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A PROPOSED TECHNIQUE FOR COMBINED 226-RADIUM
AND 228-RADIUM ANALYSIS

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Abstract

A new program was undertaken to evaluate a new method for analyzing ^{226}Ra and ^{228}Ra in sea water. The concentrations of these two isotopes could be used as tracers to assess the nature of the interaction between the bottom, the shore and an Ocean Thermal Energy Conversion (OTEC) facility. The method tested was not entirely successful, and more standard methods are recommended, such as using scintillation counting for ^{226}Ra via ^{222}Rn emanation and some other technique such as alpha spectrometry for ^{228}Th .

I. INTRODUCTION

An Ocean Thermal Energy Conversion (OTEC) facility is designed to extract energy from the temperature difference between deep and surface waters in warm tropical seas. By its very nature, such a facility will alter its surroundings, introducing, as well as altering, nutrient and trace element distributions with concomittant biological effects. The recent shift in emphasis of OTEC planning from open ocean to near shore installations adds to the simple pertubation of the OTEC plant on the local environment. The effect of the shore, whether island or mainland, on circulation and chemistry near the OTEC plant, the potential effects on the shore due to OTEC operations and the probability that, as a result of proximity to the shore, the cold water intake will be considerably closer to the bottom than in an open ocean site, all suggest that some method to assess the nature of chemical communication between the bottom, the shore and the OTEC facility is required.

This assessment may be carried out in several ways. Direct physi-

cal measurement of water mass motions could provide the necessary information but at great cost in time and effort. Artificial tagging of water masses with, for example, dyes, or drifters (neutral buoyancy floaters) might also provide the necessary information but again, the techniques are expensive and time consuming and require careful planning and evaluation.

Natural stable-conservative tracers, temperature and salinity, can be used along with the density field calculated from them, but, being stable-conservative tracers, they do not directly incorporate a time dependent sense. Non-conservative tracers, whether stable like oxygen and the nutrients, or radioactive like ^{14}C require either measurement or estimation of their consumption/production rates which may evolve into a difficult problem.

Radioactive-conservative tracers have time dependent decay terms. The requirements for a useful radioactive-conservative tracer are relatively simple to state. The tracer should be emitted from a source within the system of interest, in this case the bottom, the shore, or the OTEC facility itself. In the case of pre-deployment measurements, this is limited to the bottom-shore combination. The tracer should have an appropriate decay constant such that the time resolution is appropriate for the time scales in question. The tracer should be measureable.

^{228}Ra was chosen for tracer studies in the OTEC program. ^{228}Ra is emitted from sediments on both the ocean bottom and its outcrop at the shore line. Negligible amounts of ^{228}Ra are produced in the water column as its parent, ^{232}Th , is extremely insoluble, rapidly moving to the sediments. The half life of ^{228}Ra is 5.7 years which gives it a

time resolving capability in the range of about one to thirty years. Finally, ^{228}Ra is measureable, although routine use is not common due to a combination of modest analytical difficulty, the newness of the technique, and a dearth of problems with the right time scale.

Because the OTEC program includes the appropriate time scale and environment, we proposed to develop a compact and relatively simple technique to measure ^{228}Ra in seawater. This technique also includes the measurement of ^{226}Ra , an isotope of much longer half life (approximately 1600 years) with a daughter nuclide, ^{222}Rn having a short half life (3.8 days), which may be applicable for the study of short term variations and rapid processes.

In the following report we will review previous studies and techniques of radium measurements, then we will describe in detail the technique developed for the OTEC program and the results to date. In the last two sections of the report we will make some recommendations for future application of the technique and for the possible inclusion of other measurements, and will propose to continue the radioactive-conservative measurement program with or without the addition of ^{222}Rn .

A. Previous studies of ^{228}Ra in seawater: a literature review.

In early work, both Moore (1969) and Ku (1972) have emphasized the probable applications of both Ra isotopes to oceanic mixing studies. ^{228}Ra , as discussed by Reid, Moore and Sackett (1979) with its half life of 5.714 years and primary source from bottom sediments is ideally suited for investigating natural processes over the span of 1 to 30 years.

Disregarding for the moment a discussion of specific analytical procedures and problems (which of necessity dictate to a certain extent the usefulness of a tracer tool), a review of results to date using radium radionuclides as natural tracers follows.

Trier, Broecker and Feely (1972) found that order of magnitude estimates of the coefficient of vertical diffusion may be made from ^{228}Ra profiles (such as the one investigated at the second GEOSECS intercalibration station, 1970, near Bermuda) in the presence of strong horizontal advection.

Knauss, Ku and Moore (1978) determined Ra and Th values in the surface water of the East Pacific and coastal Southern California. They modelled ^{228}Ra activity of surface water as a one-dimensional diffusion process and indicated the possibility of different flow regimes across the Peru current. Perturbing effects of upwelling and advection were noted. Differences in supply of ^{226}Ra from continental shelf sediments and upwelling were noted. Latitudinal trends in the insoluble daughter/soluble parent activity ratios ($^{228}\text{Th}/^{228}\text{Ra}$ and $^{234}\text{Th}/^{238}\text{U}$) were tentatively correlated with productivity variations.

Li, Feely and Santschi (1979) utilized ^{228}Ra and ^{228}Th data from seasonal water samples in the New York Bight and a simple box model to show exchange rates between the shelf and slope waters. Mean residence times of the shelf water were determined and average ^{226}Ra and ^{228}Ra fluxes per unit area of the coastal sediments were determined.

Reid, Moore and Sackett (1979) measured the surface and near surface distribution of ^{226}Ra and ^{228}Ra in the Gulf of Mexico. They found

the observed distribution (particularly the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio) could be explained by already known circulation patterns or, more importantly, provided insight into not well understood surface currents. The temporal distribution of ^{228}Ra was found to be naturally variable over a time period of less than or equal to 5 years probably related to changing residence times for the near surface water or variation in the relative dominance of the two sources of waters entering the eastern Caribbean. Because of this time variability, they postulated that the usefulness of ^{228}Ra in calculation of eddy diffusion coefficients is limited for the Gulf of Mexico.

Li, Feely and Toggweiler (1980) fitted ^{228}Ra data obtained in profiles of near surface and near bottom samples and potential temperature data to vertical diffusion models to calculate upwelling rates and vertical eddy diffusion coefficients in the upper water column of the equatorial Atlantic.

Feely et al. (1980) found mean residence times of Th in the surface water of the New York bight, calculated from $^{228}\text{Th}/^{228}\text{Ra}$ activity ratios. They found vertical profiles in the surface mixed layer and thermocline of the open ocean qualitatively resembled nutrient concentration profiles. They hypothesized the process that produced the rapid removal of Th from surface water, included uptake by phytoplankton, ingestion by zooplankton and final inclusion of the Th in rapidly settling fecal pellets.

These studies indicate the expanding scope of oceanographic and geochemical questions that may be addressed through a study of natural radionuclide tracers. The techniques and methods of analysis were only

recently established; consequently abundant data is lacking. The potential is very great indeed for their usefulness in understanding transport, residence and origin of oceanic water masses.

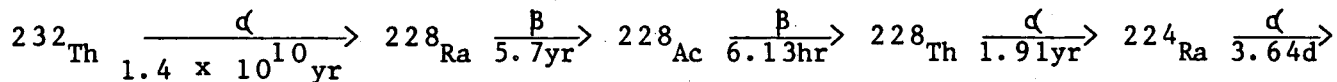
B. Methods of ^{228}Ra and ^{226}Ra collection and analysis

The ultimate goal was the measurement of ^{228}Ra and ^{226}Ra distributions rapidly and efficiently in spatial and temporal profiles at potential OTEC sites. Data collected would be used in cooperation with physical oceanographic measurements and models to study the transport of material on the one-to-thirty year time scale.

In order to conduct the measurement program, a simple and compact technique for ^{226}Ra and ^{228}Ra measurement was tested. Since there is only one common technique for counting both ^{226}Ra and ^{228}Ra , alpha particle spectrometry, we based our technique on this method. Previous methods had required either the return of large quantities of water to the home laboratory for processing (Koide and Bruland, 1975) or the use of scintillation counting for ^{226}Ra via ^{222}Rn emanation and some other technique for ^{228}Ra determination, generally alpha spectrometry for ^{228}Th . The manganese fiber collection technique (Moore, 1976) and the ^{223}Ra isotope dilution technique (Koide and Bruland, 1975) had never been combined. It seemed clear that such a combined method would be advantageous since it would be simple and compact in the field and involve only a single chemistry, a single sample preparation, and a single counting technique. The following describes the theoretical basis for the technique.

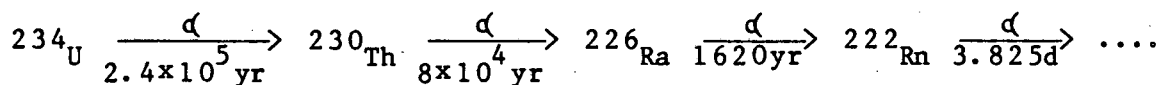
1. Radium decay chains.

a. ²²⁸Radium. ²²⁸Ra has a decay chain in brief as follows:



where the main decay mode for each nuclide is indicated above the arrow and the half life is indicated below the arrow. Figure 1 shows the complete and more detailed scheme. The half life of ²²⁸Ra, 5.714 years, was recently determined by Reid (1976).

b. ²²⁶Radium. ²²⁶Ra has a decay chain in brief as follows:



2. Counting techniques for radium isotopes.

a. ²²⁸Radium. Alpha particles are emitted from the nucleus with distinct energies rather like photons from the electron shells. Beta particles are emitted in conjunction with neutrinos. The variable energy partition between beta and the neutrino leads to a broad and diffuse distribution of beta energies. For this reason, energy dispersive spectroscopy of beta particles is much more difficult because of the overlap of the broad beta peaks. Alpha spectroscopy is a superior method for counting mixtures of nuclides because of the narrow peaks and the high resolution of modern detectors. A tabulation of alpha particle energies for the nuclides of interest is included in Table 1 and Fig. 2.

²²⁸Ra decays by beta emission. Fortunately the decay chain of ²²⁸Ra leads rapidly to ²²⁸Th and ²²⁴Ra. Both ²²⁸Th and its short-lived daughter ²²⁴Ra are alpha particle emitters. Since the decay times in

the chain are relatively short, ^{228}Th and ^{224}Ra accumulate rapidly in the sample planchet. Exact expressions for the parent:daughter ratios as a function of time may be calculated from Bateman's equations (c.f. Friedlander, Kennedy and Miller, 1964, p. 76). A graphical presentation of relevant decay curves is shown in Fig. 3. The counting technique chosen for this study consists of electroplating a thorium-free radium sample onto a platinum planchet (see below for chemical and electroplating details). When the sample has aged sufficiently (3 to 12 months) for ^{228}Th and ^{224}Ra to be countable, the planchet is counted in the alpha spectrometer and the ^{228}Ra abundance calculated.

The beta decay of ^{228}Ra and its very short lived ($t_{1/2} = 6.13$ hours) daughter ^{228}Ac may be used to measure ^{228}Ra directly. Because of its short half life, ^{228}Ac will grow into secular equilibrium with its parent ^{228}Ra in a matter of days. Koide and Bruland (1975) used a low-level beta spectrometer to measure the beta activities of their planchets. A thin aluminum foil absorber was placed over the planchet to prevent the alpha emissions (which have a very short penetration range) from entering the gas proportional counter. This absorber has only a small effect on the beta spectrum which tranverses the foil readily.

The use of beta counting for ^{228}Ra determination has both advantages and disadvantages. The primary advantage is that the total time from sample collecting to data production can be kept short since there is no need for the delay necessary for the accumulation of ^{228}Th and ^{224}Ra in alpha spectroscopy. The disadvantages were twofold. First, we would have to introduce a new counter and counting technique. Secondly, the calibration of the beta counting technique required the production

of ^{228}Ra standards and calibration of the efficiency of the beta spectrometer relative to the alpha spectrometer. We saw no real advantage to the technique when sufficient time is available for alpha spectrometry.

b. $^{226}\text{Radium}$. ^{226}Ra is an alpha particle emitter; consequently it can be counted directly by alpha spectrometry as discussed above. No waiting is required and the only constraint on counting is that a thin sample be prepared so that the alpha spectrum is not broadened by energy loss while traversing the sample itself. ^{226}Ra produces ^{222}Rn , a short-lived daughter, which can interfere with the alpha counting of other nuclides. For this reason, samples are flamed to orange heat immediately before counting to degas the radon and other volatile daughters.

^{226}Ra is commonly measured by the radon emanation method (e.g., Broecker, 1965). The ^{222}Rn emitted from the ^{226}Ra is collected and counted in an alpha scintillation counter. Since radon is a noble gas, chemical cleanup is relatively simple and the technique has been used to great effect in the past. Unfortunately, radon counting does not provide any information about ^{228}Ra which must be counted by other means.

3. A combined technique for ^{226}Ra and ^{228}Ra .

Although using separate techniques for independently determining the activities of ^{226}Ra and ^{228}Ra is advantageous in that cross checking of results is possible, time, equipment and analytical limitations are also significant considerations. Lacking the equipment for the classical scintillation counting method for ^{226}Ra , desiring a time efficient

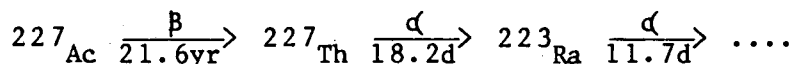
scheme for the determination of both ^{226}Ra and ^{228}Ra , and having no requirement for this study of in situ ^{222}Rn measurements, we proposed a combined alpha particle spectroscopy scheme as advantageous.

The alpha spectroscopy methods for radium determinations as described above are combined into a single operation. The radium isolate is plated directly onto a planchet, flamed and counted for ^{226}Ra . After a sufficient time period for ingrowth of ^{228}Ra daughters, the planchet is reflamed and ^{228}Ra is determined by ^{224}Ra assay with cross checks on ^{228}Th activity (subtracting appropriate ^{222}Rn counts).

This combined technique has the obvious advantages of use of a single planchet and method for both radium isotopes. In addition, chemical separation of the ^{228}Th and individual plating and counting is eliminated. The extra equipment and analytical time required for scintillation counting of ^{222}Rn for ^{226}Ra determination is also eliminated.

a. Calibration using isotope dilution via ^{223}Ra spike. In order to effectively monitor the chemical yield and to determine accurately the specific activities of radium isotopes of interest, it is preferable to calibrate the system. This is accomplished by introducing an extraneous isotope which has similar chemical properties, whose specific activity is well known and which can be accurately determined after all chemical and counting steps.

A variety of spike nuclides are available. After considerations, ^{223}Ra , the decay chain of which follows:



The detailed decay series is included in Table 4 (Friedlander, Kennedy

and Miller, 1964) and the relevant energies of decay particles are included in Table 1 and Figure 2.

^{223}Ra was selected because it is 1) not naturally occurring, preventing any confusion in its origin; 2) a radium isotope, having the same chemical behavior as the radium isotopes of interest (^{228}Ra , ^{226}Ra and ^{224}Ra); 3) a short-lived nuclide ($t_{1/2} = 11.7$ days), ensuring its elimination after initial counting before ingrowth of ^{228}Th and ^{224}Ra ; and 4) an alpha emitter, allowing measurement by alpha spectrometry. ^{233}Ra must be isolated chemically from the Ac and Th parents. After which, optimal ^{223}Ra activity levels were selected before addition to the sample solution. Koide and Bruland (1975) discuss the necessary considerations. Corrections were made for small tailings of ^{223}Ra counts into the ^{226}Ra count region. Last, the activity level selected should be appropriate for the time necessary for sample processing and for decay of any unsupported ^{224}Ra which may be present in near shore waters.

II. EXPERIMENTAL

A. Sample collection

Necessary samples were collected on a cruise off St. Croix, U.S. Virgin Islands (VOTEC site) in February, 1980. On each of two days 50 L of water from each of five depths (74, 300, 500, 700 and 900 m) were obtained using two 30 L teflon[®]-coated Go-Flo[®] bottles for sampling at each depth interval.

On day one, the water samples were filtered through Mn-fiber columns at rates of about 0.25 L/min. The water was not spiked and the

fiber samples were reserved for ^{226}Ra determination by the ^{222}Rn emanation method by Dr. David Reid of NORDA.

On day two, 50 L water samples were again collected and individually spiked with ^{223}Ra solution. Samples were shaken to mix the spike and allowed to equilibrate for about 1 hr. They were then filtered through Mn-fiber columns. Fiber was squeezed free of excess moisture, bagged and labelled for transport to the laboratory. Unspiked fiber samples were sent to David Reid.

B. ^{223}Ra spike preparation

In the laboratory, a solution of ^{223}Ra was prepared from a solution of ^{227}Ac , following the method of Hageman (1950) and Koide and Bruland (1975). Separation relies on the fact that at different pH, thenoyltrifluoroacetone (TTA) in a benzene solution will selectively extract specific elements. Figure 4 (from Hageman, 1950) shows the per cent extraction of Th, Bi, Pb, Tl, Ra and Ac from aqueous solution by an equal volume of 0.25 M TTA-benzene solution as a function of pH.

The solution containing ^{227}Ac , ^{227}Th and ^{223}Ra was taken to dryness and redissolved in 2.5 N HCl. The pH was adjusted to 2 by addition of 15% NH_4OH solution. The solution was shaken vigorously with an equal volume of TTA after which the two immiscible liquids were allowed to separate (or centrifuged for quicker separation). The ^{227}Th bearing TTA was removed and discarded. The entire procedure was repeated one to two additional times. Next, Ra was separated from Ac. The pH of the solution was adjusted to 5.5-6.0 with NH_4OH and an approximately equal volume of TTA/benzene was added. The mixture was shaken vigorously.

The two liquids were separated after settling or centrifugation. The extraction was repeated one to two times. ^{223}Ra remained in the aqueous phase.

The ^{227}Ac contained in the TTA fraction was re-extracted with an approximately equal volume of 2 M HNO_3 . The two liquids were separated and the procedure repeated one or two times. TTA was discarded and the Ac solution reserved for later extraction of ^{223}Ra .

Once the ^{223}Ra was isolated, it was further purified by passing through a cation exchange column. We used a quartz column, 0.9 cm in diameter, filled to a depth of 9.5 cm with Dowex cation-exchange resin (Bio-Rad AG 50W-X8, 200-400 mesh). Columns were calibrated using a high activity aliquot of ^{223}Ra and counting small elution intervals (volumes) on a gamma spectrometer adjusted for the 270 keV Ra peak. The purification was accomplished by loading 1 mL of the ^{223}Ra solution (in 2.5 N HCl), elution of 130 mL 2.5 N HCl, and final elution of 40 mL 8 N HCl which contained the purified spike. Flow rate was approximate 0.5 mL/min. The final eluate was taken to dryness, redissolved in 2.5 N HCl and subsampled for plating to determine ^{223}Ra specific activity on the alpha spectrometer.

Once spike activity was determined, a volume with appropriate activity was selected for addition to the 50 L water samples. The 50 liter carboy and spike was shaken and allowed to equilibrate for one-half to one hour.

1. Spike purification.

Prior to the VOTEC cruise, methods of ^{223}Ra spike purification were

judged sufficient. After sample processing and counting, it was discovered that separation of ^{223}Ra had been incomplete leaving significant quantities of parent ^{227}Ac in the spike. Purification removed ^{227}Th but not parent ^{227}Ac .

It is possible, but more unlikely, that ion-exchange columns were contaminated with ^{227}Ac . The continued presence of ^{227}Th and ^{223}Ra hampered measurement of ^{228}Ra via the ingrowth of ^{228}Th and ^{227}Ra . The techniques of ^{223}Ra extraction described previously can produce clean solutions, however, any ^{223}Ra spike produced in this way should be monitored for ^{227}Th in growth for several days to ensure a clean separation from ^{227}Ac .

Another procedure has been investigated which appears both time and yield efficient. An aliquot of the Ac-Th-Ra solution is taken to dryness and redissolved in 3 mL of 0.05 N HCl. pH is carefully adjusted to 6 with approximately 1.6 mL of 0.1 N NaOH. The solution is transferred to a round bottom centrifuge tube with cap. Approximately 5 mL of TTA benzene solution are added and the solutions are vigorously shaken by hand for 2-3 minutes. The vial is centrifuged to separate the two liquids and the TTA phase containing both Ac and Th is withdrawn by disposable pipette. The pH is checked and adjusted to 6 as necessary. The procedure is repeated twice. Both Th and Ac are re-extracted into 2 M HNO_3 as previously described. The aqueous phase now contains a pure or nearly pure solution of ^{223}Ra . A small aliquot may be used check for yield and purity. If required a small ion exchange column purification is used. An aliquot of the spike solution is plated and checked over several days for ^{223}Ra decay and ingrowth of ^{227}Th (which would indicate

the unwanted presence of the parent ^{227}Th).

A single extraction of TTA benzene with the Ac-Th-Ra solution at pH 5.5-6.0 resulted in approximately 70% extraction of ^{223}Ra and elimination of 99% Th and 85% Ac. After two more extractions approximately 35% of the original Ra will be retained while only 0.0001% of the Th and 0.3% of the Ac remains. A small column cleanup would extract the remaining Th and Ac to only trace levels, unimportant in the final analysis.

C. Fiber preparation and filtration

Mn-fiber to be used for filtration (Moore, 1976) was prepared in the laboratory. 200 g of dry acrylic fiber (Monsanto Acrilan 3.0 denier, type B-16 donated by Monsanto, Moore, 1976) was added to 4L of 0.5 M potassium permanganate solution in an 8 L capacity stainless steel Bain-Marine beaker at 80°C. The mixture was maintained at 80°C for 5 min. with frequent stirring. After this period, and when obvious quantities of gas were apparent from the reaction between the fiber and permanganate, the fiber was quickly removed with tongs or in an open mesh nylon bag to a cooling bath of double-distilled H₂O in another 8 L Bain-Marine beaker. The impregnated fiber was rinsed four to five times with double-distilled H₂O and finally squeezed free of excess moisture using plastic gloves.

Shortly before actual use, a fiber bag was opened and the fiber was "fluffed," i.e., separated into non-clumped fibrous strands. The fiber sample was then placed into a plastic column (3.4 cm diameter, 13 cm length) with a plastic frit on one end. The column top was sealed by a

one hole rubber stopper and Bevaline[®], teflon lined plastic tubing, used to connect the fiber column to the water sample.

The plastic column was inverted to purge bubbles of trapped air and to insure a complete flow of water through the fiber. Flow rates were about 0.2-0.4 L/min. The total volume of water passed was measured by marking the beginning and ending water levels on the plastic carboy and calibrated later in the laboratory.

Once filtration was complete, fiber samples were removed from the plastic columns, squeezed to remove excess liquid, and stored in plastic bags.

D. Radium purification

In the laboratory, fiber samples were immersed in one-fiber volume of 8 N HCl and heated gently to boiling under a fume hood. Heating was stopped when the fiber was completely white. The HCl solution and fiber was next filtered (0.45 μm nuclepore[®] filter). The fiber mass was then placed in the filtering bowl and rinsed several times with 8 N HCl to ensure complete removal of leachate. The leachate (approximately 1 L) was transferred to a large beaker. Fiber samples were reserved after rinsing in double distilled H₂O.

The 8 N HCl leach of Mn-fibers was chosen because of the good yields obtained. Experiments using 2 N HNO₃ resulted in lower yields. The 2 N HNO₃ had resulted in lower yields. The 2 N HNO₃ leach deserves further investigation because copious quantities of Mn in solution are not produced as with the HCl method.

1. BaSO_4 - Radium co-precipitation and BaSO_4 fusion.

To further concentrate radium, a saturated solution of BaNO_3 was prepared and a 2.5 mL aliquot was added to the HCl solution. Next, 35 mL of 17% H_2SO_4 solution was added slowly. The solution was warmed gently and slowly stirred with a magnetic stirrer for approximately one hour. The BaSO_4 precipitate with co-precipitated radium was collected on a 0.45 μm cellulose acetate milled R filter.

To convert the insoluble BaSO_4 precipitate to Ba-Ra carbonate which may be dissolved in HCl the precipitate of the step was transferred (while still on the cellulose acetate filter) to a platinum crucible and ashed over a gas burner. Subsequently, 2.5 g each of K_2CO_3 and Na_2CO_3 were mixed and added to the cool crucible. The three phases were mixed and heated over the gas burner to liquid. After cooling the light blue fusion cake was put in a 1 L beaker and covered with approximately 800 mL of double distilled H_2O .

The fusion cake was agitated ultrasonically to promote disintegration of the cake and solution of soluble sulfates. The liquid and solid suspension was then heated for approximately 30 minutes and filtered through a 0.45 μm nuclepore R filter. The barium-radium carbonate caught on the filter was resuspended and washed several times in a total of 200 mL of hot, double distilled H_2O .

The filtration bowl and filter holder were transferred to a smaller collection flask and the material on the filter dissolved in 2.5 N HCl. This filtrate was transferred to a 100 mL beaker and slowly taken to dryness.

This coprecipitation and fusion presented no major difficulties. Initially we had hoped to forego both steps and proceed with a concentrated fiber leach solution directly to an ion exchange column. Unfortunately, the quantities of Mn in the solution overloaded the exchange capacity of the columns. The size and capacity of columns required to separate radium from manganese in these solutions was prohibitive.

After conversion to Ba-Ra carbonate during the fusion process, the selective dissolution of sodium, and potassium sulfates in water presented some problems. Dissolution always appeared complete initially, but transfer of the Nuclepore[®] membrane containing the Ba-Ra carbonate residue to a beaker and washing with HCl usually resulted in a solution with a fine precipitate of, presumably, barite. This condition was eliminated when HCl solution was added directly to the filtering apparatus without removal of the filter.

2. Ion-Exchange column separation of Ba and Ra.

In order to remove Ba and other impurities from the above isolate, we proceeded to use a cation exchange resin column technique. Columns were 2 cm in diameter filled to a depth of 12 cm with Dowex cation exchange resin (Bio-Rad AG 50W X-8, 200-400 mesh).

The isolate was redissolved in 5 mL of 2.5 N HCl and loaded onto the column. An elution of 650 mL of 2.5 N HCl removed the bulk of Ba. Next the Ra fraction was eluted with 300 mL of 8 N HCl. This fraction was taken to dryness and redissolved in 5 mL of 2.5 N HCl. The large column elution procedure was repeated. The final 8 N HCl fraction was taken to dryness and redissolved in 1 mL of 2.5 N HCl. Final purifica-

tion involved a small column purification identical to that described above for the ^{223}Ra spike final clean up. The 40 mL 8 N HCl eluate from this column was taken to dryness and generally appeared very free from Ba contamination and other visible residue.

Ion-exchange column separation methods require significant improvement. Column calibration and purification of the spike were straightforward, but calibration of the large columns was different with a relatively pure radium solution from that with a solution containing high Mn and Ba impurities. Yields depended upon the amount of initial material introduced and number of ion-exchange pass elutions. The final procedure is a compromise between purity and yield. More elutions resulted in higher purity but lower yields and, in general, required more time. Although the procedure we have outline is adequate, more experimentation with column size, calibration, resin mesh size, and acid strength, etc. would be profitable.

3. The electrodeposition of radium.

In order to mount the final isolate of radium on planchets suitable for counting, we followed the basic procedure as outlined by Koide and Bruland (1975). This involves cathodic deposition of radium onto a 2.1 cm^2 area of a 2.5 cm diameter platinum planchet. Platinum planchets must be used due to the repeated flaming necessary to purge ^{222}Rn gas.

The plating cell was constructed following their design with the single exception that the millepore $\text{\textcircled{R}}$ clamp did not provide sufficient force to seal the bottom of our cell and a ball joint clamp (Thomas, No. 28) with a screw down closure was substituted. An unregulated power

supply was constructed for electroplating consisting of a 36 volt (rms) transformer, a full wave recifier and a 1300 μ f capacitor producing approximately 50 v D.C. and a 2 watt 2000 ohm potentiometer in series with the cell. The cell was operated at 40 volts and 100 mA by varying the cathode-anode spacing and the series resistance.

The final radium isolate described above was redissolved in 0.5 mL of 0.05 N HCl and transferred to the electrodeposition plating cell via rinses with 2-propanol to a final volume of 5 mL. The planchet formed a cathode at the base of the cell. A specially designed platinum anode was then flamed and inserted into the liquid 1-2 mm from the cathode face. Current was kept between 100-150 mA at approximately 40 V for 20 minutes. After this interval, the anode was withdrawn, several drops of 15% NH_4OH added to the cell, power shut off, the liquid decanted and the cell rinsed with 2-propanol. The planchet was removed and flamed to prepare for counting.

E. Alpha particle spectroscopy

The flamed planchet is transferred to the alpha spectrometer and counted for an appropriate time as described above in the discussion of the combined ^{226}Ra , ^{228}Ra spectroscopy technique.

IV. RESULTS

A. Counter efficiencies and electrodeposition yield

A standard solution of ^{226}Ra (Amersham) was obtained and diluted to a solution containing 1485 dpm/mL. A 0.1 mL aliquot was evaporated onto a platinum planchet. A 0.1 mL aliquot was also electrodeposited by the

previously described method.

Results are indicated below.

Evaporated ^{226}Ra Std:

$$\frac{56746 \text{ counts}}{108050 \text{ sec}} = 56746 \pm \frac{238 \text{ cts}}{1800.8 \text{ sec}} = 31.510 \pm 0.132 \text{ cts per min (cpm)}$$

Electrodeposited ^{226}Ra Std:

$$\frac{54842 \text{ cts}}{108050 \text{ sec}} = \frac{54842 \pm 234 \text{ cts}}{1800.8 \text{ min}} = 30.454 \pm 0.130 \text{ cpm}$$

YIELD: $\frac{30.454 \pm 0.130}{31.150 \pm 0.132} = 96.65 \pm 0.08\%$

EFFICIENCY OF COUNTER (FROM EVAPORATED STANDARD):

$$\frac{31.510 \pm 0.312 \text{ cpm}}{148.5 \text{ dpm}} = 0.2122 \pm 0.0009 \text{ cpm/dpm}$$

Our electrodeposition technique resulted in a 96.7% yield as compared to an evaporated standard. Counter efficiency was calculated as 21.22%. Several replicate experiments confirmed these results within the recorded uncertainties.

The efficiency of each individual detector should be conducted and the plating yield of the electrodeposition method should be improved. Nevertheless, these yields and efficiencies are on the order of those reported by Koide and Bruland (1975).

B. Fiber and column (ion-exchange) yields

Because of lack of numerous quantities of platinum planchets, precise yields could not be calculated at each stage of the analytical procedure. Yields sufficient for experimental purposes were approximated

using gamma spectroscopy of ^{223}Ra spike.

The Mn-fiber was found to be a quantitative scavenger of radium in sea water solution. Our total method yield calculated in this way ranged from 16-44%, which is not acceptable. Our separation and plating method yields were so erratic and low (16-44 %) that the results are not presented.

C. Blanks and Background

Blank contributions should be determined for non-impregnated fiber, and for BaSO_4 precipitation and fusion steps. This requires several experiments with spiked and non-spiked material from which aliquots will be separated and plated at appropriate stages in order to calculate the contribution of the analysis material to the counts for radium. Precise yields at various stages of the method should be determined.

The background of the detectors in use is practically zero when new. Frequent analyses with different levels of activity and various nuclides create a higher background level by contamination of the counter surfaces.

D. ^{226}Ra and ^{228}Ra results from St. Croix

1. ^{226}Ra by ^{222}Rn emanation.

The ^{226}Ra results from the ^{222}Ra emanation method provided by Dr.

David Reid are as follows:

Depth (meters)	^{226}Ra in sample (dpm)	No. of replicates	Vol. of sea water passed (liters)	dpm/100L
75	3.82 + 0.16	3	50	7.64 + 0.3
300	3.40 + 0.23	3	46	7.39 + 0.5
500	3.85 + 0.19	4	50	7.70 + 0.38
700	5.02 + 0.17	4	48	10.46 + 0.35
900	5.70 + 0.21	4	51	11.18 + 0.41

The mean presented is the arithmetic average. The standard deviation is the larger of the individual counting statistics or the standard deviation of the mean of the replicates, whichever is greater.

2. ^{228}Ra results.

Since our spike was contaminated with ^{227}Ac , the long lived (21.77 year half life) parent of ^{223}Ra , the sample planchets will contain abundant ^{223}Ra long after the ^{228}Ra is decayed away to unmeasurable levels. Therefore, we could count ^{226}Ra , but not ^{228}Ra .

^{228}Ra might be determined by examining its daughter nuclides ^{220}Rn ($t_{1/2}$) = 55.6 sec., 6.287 MeV, 100%) and ^{216}Po ($t_{1/2}$) = 0.15 sec., 6.777 MeV, 100%). The spectrum on the 6-8 MeV scale provides the information necessary to calculate ^{228}Ra abundances (see Fig. 3).

Both the ^{220}Rn and ^{216}Po peaks are contaminated by ^{223}Ra daughter nuclides, ^{211}Bi ($t_{1/2}$) = 2.14 min., 6.289 MeV, 15.9%) and ^{219}Rn ($t_{1/2}$ = 3.96 sec., 6.817 MeV, 81.0%) respectively. The counts due to ^{223}Ra daughters must be subtracted from the ^{220}Rn and ^{216}Po peaks regions. To calculate these quantities the ^{223}Ra daughter, ^{215}Po ($t_{1/2}$ = 1.78 ms, 7.384 MeV, 100%) is counted. The contribution to the ^{220}Rn and ^{216}Po peaks is found by counting an old sample of the original ^{227}Ac parent

solution. This gives the counts from ^{211}Bi in the ^{220}Rn and ^{219}Rn in the ^{216}Po region relative to the counts in the ^{215}Po peak. In the sample spectra, we measure the 215 peak counts and calculate the ^{211}Bi and ^{219}Rn counts, subtract from the counts in the ^{220}Rn and ^{216}Po regions and assign the difference to the ^{228}Ra daughters. Since the corrections are large, the uncertainties in the results are much larger than would have resulted from if the ^{223}Ra spike had been pure.

One of the possible objections to this technique might be that ^{219}Rn and ^{220}Rn are noble gas isotopes and will be lost from the samples. This possibility has been investigated and found to be unimportant for ^{219}Rn in the 227 spike sample. In this sample both ^{215}Po and ^{211}Bi are as abundant as ^{223}Ra . Since they are ^{219}Rn daughters, they would be depleted if ^{219}Rn were leaking out of the samples. We made the same assumption for ^{220}Rn since it also has a very short half life; 55.6 sec. vs. 3.96 sec. for ^{219}Rn . The assumption is incorrect for ^{222}Rn coming from ^{226}Ra which has a much longer half life (3.82 days) and is present in our samples at about one-fourth of the ^{226}Ra abundance. The diffusion time of Rn is clearly of the order of a day or so, several thousand times longer than the decay times for either ^{220}Rn or ^{219}Rn . Consequently, the use of ^{220}Rn and ^{219}Rn to measure their parent nuclide abundances is justifiable.

The following table shows our measured ^{228}Th abundances and the ^{228}Ra abundances calculated from them and the $^{228}\text{Ra}/^{226}\text{Ra}$ ratios calculated from the ^{226}Ra data in the preceding table. Because of the large uncertainties in the ^{228}Ra calculations we are reluctant to assign an error factor to these data at present, although we suspect that the

errors are roughly a factor of two; that is, the $^{228}\text{Ra}/^{226}\text{Ra}$ ratios may be as much as twice or as little as half as large as those shown here. We believe that most of the error is systematic and that if one value is, say, twice the true value, all are twice the true value. The ultimate precision of the measurement of the 228/226 ratio is of the order of + 10% with the ratio varying from essentially zero to values as high as 5.0.

Depth	^{228}Ra cpm on planchet	^{226}Ra cpm on planchet	$\frac{^{228}\text{Ra}}{^{226}\text{Ra}}$	^{228}Ra dpm/100 L
75	0.700	0.692	1.012	1.13
300	0.189	1.638	0.115	0.85
500	0.051	1.672	0.031	0.24
700	0.126	2.183	0.058	0.61
900	n.d.	0.187	n.d.	n.d.

V. RECOMMENDATIONS FOR FUTURE DEVELOPMENT

A. Continuation of the Present Technique

The present technique is inadequate to continue in an active field measurement program. With some experimentation we could use our technique to measure ^{226}Ra and ^{228}Ra concentrations in field samples using the ^{223}Ra spike technique. We are also at a less than satisfactory point with regard to the VOTEC samples as the ^{228}Th is still growing in from ^{228}Ra at a relatively rapid rate and the ^{228}Ra determination in those samples will continue to improve with age for a couple of years.

B. Addition of ^{222}Rn Counting

The addition of ^{222}Rn counting capability to the project would add

to its usefulness in several ways. The measurement of ^{226}Ra by the ^{222}Rn emanation method is a venerable technique with no new development required. Once a radium sample is sealed into the sampling system, one can continue to count ^{226}Ra until, as Key et al (1979) put it, "Texas freezes over." This means that the ^{223}Ra spike is no longer required as the radon counter gives the abundance of ^{226}Ra . If we continue our $^{228}\text{Ra}/^{226}\text{Ra}$ measurement program and use the radon counter to measure ^{226}Ra we get the necessary data, namely the ^{226}Ra concentration, the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio and consequently, the ^{228}Ra concentration.

In addition to making the ^{223}Ra spiking unnecessary, a ^{222}Rn counting system would make possible the determination of unsupported ^{222}Rn which is another circulation tracer but of much shorter timescale (3.82 days vs. 5.71 years) than ^{228}Ra . This adds to the dynamic range of the measurements which could be made and the information which could be generated.

We are strongly in favor of ^{222}Rn measurements as an addition to the program. We would require a modest period of time to construct a radon counter and learn its operation. Such an addition would be of great use in the study of sediment-OTEC communications and would simplify the radium determinations as well. We believe that it would make an important contribution to understanding the OTEC site environment.

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90	Th	Th^{232} , Th (thorium) 1.39×10^{10} years		Th^{228} , RdTh (radiothorium) 1.90 years		
89	Ac		Ac^{228} , MeTh ₂ (mesothorium 2) 6.13 hours			
88	Ra	Ra^{228} , MeTh ₁ (mesothorium 1) 5.75 years		Ra^{224} , ThX (thorium X) 3.64 days		
87	Fr					
86	Rn			Rn^{220} , Tu (thoron) 54.5 seconds		
85	At					
84	Po			Po^{218} , ThA (thorium A) 0.158 second		Po^{212} , ThC' (thorium C') 3.0×10^{-7} second
83	Bi			Bi^{212} , ThC (thorium C) 60.6 minutes		
82	Pb			Pb^{212} , ThB (thorium B) 10.6 hours		Pb^{208} , ThD (stable lead isotope)
81	Tl					Tl^{208} , ThC'' (thorium C'') 3.1 minutes

Figure 1. The ^{232}Th (^{228}Ra) decay scheme.
(Adapted from Freidlander *et al.*, 1964,
p. 10, with information from Reid, 1976)

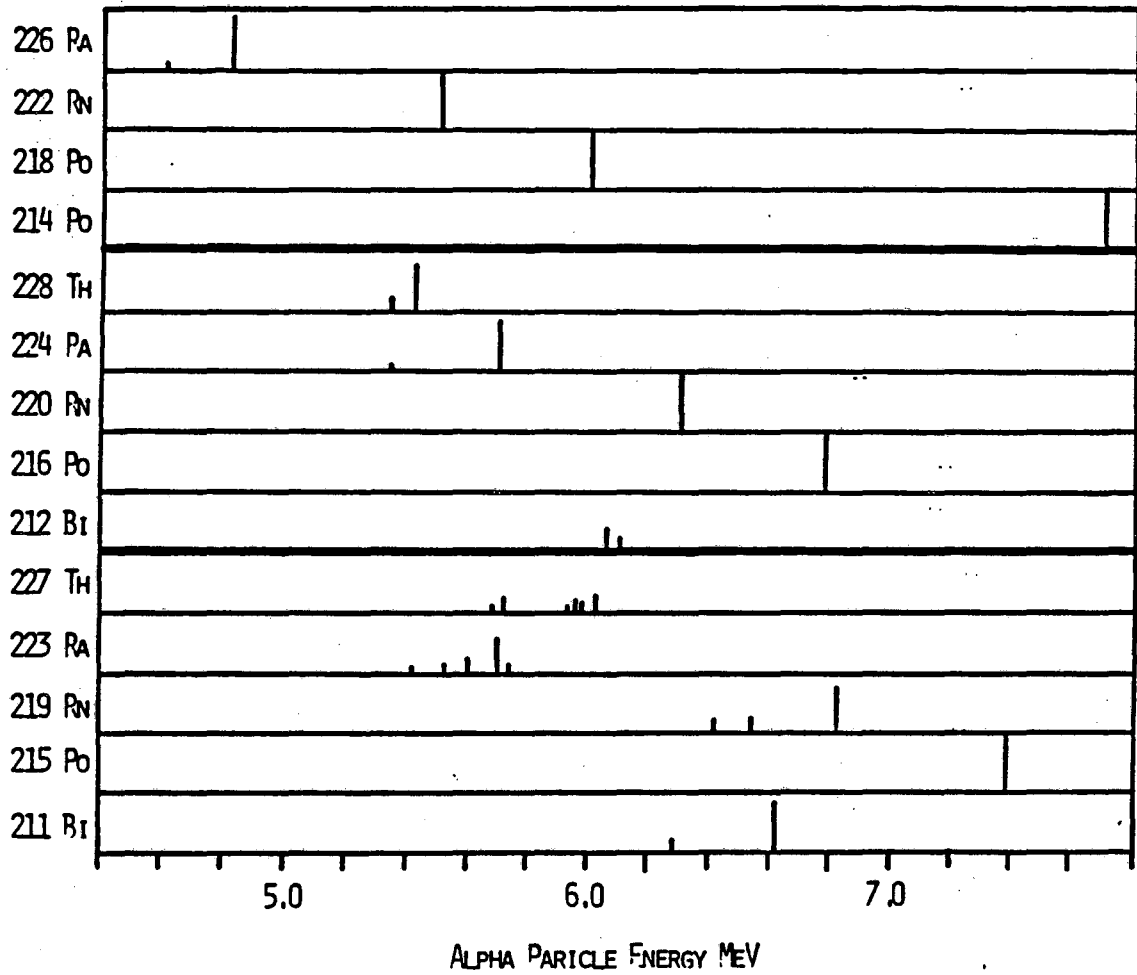


Fig. 2. Alpha particle energies of the nuclides of interest in the 228, 226 and ²²³Ra systems. Vertical bars are approximately proportional to the relative intensities of the peaks.

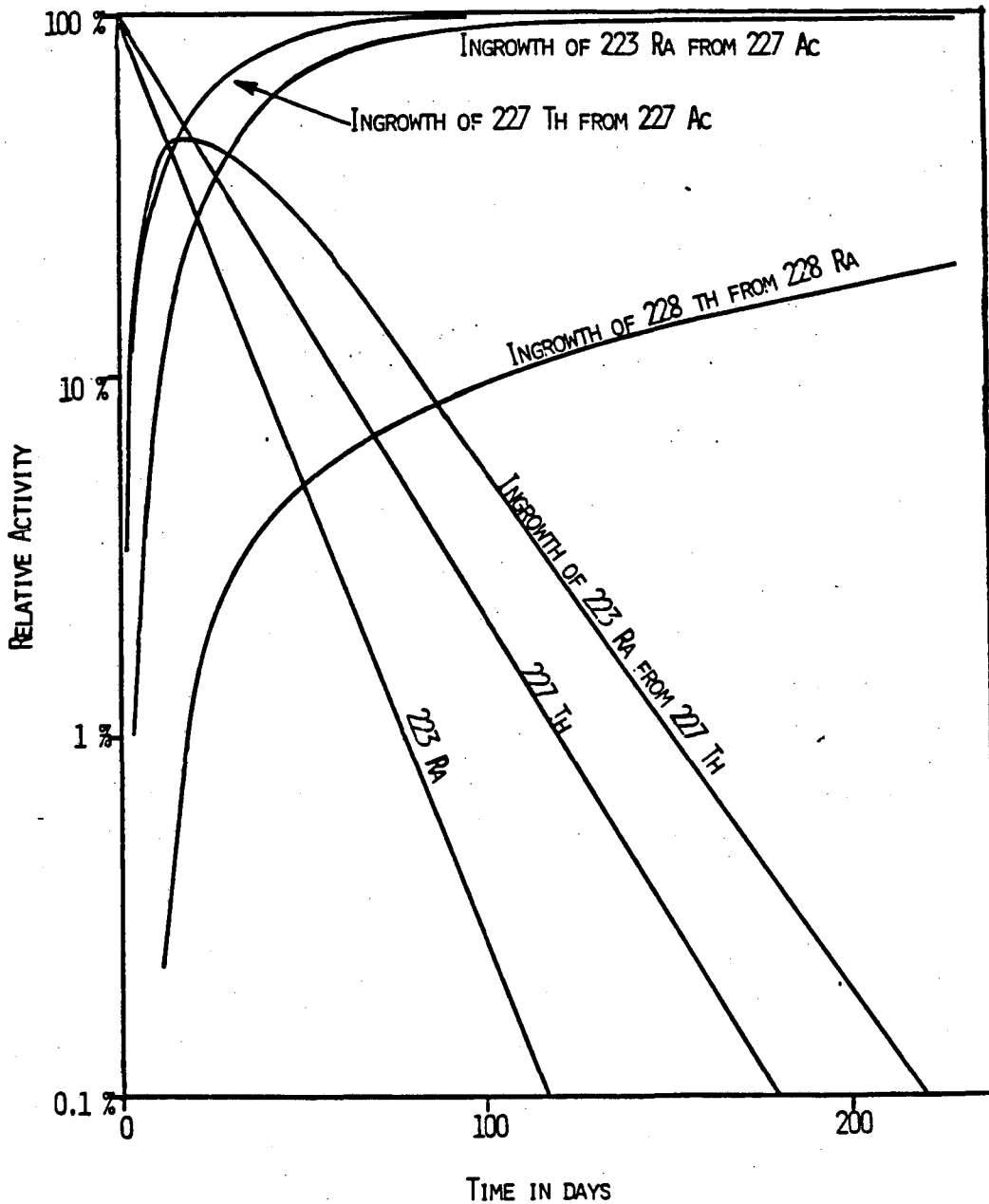


Fig. 3. Graphs of the solutions of the decay equations for ^{228}Ra , ^{223}Ra and ^{227}Th . The decay curves of unsupported ^{223}Ra and ^{227}Th are straight lines. The same nuclides when supported by ^{227}Ac are asymptotic to the 100% axis because of the long half life of ^{227}Ac . ^{223}Ra in transient equilibrium with unsupported ^{227}Th rises rapidly and then declines. ^{228}Th grows in from the beta decay of ^{228}Ra .

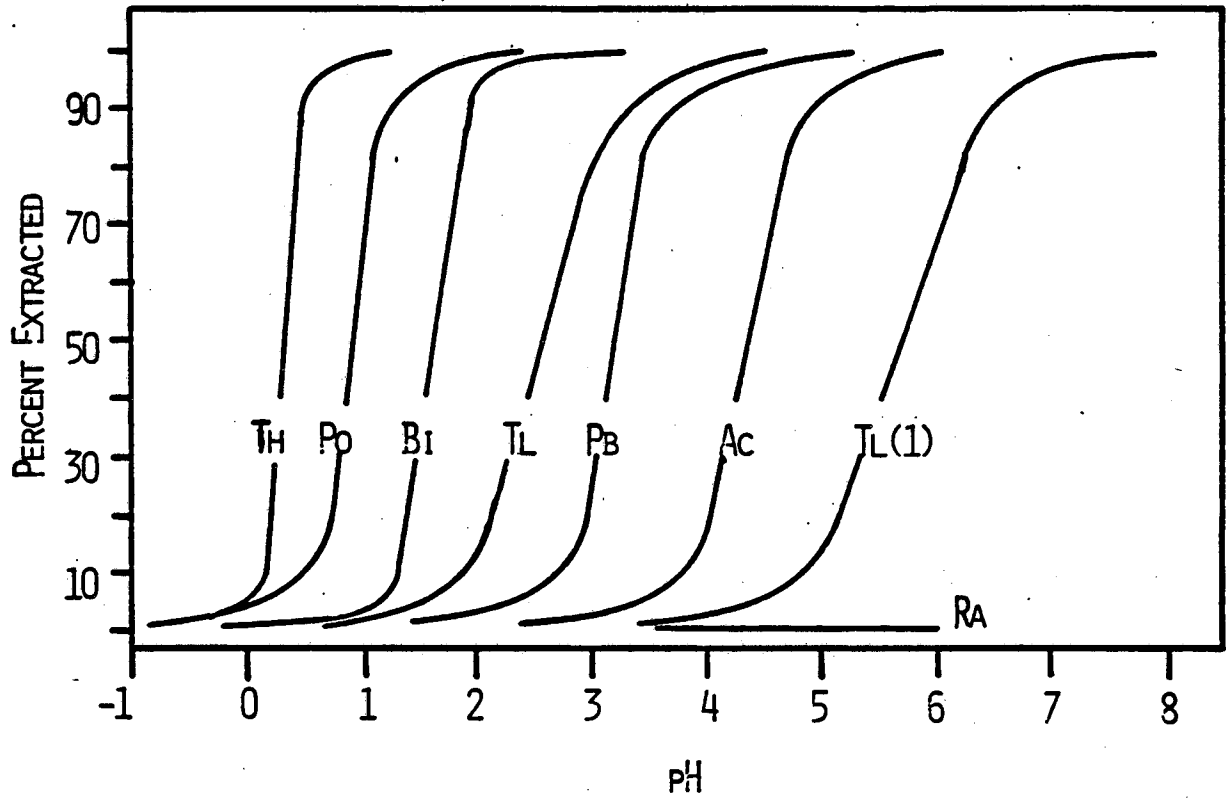


Fig. 4. Extraction efficiency for several elements in TTA-benzene as a function of the pH in the aqueous phase.

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