by the law of mass action. The chief differences between reactions of these compounds with ions in solution and the reactions between ions which are all homogeneously dispersed in solutions, is the rate at which equilibrium is approached.

In general, the mass action law which holds for granular exchangers where all of the exchange takes place in the interior of the particles having a porous gel structure, takes the form of the Kerr (7) equation:

$$A^+ + BX \rightleftharpoons AX + B^+$$

$$\frac{m_{AX}}{m_{BX}} = K \frac{(A^+)}{(B^+)} \quad \text{or} \quad \frac{m_{Ca}}{m_{Na}^2} = K \frac{(Ca^{++})}{(Na^+)^2}$$

An equation of this type expresses the well-known fact that the distribution of two ions of unequal charge depends upon the dilution; the more dilute the solution, the greater the proportion of the higher valence ion in the exchanger.

In ion exchange as in other chemical equilibria, the reactions are reversible; that is, in the forward direction we have the exhaustion and the reversed direction we have regeneration. In our particular case with IR-120 it is recommended that a 10% solution of NaCl be the regenerant in the sodium cycle; in other words, the regenerant will displace all cations other than sodium from the resin and thereby rejuvenate the resin. With sea water, we are confronted with the difficulty that we have appreciable amounts of regenerant sodium ions in our exhaust solution. Hence it can be seen from our equilibrium equation that the exchanged form, AX, is lowered by the increase in B. Or it may be said that our resin exchange capacity is now lower. It was therefore essential to conduct experiments to determine exactly how the capacity of the resin varies with the concentration of sodium ions in the exhaust solution because our determination of uranium is quantitative. Furthermore, capacity variations under such conditions has not been recorded in the literature.

PRINCIPLE OF CO-PRECIPITATION

There is a fundamental difference between the

chemistry of extremely small amounts of the radio-elements and that of the weighable quantities in chemical analysis. Thus, the condition for co-precipitation is not so much one of isomorphism as the formation of a precipitate consisting of a compound whose anion forms an insoluble compound with the radio-element. Fajan's rule as stated by Hevesy and Paneth (8) is as follows: "A cation will be absorbed by a difficult soluble salt when it forms with the anion of the absorbing salt a compound, the solubility of which in the solvent is small." The less the solubility of the compound involved and that of the absorbent, the stronger will be the absorption. In the following table, (Table 1) most of the radio-elements are isotopes of the co-precipitators or of one other element, of the series. For example, of the radio-elements co-precipitated with bismuth, the C and E products, isotopes of bismuth, the remainder are isotopes of polonium. The very short lived "C" products of thallium need not be removed.

Table 1	
Co-Precipitation of the Radio-Elements (9)	
Element added and precipitated	Radio-elements precipitated as isotopes or co-precipitated
Ce (as oxalate) Bi (as sulphide)	Io UX UY--Ac RaAc---Th MsTh ₂ RaTh RaA RaC RaC' RaE Po---AcA AcC AcC'-- ThA ThC ThC'
Pb (as sulphide) Ba (as sulphate) Fe (as Hydroxide)	RaB RaD----AcB---ThB Ra--AcX--MsTh ₁ ThX U-238 U234 U-235

EXPERIMENTAL

Evaluation of Resin.

A simple experimental column, as illustrated in figure 1, was constructed to test the performance of the exchange resin, Amberlite 120, and also to obtain sufficient data to construct a larger column for our actual determination of uranium in sea water. A glass column 1.5 inches in diameter and 10 inches long with a medium porous plug which ^{was found} most convenient to handle and afforded excellent visibility was used for these preliminary experiments. The sintered-glass plug prevented entrainment or retention of regenerant or other solutions. In such a column, packing and channeling of the resin was avoided.

A T-tube was attached to this column by means of a rubber joint and each projecting part of the T-tube was fitted with a piece of rubber tubing and a Hoffman screw clamp for regulation of flow at the desired rate. A stopper at the top fitted with a three-way T-tube as illustrated in figure 1 completed the apparatus. The arms of this T-tube provided for escape of effluent in back-wash or upflow operations, and for entrance of exhausting solutions in downflow operation. Connections to the upper T-tube were controlled by means of pinch clamps and when any one of these were removed, the downflow rate was controlled by the Hoffman clamp at the bottom of the column serving as an outlet.

A strip of ruled or coordinate paper was pasted

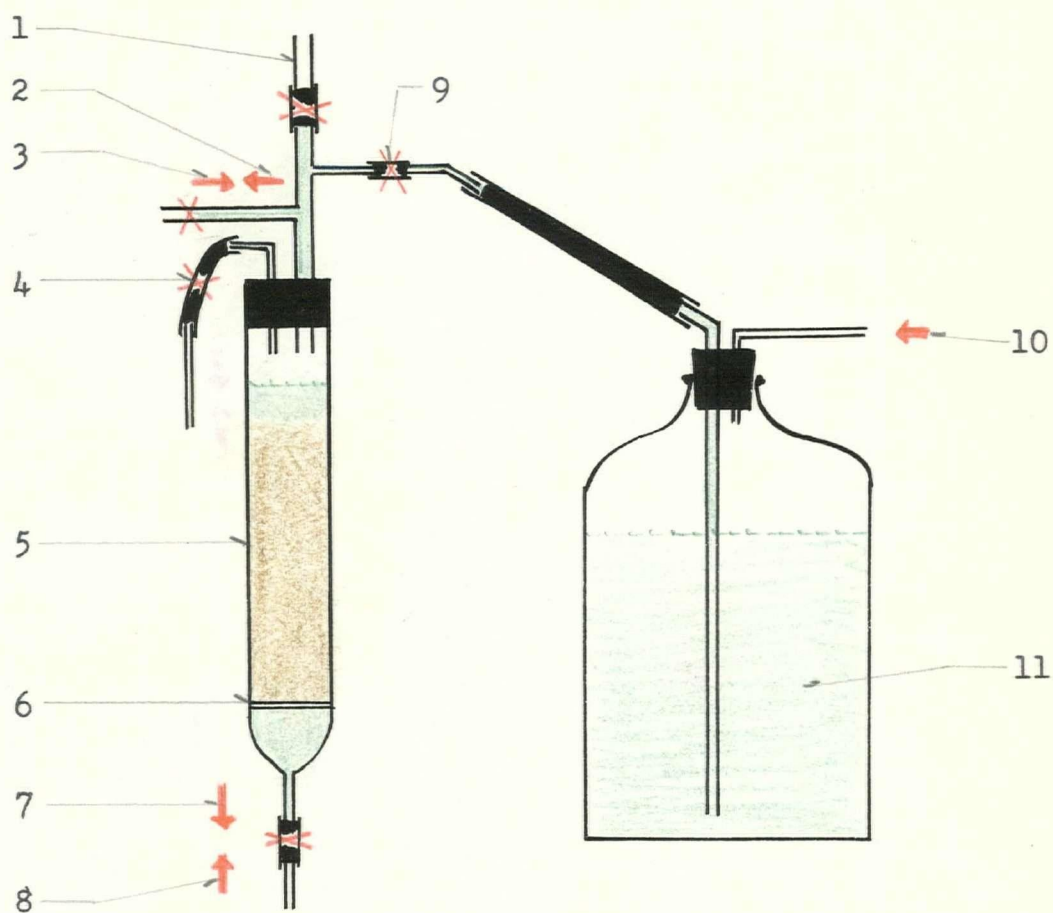
along the side, the column was calibrated conveniently in terms of linear scale units by pipetting successive 10 milliliter samples of water on top of the glass plug and the scale reading of the meniscus was recorded each time. This was done after the bottom of the column had been filled with water up to the plug with the clamps of the T-tube closed. From this data an average "column factor", the number by which the height of a section of column must be multiplied to give its volume, was obtained. Resin bed volumes in milliliters were then calculated directly from the product of the number of scale units between the limits of the bed and this column factor.

Two reservoirs were required, one as a source of solution to be treated, and the other to furnish regenerant for the resin. Since the flow must be controlled accurately, the solutions were forced to the top of the column by compressed air under a constant pressure maintained by a T-tube arrangement in mercury as shown in figure 1.

Amberlite 120 contained sufficient moisture so that there was relatively little swelling upon wetting. Thus a given desired volume was measured out directly before introduction into the column using the exchanger as received. The resin was slurried first in a beaker and washed into the column through a funnel. After the column was charged as described, the column was washed at a rate sufficient to cause 50 to 70 percent bed expansion. This was done in order to

Figure 1.

EXPERIMENTAL COLUMN.



X Pinch clamps

NOTATION FOR FIGURE 1 ----EXPERIMENTAL COLUMN

1. Exhaust Solution.
2. Drain
3. Rinse
4. Level control
5. Ion-exchange resin----Amberlite IR-120
6. Porous plug
7. Effluent
8. Backwash
9. Regenerant
10. Compressed air
11. Regenerant solution

remove the fines which remain in the resins when shipped. This residue was removed to prevent excessive resistance to downflow operation. The backwash was continued until the fines had been washed from the bed. In the glass column technique it was simple to observe when this condition had been reached and prevented the loss of the larger particles by proper flow regulation. The proper backwash caused the resin particles to move up and down freely within the bed and this served to classify the bed hydraulically in increasing particle size from top to bottom. Such a classification improved operating characteristics of the resin.

The backwash which prevented packing of the resin, was carried out using distilled water and backwashing was repeated after each exhaustion cycle. When the backwash was completed, it was necessary to determine the bed volume upon which capacity data were calculated. It has been demonstrated that reproducible bed volume results could be obtained by draining the bed following backwash to ^agiven height of water above the resin, usually chosen as one inch. The bed volume was then determined from the column calibration as previously explained.

The resin was allowed to settle by gravity before draining was begun and all bed volumes referred to will be this backwashed and drained bed volume. The flow rate at which this draining was carried out is relatively critical because the water must not run out fast enough to cause ex-

cessive settling and hence pack the resin bed.

The bed was never allowed to drain dry as this would cause air pockets to appear in the bed causing subsequent faulty contact of the exhausting or regenerating solution with the resin and limiting exchange. Moreover, it was desirable to have a small amount of water above the bed to cushion the incoming stream during the exhaustion cycle and thus prevent the bed from being disturbed excessively.

The column was operated downflow by running the exhausting solution through the resin from top to bottom. The extent to which the material being exchanged is removed depends primarily upon the quantity of regeneration material used and the composition of the exhausting solution, and secondarily upon the exhausting solution flow rate per unit volume of exchanger. The quality desired in the treated effluent is the factor which determines the length of time between regenerations for any given regeneration value. The total exchange of divalent or higher valence ions are desirable and therefore it was necessary to regenerate our resin to the level which gave the optimum capacity. To determine the variation of capacity with various sodium ion concentrations, solutions of .1 equivalents in copper ions per liter with various concentrations of sodium chloride were run through the small experimental column just described. Each solution was run through the column after the usual steps of regeneration and backwash etc.

The exchanger effluent was sampled from time to

time with Na_2S to detect the first leakage of copper ions and the volume of the exhausted solution was noted when the first leakage was detected. This procedure was repeated for three samples of the same solution and in each case the results were in perfect agreement. The capacity was found to decrease rapidly with increasing concentrations of sodium ions in the exhaust solutions as expected. The data obtained in this experiment is given in table 3 and a plot of this is shown in figure 2. From such a plot, and knowing the desired total bed capacity for our subsequent determination of uranium in sea water, the volume of resin to be employed may therefore be easily found. The following table (Table 2) gives the operating conditions of our small column as specified by the producers of Amberlite 120, (10)

Table 2.
Operating Specifications for - Amberlite 120

Volume of Resin	120cc
Regenerant concentration	10%
Regenerant flow rate	15.9cc/min.
Regenerant level	13.7Meq./cc resin, or 866cc(10%sdn.)
Rinse flow rate	15.9cc/min.
Rinse water requirement	800cc
Service flow rate	31.8cc/min.
Capacity	.197 equiv.

Figure 2.

THE CAPACITY OF AMBERLITE IR-120 vs SODIUM CONCENTRATION.

(Meq./cc vs % Na by weight)

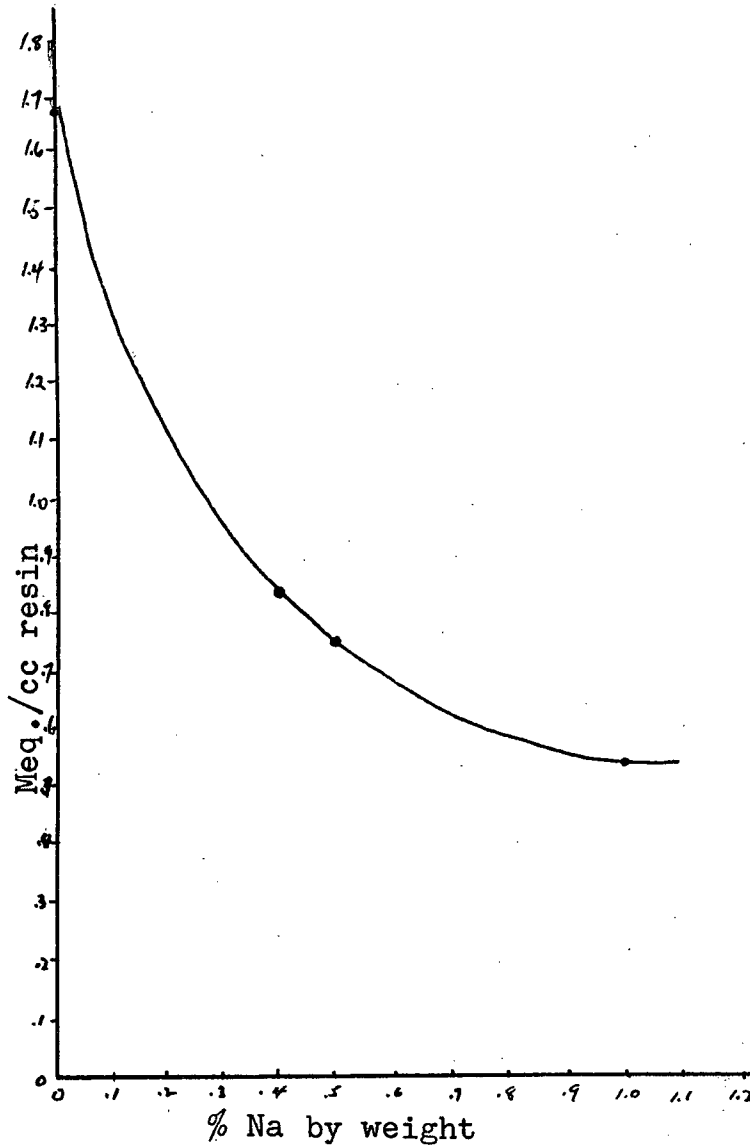


Table 3.
Variation of Capacity with Sodium Ion Concentration

Conc. of Cu^{++} equiv./liter	Conc. of Na^+ % by weight	Max. Vol. of exhaust soln.	Capacity Meq./cc resin
.1	0.0	1990cc	1.66
.1	0.39	1000cc	0.833
.1	0.50	900cc	0.750
.1	1.0	325cc	0.541

Analysis of Sea Water Sample

In order to determine as accurately as possible the maximum volume of sea water sufficient to just exhaust the resin, analysis of the sea water sample must be performed. Of the major cation constituents of sea water, magnesium and calcium comprise the greatest portion of the di-valent and higher valence ions (11). As has already been stated, it is the di-valent and higher valence ions which are exchanged in the sodium cycle. Consequently, the exhaustion of our column is totally dependent upon the concentration of calcium and magnesium ions and also the sodium and potassium ion concentrations which determine the capacity of the column. It has been found that the sodium, potassium, calcium and magnesium ion concentrations may be easily found once the chlorinity is known and the following ratios as given in table 4 are found to hold. The chlorinity was found by the Volhard titration with silver nitrate and the chlorinity was found to be 16.383. Table 4 gives the various

major constituents in our sample of sea water.

Table 4.			
<u>Major Constituents in Sea Water Sample</u>			
Ion	Ratio to Chlorinity	Weight in gms./l	Equiv./l
Na ⁺	.5509	9.27	
K ⁺	.0200	0.334	
Mg ⁺⁺	.06695	1.12	0.0922
Ca ⁺⁺	.02106	0.352	0.01755

The above data also supplied enough information for us to make up artificial sea water for our control determinations with conditions very similar to those found in the actual sample. The C.P. salts of sodium, potassium, magnesium and calcium were used and the amounts used per liter of solution were as follows:

Table 5.	
Salt	Weight gms./l
NaCl	23.6
MgCl ₂ · H ₂ O	9.38
Ca(NO ₃) ₂ · 4H ₂ O	2.07
KCl	0.638

For the separation of uranium from sea water a new column was constructed consisting mainly of three pyrex glass tubes each 6cm. in diameter and 124 cm. in length. To allow for a glass wool plug and sand to cushion the resin bed and

and to allow for sufficient expansion of the resin bed in the backwash operation, the actual resin bed was only 75cm. in height. The total volume of the resin in the three columns was therefore 6,360 cc. A diagram of this column is given in figure 3.

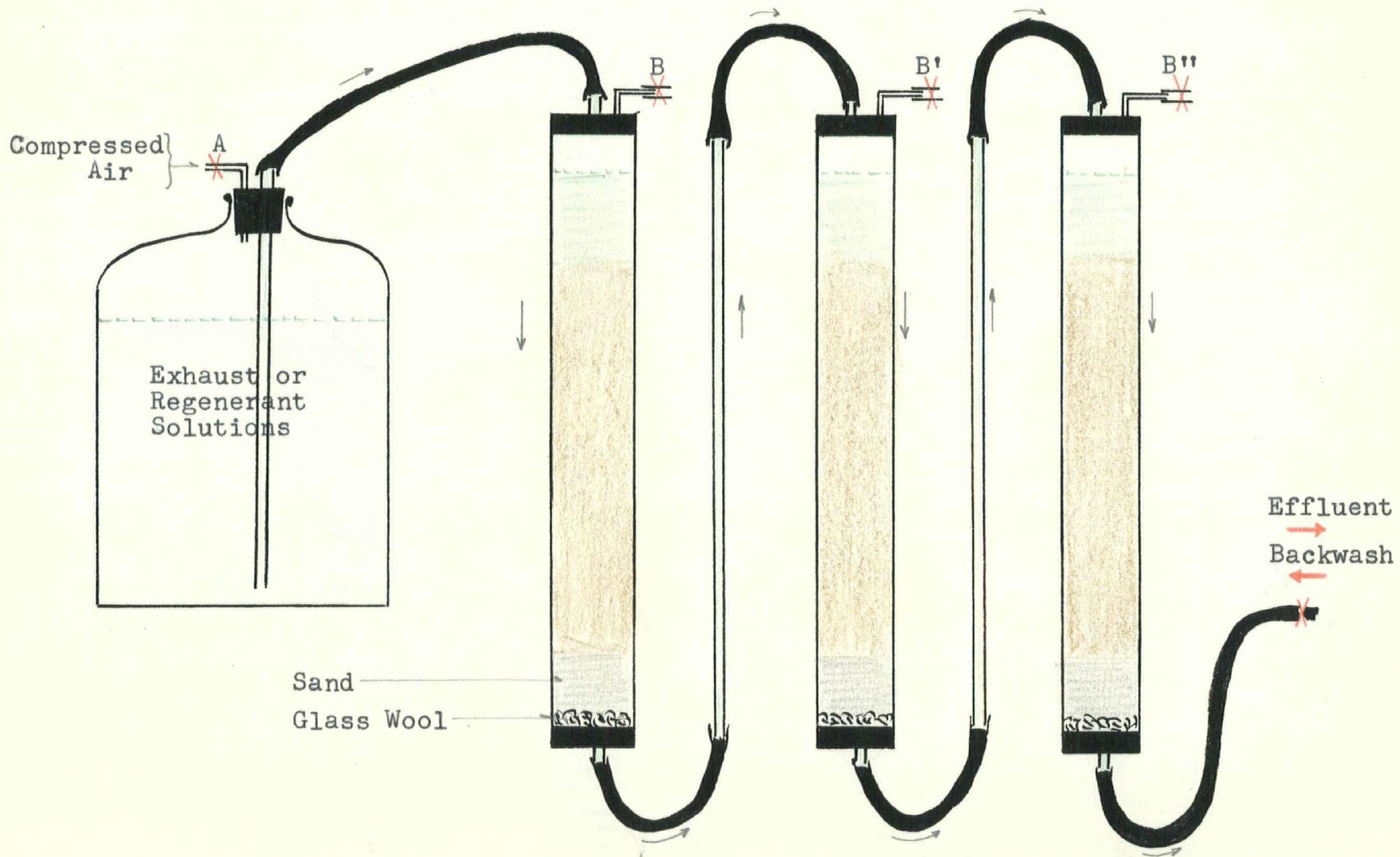
The capacity per cc. of resin at the sodium ion concentration of 0.924% is 0.560 milliequivalent per cc. resin as determined from the graph and table 4. The total equivalents of magnesium and calcium per liter from table 4 is 0.110. The following table (Table 6) gives the operating specifications of our new column.

<u>Table 6.</u>	
<u>Operational Specifications for 6,360 cc Amberlite IR-120</u>	
Conc. of Na in exhaust soln.	0.924%
Total resin capacity	3.57 equiv.
Max. vol. of exhaust soln.	32.4 liters
Exhaust service flow rate	80 cc/min.
Regenerant conc.	20% (approx.)
Regenerant flow rate	80 cc/min.
Regenerant level	11.25 lb.
Rinse requirement	85.5 liters
Backwash time requirement	10 min.

The Separation of Uranium From Sea Water

an
In actual run(5) after the usual preparations of regeneration and washings of the resin bed, the samples were pumped through the column from a 40 liter carboy by compressed

Figure 1.
EXCHANGE COLUMN.

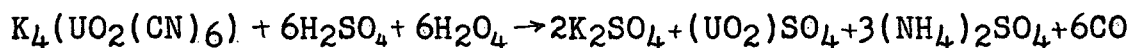


air regulated by a safety valve, A. The actual route of the samples through the column was as indicated in diagram 3. After 30 liters had been run through the column, instead of 32.4 litres allowing for a safety margin, the column was back-washed with pure water for five minutes and then drained until the surface of the liquid in column 1 was just that of the resin bed. This was done by regulating valves B, B' and B''. The eluting agent, 100 cc of 25% sodium cyanide solution, was allowed to run through the column at the rate of 50 cc per minute. The resin bed was always submerged in water by admitting water on top of the cyanide solution at 50 cc per minute. In this way the cyanide solution was in between two water layers in going through the column. The first eluent was collected when cyanide was detected by ferric chloride and collecting was continued until no cyanide could be detected by ferric chloride after which another 100 cc was collected. In this way, approximately 1600 cc was collected each run. A total of four runs were made----two controls and two sea water samples.

Treatment of the Eluent.

The solutions were then evaporated to 150 cc and cooled. Then 250 cc of concentrated sulfuric acid was added to each of the solutions and evaporated to dryness to decompose the cyanide complexes (14). The treatment in concentrated sulfuric acid was accomplished in porcelain casseroles placed in an inclined position over the flame, and the flame directed against the upper part of the crucible. The heating was continued until ^{the} fumes of sulfuric acid ceased to come off. The

residue consisted of the alkali sulfate and anhydrous heavy metal sulfates and uranyl sulfate. This residue was heated gently with 10 cc of concentrated sulfuric acid and water was added little by little until 25 to 30 cc was added and the sulfates were readily brought into solution. It is presumed the following reaction took place;



2 cc of one normal ferric chloride and 2 cc of one normal aluminum chloride were added to each solution and the solutions heated up to boiling. Ammonium hydroxide was carefully added to neutralize the sulfuric acid and finally to precipitate the aluminum and ferric hydroxides which would co-precipitate any uranium. This co-precipitation procedure was repeated twice to ensure complete removal of uranium. This precipitate was washed with a dilute solution of ammonium chloride and the precipitate finally dissolved in purified hydrochloric acid and the solution treated by the following co-precipitation technique.

Analytical Procedure.

The chemical separation of uranium, which is shown schematically in table 7 is adapted from the procedure given by Urry in his procedure for the analysis of rock samples (15).

Table 7.

Preparation of Uranium Free from Other Radio-elements.

Oxidize Fe in the filtrate with HNO_3 .
Evaporate to dryness.
Dissolve in HCl.

Precipitate from the boiling soln. with NH_4OH in slight excess, Fe, Al, U, Rare Earths, Th, Zr, Tl, some Mn etc.

Dissolve ppt. in HCl.

Add 20 mg. Ce as $\text{Ce}(\text{NO}_3)_3$.

Evaporate in HCl and HNO_3 :

Dissolve in smallest amount of HCl and make up the vol. to 150cc.

Precipitate with a saturated soln. of Oxalic acid, stir vigorously and allow to stand overnight.

Filter and discard ppt. of Ce, Th, Io, Ac.

With the filtrate twice repeat the treatment with Ce.

Evaporate the final filtrate with HNO_3 to remove oxalates,

Remove HNO_3 by evaporation with HCl.

Dissolve in 4% HCl.

Add 10 mg. each of Bi, Pb, and Ba as chlorides.

Precipitate the Ba (with some Pb) with a few drops of a Satd. solution of K_2SO_4 .

Allow to stand six hours with frequent stirring and precipitate Bi and Pb with H_2S .

Filter and discard ppt. of Bi, Pb, Ba.

With the filtrate, twice repeat the treatment with Bi, Pb, and Ba, removing the H_2S between treatments.

To expel the H_2S and oxidize the Fe in the final filtrate with HNO_3 .

Evaporate to dryness.

Dissolve in HCl and precipitate with NH_4OH in slight excess from the boiling solution; Fe, Al, U, etc.

Filter and dry the ppt. of Fe, Al, U. etc.

The sequence in which the co-precipitators are added is important. For example, were the bismuth and lead to be added prior to the cerium precipitation, it is possible that the cerium and later the barium would re-introduce the radio-elements removed by the bismuth and lead.

In all cases it was important to use the same quantities of reagents as far as possible and the treatment of each solution was exactly identical so that our correction as determined by our control tests may be applicable. Exact volumes of standard solutions of the co-precipitators were used by adding each one with its individual burette.

Preparations of the Reagents. (see p. 33 for details)

The water was from the laboratory still. Hydrochloric and nitric acids were distilled from constant-boiling mixtures of the "Reagent" acids. Cerium nitrate was purified by dissolving the CP salts in distilled water and precipitating the hot solution with oxalic acid. The precipitate was dissolved in concentrated distilled nitric acid and evaporated to dryness. The precipitation procedure with oxalic acid was then repeated twice and crystals recrystallized three times. Bismuth, lead, and iron were precipitated three times as sulfide to remove the iron group since they must not contain Th, Io and Ac in addition to uranium. The sulfides were dissolved by boiling with purified nitric acid and after filtering off the free sulfur, the nitric acid was boiled off in hydrochloric acid and the resulting chloride salts recrystallized three times. Barium chloride was recrystallized three times by sol-

ution in distilled water. The potassium sulphate was recrystallized four times.

Radioactive Measurement with Nuclear Emulsions.

The nuclear emulsion records tracks of all alpha particles that enter the recording medium provided that their residual energy exceeds a minimum value. Although the tracks of minimum discernibility vary with the emulsion composition, sensitivity, and the microscopic resolution, it is unnecessary to consider the complex variation in ionizing power along the trajectory and the effective area of the counting chamber which are important factors in electronic counting instruments. This simplifies the translation of the microscopically determined track count into a disintegration rate, as each track irrespective of length corresponds to the emission of an alpha particle by the source. The processed plate carries a record of the number of tracks and also exhibits their approximate line of incidence into the original emulsion. From purely geometric considerations particles entering the emulsion at right angles should appear dimensionless. However, after fixation the gelatin dries to a very thin layer and the vertical tracks become distorted. The visibility of these erect tracks is further enhanced under dark-field illumination by the light scattered from the compressed column of silver grains. With thin sources weighing less than 1 mg. per cm^2 , over 90% of the particles enter the emulsion with energies and orientation favoring optimum track visibility.⁽¹⁸⁾ Tracks of alpha

particles that spent the greater part of their energy in traversing the source are the most difficult to discern because of their short recorded length.

A radioactive source is considered thin when its effective thickness, which is the thickness of the source in equivalent air-centimeters, is less than the effective mean range of alpha particle system in dry air at 15°C. The mechanical thickness or weight per unit area varies with the permeability of the carrier but will in general reside below 2 mg. per cm.² In our determination the sample thickness lies well below this value and may therefore be considered a "thin" source. Geometric considerations, the details of which are discussed by Evans (16, 17) in conjunction with alpha pulse counter, show that:

$$d = \frac{2n_r}{1 - \frac{T - 2L}{2(R-p)}} = n_r k_w$$

where:

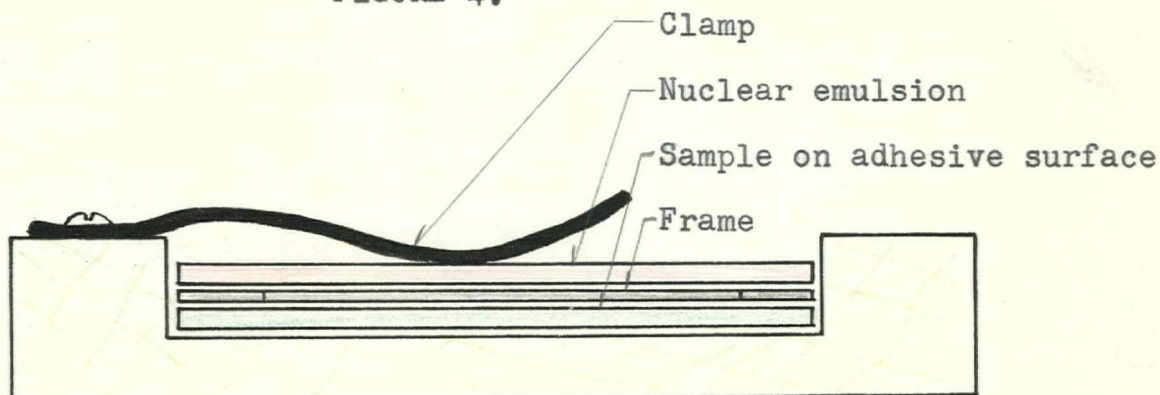
- d is the number of disintegrations in the source during exposure.
- n_r is the total number of tracks recorded during exposure.
- T is the thickness of the source in equivalent air-centimeters.
- L is the distance between source and emulsion in air-centimeters.
- p is the track length in air-centimeters of minimum discernibility.
- R is the effective mean range of alpha particle system in dry air at 15°C.

It is evident from this equation that L is an important factor in governing the proportion of alpha-particle tracks recorded by the emulsion. Yagoda has computed several values of k_w for various radioactive compounds (18). The

tracks are distributed at random, and, when L is about 0.05 air-cm., 98% of the tracks are confined to an area of the same dimensions as the source. n_r was therefore determined indirectly by a restricted count on representative areas of the emulsion.

The actual recording of the activity in our samples were made with Eastman NTB plates with emulsion thickness of 100 microns. The hydroxides were ignited to form the oxides and were ground to a powder in their respective crucibles. Each sample was sprinkled onto an adhesive surface bordered by an aluminum frame 0.05 cm. thick and leaving an exposed adhesive area of 10.0 cm.². The sample was sprinkled in excess onto the adhesive surface to cover the entire surface after which the excess was removed by gentle tapping with the surface inverted. The nuclear track plate was then placed over the sample and clamped to commence the exposure. In this way the sample was "thin" and kept at a known distance from the track plate. This arrangement is illustrated in figure 4.

FIGURE 4.



Because the samples were expected to be very weak, the exposure was for $24\frac{1}{2}$ hours. The development of the plates were done according to instructions from the Eastman Kodak publication (19).

The tracks were counted under dark-field illumination using a 45X dry objective whose aperture was reduced by suitable dark-field stops. The reduction of the aperture is of paramount importance in quantitative track counting. It increases focal depth so that all tracks, irrespective of their position in the gelatin layer, are brought into view with one focal setting. When the exposure is made with an external source the tracks reside close to the upper surface of the gelatin. The tracks were counted in a restricted area of the microscope field with the aid of a graduated ocular diaphragm. With the use of such a diaphragm all the tracks were counted along a strip which extended from one side of the track plate to the other.

RESULTS.

The results of our experiments are as enumerated in Table 8. The tracks were counted as previously described and the uncertainty in the count is 2.3% as suggested by Yagoda (20). The correction factor was determined from the results of the control tests. The activity of the 15 cc of solution was $3.71 \cdot 10^6 \pm .085 \cdot 10^6$ but the control results were $2.07 \cdot 10^6 \pm .0476 \cdot 10^6$ and $2.02 \cdot 10^6 \pm .0465 \cdot 10^6$. The results of the controls varied from the total added amount by factors of 1.78 and 1.83 respectively and yielding an average factor of 1.81.

<p style="text-align: center;">Table 8.</p> <p style="text-align: center;">THE DETERMINATION OF THE URANIUM CONTENT FROM THE RADIOACTIVE MEASUREMENTS.</p>				
Sample	Sample volume (liters)	Total weight of oxides.	Weight of oxide examined.	Alpha particles counted for $24\frac{1}{2}$ hrs. (10^4)
Sea water A	30	.7246	.0280	$1.29 \pm .0196$
Sea water B	30	.2868	.0310	$1.71 \pm .039$
Control A	30	.2393	.0174	$6.93 \pm .140$
Control B	30	.2550	.0195	$7.11 \pm .164$

Sample	Total counts for $24\frac{1}{2}$ hrs. (10^5).	Uranium g. per g. (10^8) sea water.	Correction factor.	Uranium g./g. (10^8) sea water corrected
Sea water A	$7.21 \pm .166$	2.19	1.81	3.93
Sea water B	$3.44 \pm .079$	1.05	1.81	1.90
Control A	$20.7 \pm .476$	6.32	1.81	11.45
Control B	$20.2 \pm .465$	6.17	1.81	11.10

The k_w value used was 2.17 (18).

CONCLUSIONS

The control tests indicate that small quantities of uranium can be subjected to the complex chemical processes of separation without appreciable loss. In both control tests the results were in very satisfactory agreement although the results indicate a loss of uranium. Incomplete removal by co-precipitation of any other radio-elements that emit alpha-particles results in greater activity. But, incomplete exchange and eluting processes along with inefficient co-precipitations may lead to low results. However, the results are open to criticism because a loss of uranium might conceivably be exactly compensated by incomplete removal of the other radio-elements although there seems to be no reason to doubt the efficiency of the co-precipitations which have been so well established in radio-chemistry. Our results for sea water of $3.98 \cdot 10^{-8}$ and $1.9 \cdot 10^{-8}$ grams per gram of sea water is higher than that found by Karlik whose value was $1.3 \cdot 10^{-9}$.

The difference between the two results for sea water cannot be fully explained but the solutions were handled with great care and identically. This is shown in the control tests which results were within 3.0% agreement. The sea water as shipped from the Pacific Oceanographic Labs was in two steel drums and the two samples of the sea water which were run through the column were from two different drums. As was already stated, filtering was required and it was noticed that the residue or solid impurities thus separated were composed of black solids and reddish brown solid matter, the

latter taken for rust. This residue was found to be present in the samples even though they were withdrawn from the drums within two days upon arrival.

If rust was present in the sea water samples, the uranium may possibly have been occluded or co-precipitated by the rust. This is uncertain but the co-precipitation of uranium by ferric hydroxide strongly suggests this possibility. Although the two sea water determinations differ by a factor of 2.1, the results were considered satisfactory in view of the magnitude of the concentration.

SUGGESTIONS FOR FUTURE WORK

Our separation of the micro-amounts of uranium from sea water has provided another method for the determination of other micro-elements in the sea. Since the tracing of the various members of the radio-elements in the uranium family in the sea has not been determined conclusively, such investigations would present very intriguing problems to the chemist and geo-physicist. Although many determinations on the radium content of marine life and bottom sediments have been made by Evans (21) from Pacific ocean samples, it has not established where the various quantities are distributed in the sea and surroundings. Foyn, et al. (22) had found that the radium content of sea water was $.86 \cdot 10^{-16}$ grams of radium per cc of water as compared to $.46 \cdot 10^{-12}$ grams of radium per gram of plankton as found by Evans. However, there is some evidence relative to the possible chemical extraction of

calcium by marine organisms.

From Karlik's (5) determination of uranium in sea water an average of $1.3 \cdot 10^{-9}$ grams per gram of sea water was found but the radium content as found by Foyn was only $0.8 \cdot 10^{-6}$ grams per gram of water. If this latter amount is correct then $.24 \cdot 10^{-9}$ grams of uranium per gram of water could support this amount. Instead, however, we have five times as much uranium as necessary to maintain the radium content. On the otherhand it was found by Urry (9) that bottom samples of high radium content had about one quarter as much uranium as necessary to support its radium content. The rate of deposition in the deep ocean is about one centimeter per 1,000 years and therefore the uranium and radium may not be in equilibrium but whatever the sedimentation process is, it must be efficient, since high concentration bottom samples contain tens of thousands of times as much radium per unit weight as does the ocean water. It must be remembered that the precipitation of ferric hydroxide is a method for precipitating ionium and uranium from dilute solutions and such a process might conceivably occur. It has been observed by Thompson, et al. (23) that the concentration of ferric iron in ocean water is less than it should be if all the iron received were held in solution but the precipitation of uranium would be inhibited by the presence of carbonate ions. This could contribute to the means by which the ionium-uranium ~~unbalance~~ in the sea water

and sediments are unbalanced.

In the preceding discussion the sea water, marine life and bottom sediments and rocks were not from the same locality and too much emphasis cannot be placed upon these results as it is well established by Sanderman and Utterback (24) that the radium content of ocean bottom sediments may vary appreciably with the location. Therefore, it should be a very interesting project to determine the distribution and balance of the radio-elements of uranium family in the ocean sediments and rocks and the sea water directly above it by means of analyses on cored samples and water samples.

APPENDIX.

The HCL and HNO_3 were diluted with distilled water to the approximate constant boiling compositions before being distilled. The first and last quarter of the distillate were discarded and the middle half was collected. The composition of the constant boiling HNO_3 was 68% and for the HCl 20.2%. The constant boiling points were 120.5°C and 110°C for HNO_3 and HCl respectively.

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