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WINCHESTER LABORATORY

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JANUARY 1, 1960 - MARCH 31, 1960

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INTRODUCTION

The Winchester Laboratory has been assigned the task of investigating the hazards of radioactive pollution resulting from the processing of uranium ores. Broadly this implies determination of the ultimate fate of unrecovered uranium and its daughter elements, and measurement of the biological hazards associated with environmental distribution of these materials. At present some uranium milling operations produce effluent streams containing radium and thorium at concentrations higher than the discharge levels specified in the Federal Register, Title 10, Part 20.* Furthermore, tailings piles have accumulated which contain large quantities of naturally radioactive elements; these mounds of debris are subject to the effects of wind and water erosion and the consequent distribution of their radioactive contents. The milling operations themselves present radiological hazards to personnel inhaling and ingesting naturally radioactive materials.

Work in the laboratory is concentrated at present in five critical areas:

1. The development of rapid, accurate analytical methods for measuring concentrations of radium and thorium at or below the Part 20 levels, comparing and evaluating these techniques, and determining their applicability to various chemical systems. Concomitant to this is the problem of determining isotopic ratios of radium and thorium in various systems, as well as that of developing laboratory techniques for estimating the concentrations of other radioactive species present in the ore, e.g., actinium, polonium, etc.
2. The development of simple, economical processes for decontamination of effluent mill streams so that they may be safely discharged to the surroundings.
3. Investigation of the fundamental physico-chemical behavior of radium, thorium, and other significant radioelements in a variety of chemical systems, with particular attention to coprecipitation, adsorption, and leaching properties. On the basis of the knowledge gained in these investigations, rational treatment methods can be devised to prevent the dissemination of harmful quantities of these materials into the environment.

* For radium-226, 4×10^{-9} $\mu\text{C}/\text{ml}$; for thorium-230, 5×10^{-8} $\mu\text{C}/\text{ml}$. The thorium-230 levels occurs only in a proposed revision.

4. Evaluation of the potential environmental hazards associated with the present tailings ponds and piles. Particular attention is being paid to the possible scattering of the radioactive materials by the erosive action of wind, water, and other weathering agents.

5. Evaluation of the radiological hazards of dusts arising in the milling operation or from wind erosion of tailings.

This report summarizes the work completed at this laboratory in the first quarter of 1960, and suggests the future courses of investigation. As a progress report it may be considered as a supplement to WIN-112 1/ which describes the work up to January 1, 1960.

ANALYTICAL PROCEDURES

Certain fundamental principles are common to all radiological determinations, and specifically to all low-level radiochemical procedures. The sensitivity and precision of any radioactivity determination are limited by the statistically random nature of the radioactive disintegration process 2/, 3/. Specifically, the error of a counting rate will depend on (a), the counting rate itself, (b), the length of time available for the determination, and (c) the instrument background counting rate. The relative error will be lower if the counting rate is higher, the counting time is longer, and the instrument background rate is lower. Of these three factors, counting rate is most important. There are three ways of maintaining a high counting rate for samples of a given activity in terms of disintegrations per minute per gram or per unit of volume. There are (1) use of large samples, (2) choice of methods with high chemical yield, (3) counting at high efficiency.

Radium

The measurement of radium at the levels of interest in radiological pollution work (of the order of the Part 20 levels) is one of the most exacting radiochemical determinations because of the low permissible quantities of this element and particularly of the specific radionuclide radium-226. The determination is usually made by alpha counting, because of the lower backgrounds available in such equipment. Alpha counting however introduces new problems because of the very limited penetrating power of alpha particles, only a few milligrams per square centimeter. The total quantity of material on the counting planchet must be kept very small to avoid excessive counting losses by self-absorption.

Evaluation

Four methods which have been proposed for the determination of radium were selected for evaluation. In three of these^{4/}, ^{5/}, ^{6/} the radium is finally precipitated with barium sulfate as carrier and alpha-counted. In the other^{7/}, the radium is recovered in a carrier-free condition for alpha counting. These four procedures were described in WIN-112; they have, in certain cases, been modified in use and applied to a variety of chemical systems.

The "English" method^{4/} has been found to give inaccurate results on total radium due to thorium carrying through into the final sample counted. Some time was devoted to modification of the procedure to eliminate the thorium contamination but with only marginal success. The method was finally abandoned in favor of others available.

The remaining three techniques are outlined in their final modified forms in Figures 1 - 3, with detailed descriptions presented in Appendix A. All have proved suitable for use on mill effluent samples, but have somewhat different reproducibility and accuracy, ease of manipulation, and applicability to very low levels.

In our experience, the Winchester method^{7/} has given the best reproducibility and accuracy. It is, however, time consuming, requiring some eight man-hours of sample preparation per set of four samples. Manipulations are not difficult, certainly not beyond what can reasonably be expected of a technician. At present, only one-tenth of the radium recovered is plated for counting in this method since there is some extraneous material present in the final solution, so that only 1 ml (of a total of 10) can be deposited on a two-inch planchet without self-absorption losses. While this is no disadvantage with more active samples, (100 disintegrations per minute per liter or more), it does limit the applicability of the method to lower levels. Since the radium should be recovered in a carrier-free condition, attempts are now under way to eliminate this extraneous material.

It appears that the method developed by the PHS^{6/} can give results comparable in precision to those obtained by the Winchester method with significantly lower man-hour requirements, about four hours per set of four samples. Because of the use of carrier in the form of barium sulfate, a self-absorption correction is required and it is important to deposit the barium sulfate-radium precipitate uniformly and thinly on the planchets. Improvements in plating techniques are now being developed.

FIGURE 1

Flow Sheet, Winchester Method for Radium Analysis

FIGURE 2Flow Sheet, Public Health Service Method for Radium Analysis

FIGURE 3

Flow Sheet, Idaho Falls Method for Radium Analysis

The Idaho Falls method^{5/} is rather similar to the PHS method in principle. It appears to require somewhat more care in the chemical steps, particularly in the nitric-perchloric acid oxidation of the filter paper (and other organic matter) and in the adjustment of the pH with sodium hydroxide. On several occasions, large amounts of precipitate have formed at this point. Otherwise, the Idaho Falls method appears to have potentialities and limitations similar to those of the PHS method. As presented by Ebersole, the method is designed for 200-ml samples, which would limit its applicability at the lowest levels unless inordinately long counting times were used. However, except for manipulative difficulties, there appears to be no reason why the method could not be extended to larger samples.

New Methods

In addition to the above evaluation, two new methods are under development, one of which gives a rapid estimation of the isotopic composition of the radium in the sample. These methods are presented schematically in Figures 4 and 5 and the detailed procedures are given in Appendix A.

The first of these methods is based on solvent extraction techniques. Metallic constituents including iron, thorium, bismuth and lead are selectively extracted by proper choice of chelating agent and pH control. After these elements have been removed, the radium is precipitated with barium sulfate. Because of the prior decontamination by solvent extraction, it is free of other radioactive species. In this method a self-absorption correction will probably be required, since the radium is carried on a macroscopic barium sulfate precipitate. This method requires about three hours per set of four samples. Precision appears satisfactory, but accuracy has not yet been determined.

The second of the new methods has the distinct advantage of providing information on the isotopic composition of the sample radium. In this method, the radium is purified and precipitated on barium sulfate as in the other methods. It is then converted to carbonate and allowed to stand for 36 minutes, after which the ingrown daughter elements, lead and bismuth, are separated from the radium by anion exchange techniques, using hydrochloric acid elution^{8/}. The lead and bismuth fractions are then alpha counted (the actual alpha emitter is a daughter in equilibrium). With this waiting period, by counting the alpha emitter in equilibrium with the lead-bismuth, the activity due to the various radium isotopes is quite different, as shown in the following table:

Table 1Ingrowth of Characteristic Daughter Alpha Activity into Radium

Isotope	Alpha Activity (% of original Ra activity)
Ra-223	49.83
Ra-224	0.70
Ra-226	0.45
Ra-228	0.00*

* This activity is due to thorium-228 which would probably be separated with the lead-bismuth fraction.

Note: These values were obtained by solution of the appropriate Bateman equations¹⁰ for an ingrowth time of 36 minutes.

It is apparent from this table that the lead-bismuth activity will give essentially a measure of the radium-223 activity. The total radium activity can be obtained, after measurement of the lead-bismuth daughter activity, be reprecipitating the radium-barium (which will have passed through the ion-exchange column) as barium sulfate and alpha-counting this material.

The radium-226 can then be determined by difference from the value obtained for total radium, if the quantity of radium-224 (derived from natural thorium) is small, as is usually the case in uranium ores and effluents. If the quantity of radium-224 is appreciable, it can be differentiated from radium-223 and radium-226 by the half-life of its lead daughter (10.6 hours) as compared with the shorter half-lives of those derived from radium-223 and -226 (30-40 minutes). About five manhours are required for the chemical manipulations in applying this method to a set of four samples.

Future Work

Two 25-gallon mill effluent samples (one an acid leach effluent, the other alkaline) have been requested for evaluation of the five methods above, with a number of operators using each method at a number of levels. Isotopic radium contents will be evaluated by decay and ingrowth measurements for comparison with the values obtained by the rapid isotopic technique.

With the receipt of alpha spectroscopic equipment in the near future, the problems remaining in the isotopic determination, as well as the questions of carryover of other elements and of self-absorption, should be rapidly eliminated.

FIGURE 4Flow Sheet, Solvent Extraction Method for Radium Analysis

FIGURE 5

Flow Sheet, Ion Exchange Method for Isotopic Radium Analysis

Thorium

Evaluation

Two procedures for the determination of thorium have been under investigation at the Winchester Laboratory. One of these is a modification of a method developed by the Idaho Falls Group. In the original Idaho Falls procedure⁵ the pH of the sample was adjusted to 1.2, using meta-cresol purple indicator, and hydroxylamine hydrochloride was added to prevent interference from iron. Carrier-free thorium was then extracted into TTA-benzene. The thorium was then stripped into hydrochloric acid and any iron present removed by shaking with triisooctylamine. The hydrochloric acid solution containing the thorium was then evaporated to dryness, taken up in nitric acid, and plated for alpha counting. The Winchester modifications consisted of changing the pH of TTA extraction to 0.8 - 1.0 to minimize the extraction of uranium and a simplification of the stripping procedure by substitution of nitric acid for hydrochloric acid and a direct plating of the nitric acid solution.

The other thorium procedure used was a modification of a Winchester procedure first reported in WIN-111². As modified, the procedure called for precipitation of the thorium on lanthanum hydroxide and then on lanthanum fluoride. The lanthanum fluoride was then dissolved in nitric acid aluminum nitrate, the pH adjusted to 1.0, and the thorium extracted into TTA solution, from which it was stripped into nitric acid and mounted.

Flowsheets for both of these procedures are given in Figures 6 and 7 and the detailed procedures are presented in Appendix A. Experience to date in the laboratory indicates that either method is applicable to the analysis of mill effluents at Part 20 levels, with the Idaho Falls method taking somewhat less time. On the other hand, the preliminary concentration by hydroxide precipitation makes the modified Winchester method somewhat more applicable to large, low-activity samples. This method has also given somewhat more reproducible results with dust samples, and is being used on soils for this reason.

Since these thorium methods appear satisfactory, no further work on them is contemplated at present, except for a check for radioactive contamination by alpha spectroscopy when this equipment is received.

Instrumentation

The conventional alpha counting instrumentation has been improved by the substitution of larger chambers. The new chambers (Nuclear Measurements Corporation PCC-10A) make possible the use of two-inch diameter planchets instead of the previously used one-inch planchets. With the same

FIGURE 6

Flow Sheet, Idaho Falls Method for Thorium Analysis (Modified)

FIGURE 7

Flow Sheet, Lanthanum Carrier Method for Thorium Analysis

amount of sample being counted, the thickness in the larger planchets is only one-fourth of that in the smaller, with a corresponding improvement in self-absorption losses.

More advanced counting equipment has been ordered. This includes a 256-channel analyzer, which will be used for both alpha and gamma spectroscopy. The gamma detector is a sodium iodide crystal (thallium-activated) two inches in diameter by two inches high. It is coupled to a Dumont photomultiplier tube, the combined unit being enclosed in a lead shield two inches thick and with inside dimensions 3 1/2" diameter x 8" high. The lead is enclosed in steel for mechanical strength and for attenuation of the approximately 74-kev X-ray which is emitted by lead when it absorbs gamma rays. The alpha detector is a modified Frisch grid chamber constructed after a design of National Lead Company of Ohio. It is expected that this equipment will be in operation about the middle of May.

A further avenue of investigation is in the recently-developed solid-state alpha detectors. These relatively inexpensive simple alpha detectors offer the possibility of linear, high resolution spectroscopy which may very well be directly usable in plant laboratories, possibly in combination with a single-channel analyzer. Such a combination would provide a relatively inexpensive, readily-maintained instrument selective for the radiation from a given radionuclide.

PHYSICO-CHEMICAL STUDIES

Radium Adsorption on Barite:

Previous work at Winchester^{7, 9} indicated considerable but incomplete adsorption of radium from acid leach liquors by barite (natural barium sulfate). This work suggested that it might be possible to develop a process for decontamination of mill effluents based on barite adsorption, but attainment of Part 20 levels appeared difficult, if not impossible, with single-contact batch operation.

In order to define more clearly the mechanism of barite adsorption, investigations of various parameters involved in the adsorption were initiated during the past quarter. Among these parameters were the effects of pH, sulfate ion concentration, calcium and other contaminants, and temperature. Figure 8 presents some of the data obtained under a variety of conditions, with complete details and numerical values given in Appendix B.

Particularly noticeable in the results is the strong effect of sulfate ion on the radium uptake; in the presence of even small concentrations of sulfate (0.05M) there is approximately 95% uptake of radium (1 g/l Magnet Cove barite, 100-150 mesh, one hour contact) independent of pH, while there is much less uptake in the absence of sulfate. The peak in the lower curve (Figure 8) at pH 7-8 has been observed in similar systems, but is being checked. Calcium ion, even in high concentrations, apparently has no effect on barite adsorption in either system, under the conditions of the experiments. Mechanistically one might expect excess sulfate ion to become attached to the barite crystal surface, forming many new sites available for radium adsorption. Future experimental work will be aimed at further clarifying this preliminary picture.

Figure 9, presents some preliminary results on temperature dependence of the rate of radium adsorption from a sulfate system. Extremely short (one minute) contact times were employed and some temperature dependence observed, though whether this is due primarily to increased diffusion rates in or near the crystals is still in question. Detailed rate curves under varying conditions are to be developed.

Most of the above work has been done on pure radium-226 solutions rather than on mill effluents so that control of experimental conditions can be obtained. As more information is developed it will be applied to determining why radium decontaminations obtained in the laboratory have not been duplicated in field operations.

Coprecipitation of Radium with Barium Sulfate

Coprecipitation of radium with barium sulfate has been proposed as a method of decontaminating mill effluent streams^{7/}. Simple addition of barium ions (as barium chloride solution) to an acid mill effluent gives immediate precipitation of barium sulfate. These fine crystals should include radium as they are formed and also adsorb radium from the solution.

A series of preliminary precipitations were made on a sample of acid effluent*. From 0.05 to 1.2 g/l of barium chloride were used in the runs but somewhat irreproducible results were obtained; radium removals ranged from 55 to 98 percent. For a tabulation of all data pertaining to coprecipitation studies see Appendix C. In a similar experiment on a

*Obtained from the Vanadium Corporation of America, Durango, Colorado.

FIGURE 8

Radium Removal by Treatment with Barite (1 g/l for 1 hour)

FIGURE 9

Removal of Radium by Barite Adsorption

saturated calcium sulfate solution containing radium-226 tracer, 98 percent removal of the radium was attained with 0.05 g/l of barium chloride. Further work on the synthetic system showed little dependence of radium uptake on pH, and indeed that good decontamination could be achieved in a single pass with small amounts of barium. Experiments on the treatment of two other mill effluent samples (with 0.02 g/l of barium) indicated that preliminary filtering before barium addition and the use of a flocculating agent after the addition both increased radium removal. Single pass removals of from 75 to 90 percent of the radium were attained, although on the samples in question this was not sufficient to reach Part 20 levels. Increasing the barium dose from 0.02 to 1.0 g/l increased radium removal from 89 to 99 per cent in one set of runs.

The general scatter of the results obtained to date leaves many questions unanswered. Much of the difficulty may be due to problems of mechanical stirring upon addition of the precipitant. One measurement indicates that pre-formed barium sulfate may be nearly as good a decontaminant as that formed in the radium solution. A series of checks are now being made, and the area of multiple treatment investigated.

Biological Hazards Associated with Ores and Dusts

A program for determining the size range, composition, and biological hazard of dusts from uranium milling operations was instituted in the first quarter of this year. Samples of dusts from tailings piles and from within mills themselves are to be analyzed for radium, thorium, and uranium as a function of particle size. Two Casella cascade impactors have been purchased for separation of dust samples into various size fractions ranging down to below one micron; these have been calibrated with a phase contrast microscope. A cyclone impactor has been used to separate particle size fractions in the range from 10 to 100 microns.

One dust and two ore samples have been examined to date and these only in the larger particle size ranges obtainable with the cyclone impactor. A typical plot of uranium concentration vs. particle size is given in Figure 10. The interesting increase in activity in the lower size fractions will be extended further by separation with the Casella impactors to determine concentrations at about one micron size levels. It is in this range that the dusts have particular biological significance, for it is particles of this size which appear to reach the bronchi and upper lungs. Complete radium data are not available as yet but preliminary information suggests that, in this dust sample at least, secular equilibrium exists between uranium and its daughters throughout the entire particle size range.

FIGURE 10

Dust Sample Uranium Activity as a Function of Particle
Size

FIELD STUDIES

After meetings in Winchester and Washington, a field program for studying the effects of wind and erosion on tailings piles was prepared and submitted to the U. S. Atomic Energy Commission representatives. The first stage of this operation, a study of the presently available data in the Grand Junction Operations Office and elsewhere, is completed. The data are rather complete on ore feed and tailings quantities, from which the total radium content in tailings in the plateau can be readily evaluated. The total radium content in piles is about 16,000 curies. Rainfall data is available for most of the mills, but other meteorological information is quite scanty. The second stage of the operation is a physical survey of the tailings pond and surrounding area, including topographic maps and sketches, general size and shape of tailings piles and areas, wind and drainage patterns, farm land and populated areas. Associated with and following the second stage is a third stage of sample collection and analysis.

In addition to the above program of study of wind and erosion effects, a program of tailings pond balance studies was established. In these input and output, both by volume and by activity (especially for radium-226), will be measured, giving an evaluation of the total potential effluent contamination hazard at each site. Seepage losses are of particular interest in this connection. The remainder of the field program is connected with the particle size studies.

Appendix E presents some preliminary analyses of mill effluent samples. In general, no particular trends can be detected in the mill effluent data, although the magnitude of the numbers is of interest. Some of the problems encountered in waste treatment are indicated by the results from samples G-88 and G-89, taken at the same time from two consecutive tailings ponds. Effluent from the first pond is treated with barite and sent to the second, from which it is discharged. The activity of the effluent from the second pond is higher than that from the first due to an accumulation of radium in the second pond prior to the time the barite treatment was introduced.

APPENDIX AANALYTICAL METHODSWinchester Method for Radium Analysis:

1. Adjust 500-1000 ml of a clarified sample to pH 1.0 with HNO_3 and heat to 70°C .
2. Stir with magnetic stirrer, add 5 ml of 0.5M $\text{Pb}(\text{NO}_3)_2$, and then add very slowly 60 ml of 9M H_2SO_4 .
3. Continue stirring for one hour, allow precipitate to settle (or centrifuge), and discard the supernatant solution.
4. Transfer the precipitate to a 50-ml centrifuge tube with 1M H_2SO_4 ; centrifuge, and discard the supernate.
5. Add 5 ml of 6M ammonium acetate to dissolve the precipitate.
6. Add 25 ml of 25% Na_2CO_3 solution and stir for 0.5 hour.
7. Centrifuge; discard the supernatant, add 4M HNO_3 until evolution of CO_2 stops.
8. Add a small amount of water and heat to dissolve salts. (At this point the total volume should be 5-7 ml. If total solution of the solid is not obtained, repeat steps 6, 7, and 8).
9. Place the centrifuge tube in an ice bath, and add 30 ml of red fuming nitric acid while stirring; centrifuge and discard supernatant solution.
10. Heat the tube and precipitate in a hot water bath to drive off excess acid, being careful to avoid splattering.
11. Add 30 ml of water to dissolve, and, while stirring, add 5 ml of concentrated HCl dropwise.
12. Cool the resulting PbCl_2 precipitate in an ice bath, centrifuge, and pass supernate over a 15 ml column of 100-200 mesh Dowex 1-X8 suspended in 1.8M HCl . Collect effluent at a rate of one ml per minute in a 150 ml beaker.

(Continued)

13. Add 35 ml of water to the lead chloride precipitate, heat in water bath while stirring to dissolve solid, and add 6 ml of concentrated HCl dropwise to reprecipitate PbCl_2 .

14. Cool in ice, centrifuge, and pass supernate over the same resin bed (Step 12), followed by a wash with 15 ml of 1.8M HCl.

15. Evaporate the combined column effluents just to dryness.

16. Add 10 ml of concentrated HNO_3 and re-evaporate to destroy organic material.

17. Wash the beaker into a 10-ml volumetric flask with 1M HNO_3 nitric acid.

18. Planchet an aliquot of the sample and count.

Public Health Service Method for Radium Analysis:

1. To a one liter sample add in order, while stirring, 5 ml 1M citric acid, 2.5 ml concentrated NH_4OH , 2 ml of 1N $\text{Pb}(\text{NO}_3)_2$, and one ml of standardized 0.1N $\text{Ba}(\text{NO}_3)_2$.

2. Heat to boiling, add 10 drops of methyl orange, and, while still stirring, add 1:1 H_2SO_4 until a pink color is attained; then add 0.25 ml in excess.

3. After stirring for 5-10 minutes allow to stand for at least a half-hour. Centrifuge or decant; discard supernate.

4. Collect the precipitate in a 50 ml centrifuge tube; wash with two portions of concentrated HNO_3 , discarding the washings.

5. Dissolve the precipitate in 10 ml of water, 10 ml of 0.25M EDTA, and 3 ml of 6N NH_4OH .

6. Warm and add dropwise 2 ml of glacial acetic acid, digest for 5-10 minutes, centrifuge, and discard the supernatant solution.

7. Wash the precipitate with water, centrifuge, transfer to a planchet, flame, and count.

Idaho Falls Method for Radium Analysis: Separation of Radium and Thorium

1. Adjust 200 ml of sample to pH 0.8 on a pH meter with either HNO_3 or NH_4OH . (Larger samples may be used provided there is suitable increase in the extractants).
2. Transfer the sample to a 250-ml separatory funnel, add 25 ml of 0.5M TTA in benzene, and 5 ml of 4M $\text{NH}_2\text{OH}\cdot\text{HCl}$.
3. Shake vigorously for five minutes, separate aqueous layer into another 250 ml separatory funnel.
4. Extract the aqueous layer again with another 25 ml of TTA-benzene.
5. Separate aqueous layer for radium determination, and combine and reserve organic layers for thorium.
6. Wash the combined organic layers with 10 ml of 0.2M nitric acid and add this to the aqueous extract.
7. Transfer the aqueous phase to a beaker, heat to remove benzene, cool, and discard any red iron-TTA precipitate.
8. Add 100 mg of Pb^{++} and 10 ml of 70% H_2SO_4 (by volume).
9. Allow to stand for at least 15 minutes, and filter through quantitative paper using paper pulp filter aid; discard filtrate.
10. To filter and precipitate in a 25 ml Erlenmeyer flask, add 15 ml concentrated HNO_3 , 5 ml of 72% HClO_4 , and fume to destroy the filter. (If organic material is still present, as evidenced by darkening, it may be destroyed by cautious addition of a few drops of nitric acid).
11. Evaporate to a small volume, cool to precipitate lead, and add 10 ml of 10% EDTA and 10 ml of water.
12. Neutralize with 4N NaOH, using meta-cresol purple, and then add ten more drops 4N NaOH to bring pH to 11-12.
13. Boil, cool, and filter as before, but collect filtrate in 50-ml centrifuge tube; wash filter collecting washes in same tube, and discard filter.
14. Add, in order, 1 ml of 50% $(\text{NH}_4)_2\text{SO}_4$, 5 mg of Ba^{++} carrier, and two drops of methyl purple.

(Continued)

15. Adjust to pH 4-5 with glacial acetic acid so that indicator goes purple. Note time.

16. Centrifuge, decant, wash with ten ml of water, centrifuge again, and decant.

17. Transfer precipitate to planchet with distilled water, flame, cool, and count.

Solvent Extraction Method for Radium Analysis

1. Adjust the pH of a 200 ml sample to 1.0 using either HNO_3 or NH_4OH , and transfer to a 250 ml separatory funnel.

2. Add 50 ml of 50% acetylacetone in chloroform, shake for 2-3 minutes, separate and discard the organic layer. (If excess iron is present, extract again with 25 ml acetylacetone solution).

3. Wash the aqueous layer twice with small amounts of chloroform to remove any residual acetylacetone.

4. Add 25 ml of 0.5M TTA-benzene, shake for five minutes, separate, discard the organic layer.

5. Adjust pH of the aqueous layer to 3.0 with NH_4OH , transfer to new separatory funnel, add 25 ml of TTA-benzene, and shake again for five minutes.

6. Separate, draining the aqueous layer into a 250 ml beaker.

7. Add 10 ml of 20% EDTA solution, one ml of 50% $(\text{NH}_4)_2\text{SO}_4$, and 5 mg of Ba^{++} to the aqueous solution, and let stand for several minutes.

8. Transfer to a 50 ml centrifuge tube, centrifuge, discard supernatant.

9. Wash with water, recentrifuge; discard wash.

10. Transfer the precipitate to a planchet, dry, and count.

Ion Exchange Method for Isotopic Radium Analysis

1. To 500-1000 ml of sample add, while stirring, 10 mg of Ba^{++} , plus, if the volume of the solution is large, up to 100 mg of Pb^{++} .
2. Add 2 ml of 1M H_2SO_4 , centrifuge, discard supernate.
3. Wash with 10 ml of water, recentrifuge, and discard wash.
4. Dissolve the precipitate in 20 ml of 20% EDTA, bring to pH 11-12, centrifuge to clarify, and transfer liquid to new centrifuge tube. Discard any undissolved precipitate.
5. Add several drops of 1M H_2SO_4 , and then glacial acetic acid to bring the pH to 4-5.
6. Centrifuge, wash, and add 20 ml of 25% Na_2CO_3 solution to the precipitate.
7. Boil for a few minutes, centrifuge and wash. Discard the supernatants.
8. Add 5 ml of 2M HCl to dissolve the carbonate and pour the solution onto an anion exchange column (Dowex 1-X8, 18 cm by one cm diameter).
9. Wash tube with 5 ml of 2M HCl, add this to column, and further elute with 30 ml of 2M HCl.
10. Add one ml of 1M $(\text{NH}_4)_2\text{SO}_4$ to eluate to reprecipitate radium and barium. Record the exact time of the precipitation.
11. Add to the precipitate exactly 10 mg each of Pb^{++} and Bi^{+++} .
12. After a 36 minute waiting period add 20 ml of 25% Na_2CO_3 solution to the precipitate, and heat for one minute while stirring.
13. Centrifuge, wash, retaining the precipitate.
14. Dissolve this in 10 ml of 2M HCl, heating if necessary, and transfer to a second ion exchange column.
15. Elute with 30 ml of 2M HCl.
16. Reprecipitate radium and barium from the eluate with $(\text{NH}_4)_2\text{SO}_4$, centrifuge, planchet, weigh, and count to determine total radium.

(Continued)

17. Elute column with 50 ml of 8M HCl, add chromate and neutralize with ammonium hydroxide to precipitate lead chromate.

18. Centrifuge, wash, planchet, weigh, and count as a function of time to determine the decay curve. From the amount of activity present as Pb-211 the original Ra-223 concentration may be calculated.

19. Elute the column with 30 ml of 1M sulfuric acid, add phosphate ion to precipitate bismuth, and centrifuge.

20. Wash, mount, dry, weigh, and count. Activity observed with a one-hour half life is due to the daughter of Ra-224.

Idaho Falls Thorium Analysis

1. Separate radium and thorium as was described under the Idaho Falls radium procedure; combine the organic extracts in a 250-ml separatory funnel.

2. Add 10 ml of 4M nitric acid and shake for two minutes to strip thorium into aqueous phase.

3. Separate, and rinse organic layer with an additional 5 ml of 4M nitric acid which is added to the aqueous extract.

4. Repeat with another 10 ml 4M HNO₃ followed by another wash.

5. To the combined aqueous layers add 10 ml of 20% triisooctylamine (TIA) in chloroform, shake for two minutes, and discard the organic layer.

6. Repeat step 5 until the solution is colorless, and follow with a rinse of 10 ml of chloroform.

7. Place acid layer in 100 ml beaker, rinsing the sides of the funnel with 2-3 ml of 4M nitric acid. Evaporate the solution to dryness, taking care to avoid spattering.

8. Add 3-5 ml of concentrated nitric acid and repeat to destroy any organic residue.

9. Add 3 ml of concentrated nitric acid and transfer the solution to a planchet; dry, and count.

Lanthanum Carrier Method for Thorium Analysis

1. Pipet a suitable aliquot of the sample solution (not over 25 ml) into a 50-ml centrifuge tube.
2. Add 0.5 ml of lanthanum carrier solution (12 mg La/ml) and mix well with a polyethylene stirring rod.
3. Add 10 ml of 19M sodium hydroxide solution, mix well, and digest for 5 minutes at room temperature. Centrifuge thoroughly.
4. Remove the supernatant solution with mild suction. Wash the precipitate by stirring with 5 ml of 0.05M sodium hydroxide.
5. Rinse off the stirring rod and centrifuge.
6. Remove the supernatant solution, repeat the wash step, and again remove the wash solution.
7. Dissolve the precipitate in several drops of concentrated nitric acid and add 1 ml in excess.
8. Add 5 ml of 0.4M potassium dichromate, mix well, and digest for 10 minutes in a beaker of water at approximately boiling temperature.
9. Remove from the hot water, add 5 ml of concentrated hydrofluoric acid, mix well, and digest at room temperature for 5 minutes. Centrifuge.
10. Add 0.25 ml of lanthanum carrier and stir the supernatant solution without disturbing the precipitate. Digest for 5 minutes at room temperature.
11. Centrifuge; discard the supernatant solution, leaving about 1 drop.
12. Wash the precipitate by stirring with 5 ml of 1M hydrofluoric acid-1M nitric acid containing 2 drops of 0.4M potassium dichromate.
13. Centrifuge, remove the supernatant solution, and wash the precipitate with 5 ml of 1M hydrofluoric acid-1M nitric acid until the supernatant is no longer yellow.
14. Dissolve the lanthanum fluoride precipitate by adding 5 ml of 2M aluminium nitrate and several ml of 1M nitric acid. Carefully transfer the solution to a 50-ml beaker using several distilled water washes, but keeping the volume as low as possible.

(Continued)

15. Adjust the pH to 0.8 - 1.0 with dilute sodium hydroxide; transfer the solution with several distilled water washes to a 60-ml separatory funnel.

16. Add 10 ml of 0.5M TTA solution, and extract for two minutes.

17. Allow the phases to separate and draw off the aqueous layer into a second funnel. Add to this aqueous layer another 10 ml of 0.5M TTA solution, and extract for 1 minute.

18. Discard the aqueous layer. Combine the two TTA solutions and add 10 ml of 0.2M nitric acid.

19. Shake for 1 minute and discard the aqueous layer.

20. Wipe out the funnel stem with Q-tips.

21. Strip the organic phase with 4M nitric acid and draw off the aqueous layer into a 100-ml beaker.

22. Add 5 ml of 4.0M nitric acid to the funnel and without shaking, draw off into the beaker. (This operation insures against loss of activity in funnel stem).

23. Repeat step 21 adding aqueous layer to the 100 ml beaker.

24. Evaporate to dryness on a hot plate, without spattering.

25. Add 5 ml concentrated nitric acid, evaporate to dryness again; add 3 - 4 ml concentrated nitric acid.

26. Evaporate to 1 ml and transfer quantitatively with washings to a 2" stainless steel planchet.

27. Dry under an infra-red lamp and count the planchet in an appropriate counter.

APPENDIX BADSORPTION OF RADIUM ON BARITETable 1Effect of Sulfate on Radium Removal

(1 g barite per liter; 1 hour stirring)

A. 0.05M sulfate ion present

<u>pH</u>	<u>Initial Activity of Radium (dpm/l)</u>	<u>Residual Activity of Radium (dpm/l)</u>	<u>% Radium Removal</u>
1	5140 $\pm$ 356	340 $\pm$ 38	93.5 $\pm$ 13.0
2	2530 $\pm$ 167	294 $\pm$ 10	88.4 $\pm$ 7.4
4	6120 $\pm$ 98	184 $\pm$ 8	97.0 $\pm$ 4.8
8	5930 $\pm$ 190	172 $\pm$ 16	97.1 $\pm$ 10.0
10	5800 $\pm$ 93	172 $\pm$ 8	97.0 $\pm$ 5.2
12	5250 $\pm$ 340	362 $\pm$ 48	93.3 $\pm$ 14.7
4	12800 $\pm$ 576	2570 $\pm$ 111	80.0 $\pm$ 6.2

B. No sulfate ion present

2	5000 $\pm$ 295	3520 $\pm$ 155	29.6 $\pm$ 7.4
4	5170 $\pm$ 243	3410 $\pm$ 123	32.8 $\pm$ 5.9
8	6140 $\pm$ 344	1640 $\pm$ 82	73.4 $\pm$ 7.5
10	3760 $\pm$ 282	2140 $\pm$ 115	42.8 $\pm$ 9.2

Errors estimated from counting statistics only.

APPENDIX B

(Cont'd)

Table 2Effect of Calcium on Radium Removal

(1 g barite per liter; 1 hour stirring; pH 4; 0.05M sulfate ion)

A. 0.05M sulfate ion present

<u>Calcium (Millimoles per liter)</u>	<u>Initial Activity of Radium (dpm/l)</u>	<u>Residual Activity of Radium (dpm/l)</u>	<u>% Radium Removal</u>
0.01	4920 $\pm$ 346	484 $\pm$ 50	90.2 $\pm$ 12.4
0.10	5340 $\pm$ 252	166 $\pm$ 18	95.5 $\pm$ 11.6
1.00	4650 $\pm$ 170	139 $\pm$ 16	97.3 $\pm$ 11.8
100.00*	6550 $\pm$ 252	402 $\pm$ 32	94.0 $\pm$ 8.8

B. No sulfate ion present

Saturated Ca(OH) ₂	5450 $\pm$ 399	4260 $\pm$ 172	22.0 $\pm$ 8.4
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* Precipitate appeared

Errors estimated from counting statistics only.

Table 3Effect of Temperature on Radium Removal

(1 g barite per liter; 1 minute stirring; pH 8; 0.05M sulfate ion)

<u>Temp. °C</u>	<u>Initial Activity of Radium (dpm/l)</u>	<u>Residual Activity of Radium (dpm/l)</u>	<u>% Radium Removal</u>
20	4815 $\pm$ 183	1240 $\pm$ 69	74.2 $\pm$ 6.2
40	4530 $\pm$ 96	1130 $\pm$ 22	75.5 $\pm$ 2.8
60	4530 $\pm$ 173	1210 $\pm$ 40	73.5 $\pm$ 5.1
80	5250 $\pm$ 186	700 $\pm$ 32	86.6 $\pm$ 5.8
100	4950 $\pm$ 282	577 $\pm$ 46	88.5 $\pm$ 9.7

Errors estimated from counting statistics only.

APPENDIX C

COPRECIPITATION OF RADIUM ON BARIUM SULFATE

Table 1

Exploratory Results

A. (Acid leach effluent, V.C.A.)

<u>Test</u>	<u>BaCl₂ (2.4% aq.) (g/500 ml.)</u>	<u>Vol. of BaCl₂ Soln. to vol. of effluent</u>	<u>Method of Test</u>	<u>Radium Activity (dpm/l)</u>	<u>% Radium Removal</u>
1	-	-	Untreated	2477	-
	.59	2.5/500	1 hr contact wk-end settling	41	98
2	.024	0.1/500	1 hr contact 48 hrs settling	623	75
3	-	-	Untreated	1989	-
	.024	0.1/500	1 hr contact overnight settling	899	55
4	2 x .024	2 x 0.1/500	1 hr contact 2 hrs settling*	444	78
5	.024	25/500	BaCl ₂ added dropwise over 50 min period; stirred 30 minutes	460	77

B. Saturated CaSO₄

1	-		Untreated	7632	-
	.024	25/500	BaCl ₂ added dropwise over 50 min period stirred 1 hour	148	98

* Two such cycles in succession

APPENDIX C
(Cont'd)

Table 2

Effect of Increasing Barium Ion

<u>Concentration of BaCl₂ (g/500 ml)</u>	<u>Residual radium not coprecip't'd dpm/l</u>	<u>% Radium Removal</u>
0.01	92 ± 4	89 ± 8
0.02	77 ± 4	91 ± 2.7
0.04	43 ± 5	95 ± 2.8
0.50	7.8 ± 1.4	99 ± 2.8

Acid Leach Effluent

Table 3

Effect of pH

(Saturated CaSO₄ solution, Ra-226 tracer)

<u>Trial</u>	<u>pH</u>	<u>BaCl₂ (g)</u>	<u>Radium Content (dpm/l)</u>		<u>% Radium Removal</u>
			<u>Original</u>	<u>After Treatment</u>	
1	1.6	.024	7632	148	98
2	2.0	.010	8290 ± 290	1290 ± 18	84.5
3	4.0	.010	6978 ± 230	529 ± 40	92.5
4	6.0	.010	6584 ± 370	1553 ± 80	76.4

pH at time of initiating addition of BaCl₂. The BaCl₂ was contained in 25 ml of solution and was added dropwise with stirring over a period of about 50 minutes.

APPENDIX C
(Cont'd)

Table 4

Effects of Separan and Filtration

(BaSO₄ precipitated from acid leach effluents by dropwise addition of 25 ml of a solution containing 0.020 g BaCl₂ per liter)

<u>Test</u>	<u>Sample^{a/}</u>	<u>Treatment</u>	<u>Residual Radium resisting pptn (dpm/l)</u>	<u>% Radium Removed</u>
1	G-88	Filtered - no BaCl ₂	821 ± 53	-
2	"	Filtered + BaCl ₂	92 ± 4	89 ± 8
3	"	Not filtered + BaCl ₂	212 ± 6	74 ± 9
4	G-89	Filtered - no BaCl ₂	850 ± 38	-
5	"	Filtered + BaCl ₂	206 ± 18	75 ± 5.5
6	G-88	Not filtered + Separan	520 ± 25	35.3 ± 1.5
7	"	Not filtered + Separan + BaCl ₂	63 ± 4	92.5 ± 2.7
8	G-89	Not filtered + BaCl ₂	196 ± 19	76.9 ± 5.6
9	G-89	Not filtered + Separan + BaCl ₂	146 ± 20	82.8 ± 7.1

^{a/} G-88 contained 1.1% filterable solids; G-89 contained no filterable solids.

Table 5

Comparison of Precipitated vs Preformed BaSO₄

(Acid leach effluent G-88^{a/})

<u>Treatment</u>	<u>Residual Radium (dpm/l)</u>	<u>% Radium Removed</u>
BaCl ₂ (to make 11 mg BaSO ₄)	94 ± 11	88.6 ± 6
BaSO ₄ (11 mg)	159 ± 14	80.7 ± 5.6

^{a/} See Table 4, this appendix.

APPENDIX D
PARTICLE SIZE STUDIES

Table 1
Analyses on Ore and Dust Samples

<u>Sample</u>	<u>Nominal size</u>	<u>Weight Gram</u>	<u>dpm/gm</u>			<u>Average^{1/} Size</u>
			<u>Radium</u>	<u>Thorium</u>	<u>Uranium</u>	
G-77	Full range ore	3.01	2002 2089	666	1990 1936	
G-78	"	1.97	1245 1243		1083 982	
G-80	Full range dust	3.01	1306 1322	813,867 901,917	1558	
G-77	60 μ 52 35	1.01 1.01 1.03			3252 ^{2/} 1554 1240	40. μ
G-80	77 60 52 35 26 19	3.01 3.02 3.02 1.06 0.13 0.40	 1321 1075 1249 1756 2020 2216 1797	 1164 1278	1072 1091 1242 1278 1278 1647 1445 1881 1856	 20 12.5

^{1/} By counting under microscope.

^{2/} Analytical difficulties; results being checked.

APPENDIX E
MILL EFFLUENTS

Table 1

Analyses of Mill Effluent Samples

<u>Sample</u>	<u>Mill</u>	<u>Sample Description</u>
G-81	Monticello, Utah	Pulp from tail pond feed
G-82	"	Recycled tailpond water
G-83	"	Overflow from tail pond
G-84	"	Resin from RIP Bank #5
G-85A	Rifle, Colorado	Combined plant effluent, 4 day composite
G-85B	"	Combined plant effluent, 5 day composite
G-86A	"	Effluent overflow to river, 4 day composite
G-86B	"	Effluent overflow to river, 5 day composite
G-88	Durango, Colorado	Overflow from first tailings pond
G-89	"	Overflow from second tailings pond

<u>Sample</u>	<u>pH</u>	<u>Solids</u> <u>g/l</u>	<u>Radium</u>				<u>Thorium</u>			
			<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
G-81	9.8	0	472	-	-	472	610	-	-	610
G-82	9.8	0	264	-	-	264	543	-	-	543
G-83	9.8	0	236	-	-	236	433	-	-	433
G-84	6.0	0	41620	-	-	41620	17340	-	-	17340
G-85A	2.0	.44	3890	3620	1440	5330	3720	42800	18800	22500
G-85B	2.2	.27	793	1508	409	1202	274	1524	413	687
G-86A	2.5	.16	900	263	42	944	750	2620	420	1170
G-86B	2.4	.09	2470	1090	100	2570	3205	8934	819	3324
G-88	2.5	1.10	776	5790	6340	7116	9954	5750	6296	16250
G-89	2.4	0	855	-	-	855	7420	-	-	7420

- A. Dpm/l of filtered effluent
 B. Dpm/g of solids
 C. Dpm/l due to suspended solids
 D. Total

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