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DISTRIBUTION OF RADIUM IN WATER AND SEDIMENTS  
OF RALSTON CREEK AND RESERVOIR.  
APPLICATIONS OF A DIRECT DEEMANATION METHOD OF ANALYSIS

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science of Chemistry.

Signed: Abdussalam M. Essed  
Abdussalam M. Essed

Golden, Colorado

Date: 12/30, 1981

Approved: Kenneth W. Edwards  
Kenneth W. Edwards  
Thesis Advisor

George H. Kennedy  
George H. Kennedy,  
Head, Department of  
Chemistry/Geochemistry

Golden, Colorado

Date: 12/30, 1981

## ABSTRACT

Intensive uranium ore mining and the related disposal of radioactive byproducts present significant problems in the preservation of environmental quality. Both dissolved and particulate matter discharged into rivers and streams from uranium mining operations can cause long term radioactive contamination problems.

One of the areas which has been subjected to this type of environmental stress is Ralston Creek and Ralston Reservoir near Golden, Colorado. Treated wastewater from the Schwartzwalder uranium mine is discharged into the creek at a daily rate of 700,000 to 900,000 gallons. Although most of the uranium and radium are now removed prior to discharge, the waste water still contains small amounts of dissolved and suspended radionuclides. Prior to installation of chemical treatment facilities in 1972, much larger amounts of radionuclides were apparently discharged to the stream.

The purpose of the investigation reported in the following pages was to examine the distribution of  $^{226}\text{Ra}$  (the most hazardous radionuclide of the uranium series) in Ralston Creek and Reservoir, and to evaluate the suitability of a direct emanation method for determination

of this nuclide in natural waters and sediment samples. The distribution of radium was examined by determination of its concentration (a) in true solution, (b) in suspended solids, and (c) in bed sediments of Ralston Creek and Reservoir. Each of these were measured at various sites along the stream, above and below the mine waste water discharge, and in the discharge water itself. Bed sediments were sieved to provide several particle size fractions which were individually analyzed by both the direct emanation method and by gamma spectrometry.

Dissolved radium was found to be generally low in concentration, both in the stream and in the treated mine effluent. Suspended solids were found to contain rather high levels of radium in the discharge water and in the stream. Bed sediments had concentrations of radium that varied with particle size and distance from the mine. In general, the finer particles contained higher concentrations of radium than coarse particles. All particle sizes showed a maximum radium concentration approximately 0.6 miles below the mine.

Various lixiviants were tested for their effectiveness in leaching radium from sediments. One normal hydrochloric acid was found to be most effective.

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The direct emanation method was found to be relatively simple and quite satisfactory for the radium determinations.

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## INTRODUCTION

With the public concern over the problem of radioactivity throughout the human environment, extensive attention should be paid to determination of the presence, distribution, and concentration of radioactive materials in stream water and sediments.

Among the most hazardous radioactive materials in the environment are radium isotopes. Radium is a radioactive member of the alkaline earth family and is widely distributed throughout the crust of the earth. Its isotopes occur in the three natural radioactive series (Figure 1). None of these radium isotopes would exist in nature, however, unless it were supported by its ancestor uranium and thorium isotopes. As independent radioactive materials, the only radium isotope which lasts very long is  $^{226}\text{Ra}$  due to its longer half-life (1600y). For example, after the following elapsed time for each isotope 99.9% of the original amount will have decayed and 0.1% will remain.

Radium isotope	Elapsed time
$^{226}\text{Ra}$	$1.59 \times 10^4$ years
$^{228}\text{Ra}$	57.3 years
$^{223}\text{Ra}$	114 days
$^{224}\text{Ra}$	36.3 days

	U-238 SERIES			Th-232 SERIES			U-235 SERIES		
Np									
U	U-238 4.47x10y	U-234 2.44x10y	U-235 7.04x10y						
Pa	Pa-234 1.17m	Pa-231 3.25x10y	Pa-231 3.25x10y						
Th	Th-234 24.1d	Th-230 7.7x10y	Th-232 1.40x10y	Th-228 1.913y	Th-231 25.52h	Th-227 18.72d			
Ac			Ac-228 6.13h	Ac-228 6.13h	Ac-227 21.77y	Ac-227 21.77y			
Ra	Ra-226 1600y	Ra-226 1600y	Ra-224 3.64d	Ra-224 3.64d	Ra-223 11.43d	Ra-223 11.43d			
Fr									
Rn	Rn-222 3.825d	Rn-222 3.825d	Rn-220 55.6s	Rn-220 55.6s	Rn-219 3.96s	Rn-219 3.96s			
At									
Po	Po-218 3.05m	Po-214 164μs	Po-210 138.4d	Po-216 0.15s	Po-212 0.3μs	Po-215 1.78ms			
Bi	Bi-214 19.8m	Bi-214 19.8m	Bi-210 5.01d	Bi-212 60.6m	Bi-211 2.14m	Bi-211 2.14m			
Pb	Pb-214 26.8m	Pb-210 21.3y	Pb-206	Pb-212 10.64h	Pb-208	Pb-211 36.1m			
Tl				Tl-208 3.05m	Tl-207 4.77m	Tl-207 4.77m			

● STABLE LEAD ISOTOPE  
 Figure 1. Natural Radioactive Decay Series

$^{238}\text{U}$  is the parent nuclide of the uranium series (Figure 1). After 5 decay steps (three of them by  $\alpha$ -particle emission and two by  $\beta$ -particle emission)  $^{226}\text{Ra}$  is reached, which then decays by  $\alpha$ -particle emission to  $^{222}\text{Rn}$  ( $t_{1/2} = 3.825$  d), a radioactive gas. The latter nuclide is important in measuring  $^{226}\text{Ra}$  by the emanation method or  $\gamma$ -spectrometry method. As the result of three further decay steps (two  $\alpha$ -particle emissions and one  $\beta$ -particle emission),  $^{214}\text{Bi}$  ( $t_{1/2} = 19.8$  m) is produced. The 1.76 MeV  $\gamma$ -ray emission which accompanies the  $\beta$ -particle decay of this nuclide is used for indirect measurement of  $^{226}\text{Ra}$  by  $\gamma$ -spectrometry. After five additional decay steps (two  $\alpha$ -particle and three  $\beta$ -particle emissions) a stable end product,  $^{206}\text{Pb}$  is reached.

When  $^{222}\text{Rn}$  is unsupported (i.e. is separated from its  $^{226}\text{Ra}$  parent) the total alpha radioactivity of the sample will increase to approximately three times the original activity after three hours, due to the ingrowth of  $^{218}\text{Po}$  and  $^{214}\text{Po}$  alpha emitting daughters. This ingrowth of daughters enhances the sensitivity of the emanation method of determining  $^{226}\text{Ra}$ , as described later.

Radium decay chains, as shown in the natural decay series (Figure 1), present many aspects of radioactivity hazards. The penetrating gamma rays and energetic beta

particles emitted by some of the daughters make it necessary to use massive shielding against external exposure of workers when handling large quantities of radium. The gaseous nature of radon requires precautions against inhalation. Radium in the body presents a distinct hazard because it emits highly ionizing and short-range alpha particles and because its chemistry resembles that of calcium. Radium inside the body, if available to the bloodstream, will deposit and accumulate in the bone. Once it is deposited there it is eliminated very slowly. Despite these hazardous properties,  $^{226}\text{Ra}$  and its daughter  $^{222}\text{Rn}$  have been used in medical radiation therapy for destruction of malignancies.  $^{226}\text{Ra}$ , and to a lesser extent  $^{222}\text{Rn}$ , also have been used in industrial gamma ray radiography to detect flaws in casting, and for thickness measurements (e.g. of catalyst beds) (1).  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  have been used as geological indicators for uranium and thorium, respectively.

Because of its hazardous properties and its wide distribution, the toxicity of radium, particularly  $^{226}\text{Ra}$  have been studied intensely and its concentration in potable water is of primary concern. The maximum amount (1) of  $^{226}\text{Ra}$  that may be tolerated when fixed in the body for long periods of time is 0.1  $\mu\text{Ci}$  (microcuries), and for its daughter  $^{222}\text{Rn}$  (radioactive gas) the air concentration that will

result in a maximum permissible radiation dose being delivered to the lungs is  $10^{-8}$   $\mu\text{Ci}/\text{cm}^3$ . The Environmental Protection Agency (EPA) recommendation for monitoring of radioactivity in community water systems, Part II, 1979 (2), states that "when the gross alpha particle activity exceeds 5 pCi/l [5 picocuries per liter] the same or an equivalent sample shall be analyzed for  $^{226}\text{Ra}$ . If the concentration of  $^{226}\text{Ra}$  exceeds 3 pCi/l, the same or an equivalent sample shall be analyzed for  $^{228}\text{Ra}$ ." The maximum permissible concentration (MPC) of the combined  $^{226}\text{Ra} + ^{228}\text{Ra}$  is 5 pCi/l.

#### Purpose of Study

A survey of the literature has indicated that a significant amount of radium (in terms of maximum permissible concentration in potable water) can be leached from minerals, uranium mill waste tailings, and river sediments.

Most of the prior studies dealt with rather limited aspects of the occurrence and leachability of radium in sediments and uranium mill tailings. The work reported here encompasses several aspects of occurrence, distribution and analysis of radium in water and stream sediments near a uranium mine. The important aspects of this environmental problem include the following: 1) comparison of analytical methods used for the determination of radium-226 in water

and sediments, with particular emphasis on evaluation of the suitability of a direct deemanation procedure; 2) determination of the concentrations of dissolved radium in Ralston Creek and Reservoir (Colorado) water below the Schwartzwalder uranium mine; 3) determination of the distribution of radium in the creek bed sediments and in suspended material below the mine as a function of particle size and distance from the mine; and 4) examination of the leachability of radium from stream sediments as a function of the particle size and lixiviant composition.

#### Study Area

The area selected for study is Ralston Creek and Reservoir in the foothills of east-central Colorado. The creek flows by the Schwartzwalder uranium mine owned and operated by Cotter Corporation. Treated water from this mine is discharged into Ralston Creek which flows into Ralston Reservoir and Upper Long Lake at the east edge of the foothills. These reservoirs provide drinking water for approximately 100,000 residents of the western suburbs of Denver. Radium contamination of this water supply by the mine discharge water has been moderately well documented (3).

### Location and Description of Ralston Creek and Reservoir

The area of Ralston Creek where the sampling took place is shown in Figure 2. The creek lies in a valley surrounded by the foothills of Colorado's front range and flows in a tortuous route to the reservoir in a south-southeasterly direction with a gradient of approximately 70 feet per mile. During seasonal high flows some of the creek water is diverted (at the diversion dam) into Upper Long Lake through a ditch and tunnel. The remainder of the creek water flows into Ralston Reservoir at its extreme west end. However most of the water in Ralston Reservoir is water diverted from Colorado's western slope through the Moffat Tunnel. The western slope water enters the northeast part of the reservoir near the spillway. The reservoir is located approximately 5 miles NNW of Golden, Colorado. There are a few small intermittent streams which flow into the creek, especially during the spring runoff and periods of significant rainfall, which may have some seasonal effect on the radium distribution in the creek waters.

### Radioactivity in Ralston Creek

The radioactivity found in the creek water is probably due to the high abundance of uranium mineralization in the area, and particularly to the large quantity of waste water

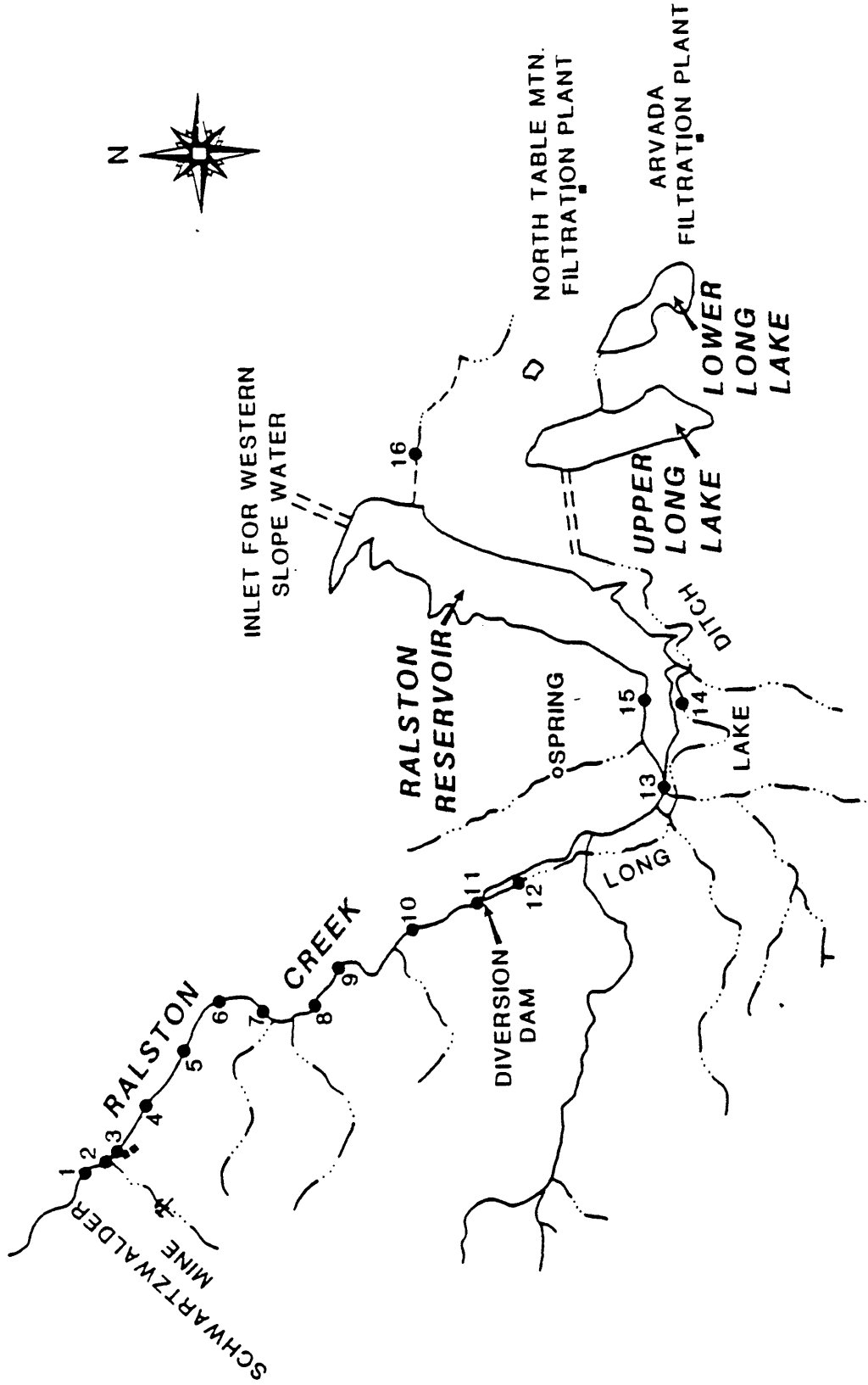


Figure 2. Map of Ralston Creek and Reservoir, Golden, Colorado. Indicated Numbers are Sample Sites.

discharged into the stream by the Schwartzwalder uranium mine (4). The mine is located on Ralston Creek approximately eight miles northwest of Golden, Colorado. Most of the waste water pumped from the mine is naturally occurring ground water. After removal from the mine, it is treated and then discharged into the creek.

#### Minewater Treatment

The water treatment plant for the Schwartzwalder mine is described in the project document (HRI Project 4135 1977) (4), which is a plan for spill prevention and containment of pollutant discharge streams at Schwartzwalder mine, prepared by Hazen Research, Inc. of Golden, Colorado (May 13, 1977) at the request of Cotter Corporation (the mine operator). Chemical treatment of the mine effluent has been the subject of a research project conducted by the Colorado School of Mines Research Institute during the years 1969 to 1972 (3). The water treatment plant units at the mine started in operation in October, 1972. A brief description of the water treatment plant follows.

Water pumped out of the mine, and recycled sorting plant water, are fed to a 9 ft. diameter by 7 ft. high steel tank equipped with an agitator (reaction vessel). Various chemicals are added to this vessel to remove most of the

radium before discharge of the water into Ralston Creek. Residence time of the water in the reaction vessel is 5.2 minutes (4). Reagents used for water decontamination are:

- a) 10% barium chloride solution. This solution is added continuously to the reaction vessel to coprecipitate radium and barium sulfates. The sulfate is present in the mine water in sufficient quantity for this coprecipitation.
- b) 10%  $\text{Fe}_2(\text{SO}_4)_3$  solution is added when the precipitation of  $\text{Ba}(\text{Ra})\text{SO}_4$  is too slow (as indicated by analysis of settling pond overflows).
- c) slaked lime is added to adjust the pH of the outflow to the creek to between 7.0 and 9.0.
- d) A weak solution of sodium hypochlorite is added to control algae buildup.
- e) Separan NP-30, a flocculating agent, is fed continuously into the outflow of the reaction vessel to enhance flocculation and settling of suspended particles.

#### Pond Settling System

The water coming out of the treatment plant is fed sequentially to four settling ponds and, in emergency conditions, to two standby underground storage ponds. The total

retention time for the entire pond system is 34.6 hours. Flow from one pond to the other and to Ralston Creek is by gravity (except underground storage areas). The total amount of solids settled per day is approximately 0.5 tons which is removed and shipped to Cotter's mill at Canon City, Colorado, about once every six months. The outflow from earthen pond No. 3 to Ralston Creek is about 700,000 to 900,000 gallons per day (4).

The uranium ore body of the Schwartzwalder mine was initially discovered by Fred Schwartzwalder in 1949 (5). The grade of uranium ore produced by the mine is in the range of 0.2% to 0.25% of  $U_3O_8$ , and it is currently mined at the rate of 600 tons per day (6). Assuming secular equilibrium in the  $^{238}U$  series, and an average ore grade of 0.22%  $U_3O_8$ , this will give about 580  $\mu g$  of  $^{226}Ra$  per ton<sup>1</sup> of ore (or 0.35 curies/day<sup>2</sup>).

#### Previous Studies of Radium in Ralston Creek and Reservoir

There have apparently been no official publications concerning the radium concentration in Ralston Creek and Reservoir, although there has been a large amount of monitoring data collected by the Colorado Department of Health

<sup>1</sup> 1 ton = 2000 lb or  $9.07185 \times 10^2$  kg  
<sup>2</sup> 1 g of  $^{226}Ra \approx 1$  curie

(3), U.S. Environmental Protection Agency (3), Hazen Research, Inc. (4), and a thesis study by Parsont (7). These reports indicate elevated levels of radium in Ralston Creek, Ralston Reservoir and Upper and Lower Long Lakes. Tables 1 through 4 are a compilation of data available from the above sources.

#### Chemical Aspects of Radium

Radium exhibits only the (+2) oxidation state in solution, and its chemistry is very much like that of barium. The hydroxide, chloride, bromide and nitrate of radium are soluble in water. Radium hydroxide is the most soluble of the alkaline earth hydroxides and is more basic than barium hydroxide. Radium chloride and bromide are less soluble than the corresponding barium salts, but radium nitrate is more soluble than barium nitrate (8). These compounds are frequently used in fractional crystallization and precipitation methods for the separation of barium and radium.

Radium phosphate, carbonate, selenate, fluoride and oxalate salts are slightly soluble, while radium sulfate is the most insoluble of the alkaline-earth sulfates ( $K_{sp} = 4.25 \times 10^{-11}$ ) at 20°C (8). Consequently the concentration of radium produced by the solubility of radium sulfate (e.g. from uranium tailings) will be  $1.5 \times 10^{-3}$  g/l in pure water

Table 1.--Dissolved  $^{226}\text{Ra}$  in Pond Effluent and in Ralston Creek Water

<u>Sample Location</u>	<u>dissolved <math>^{226}\text{Ra}</math> (pCi/l)<sup>1</sup></u>			
	<u>1980 Feb &amp; Mar</u>	<u>1978<sup>2</sup> Apr-Dec</u>	<u>1977<sup>2</sup> Jan-Dec</u>	<u>1972<sup>3</sup> Jan-Jun</u>
Ralston Creek Above Mine	0.15	0.1	0.3	0.3
Pond effluent	17.7	6.8	5.4	127.0 <sup>4</sup>
Ralston Creek Below Mine	11.1	3.6	1.9	7.0 5.2 <sup>5</sup>

<sup>1</sup>Average of data for samples collected during the indicated dates.

<sup>2</sup>Data obtained from Colorado Department of Health, Radiation and Hazardous Wastes Control Division.

<sup>3</sup>Data obtained from reference (3).

<sup>4</sup>Schwartzwalder mine effluent.

<sup>5</sup>Ralston Creek at diversion dam.

Table 2.--Dissolved  $^{226}\text{Ra}$  in Ralston Creek and Reservoir Water<sup>1</sup>

<u>Sample Location</u>	<u>Dissolved <math>^{226}\text{Ra}</math> (pCi/l)<sup>2</sup></u>	
	<u>1976 (Nov &amp; Dec)</u>	<u>1977 (Jan &amp; Mar)</u>
Above mine	0.21 ± 0.4	0 ± 0.3
Below mine	0.2 ± 0.4	0.5 ± 0.5
End property	2.2 ± 0.12	0.6 ± 0.6
First bridge below mine	2.8 ± 1.7	0.6 ± 0.6
2nd bridge below mine	0.7 ± 1.0	0.7 ± 0.5
3rd bridge below mine	1.11 ± 0.8	-
Mine outflow to Ralston Creek	0.6 ± 0.14	1.1 ± 0.9

<sup>1</sup>Data obtained from reference (4)

<sup>2</sup>Average data for samples collected during the indicated dates

Table 3.-- $^{226}\text{Ra}$  concentration in water from mine sluice, upper and lower settling basins, beaver dam pool, diversion dam and inlet to Ralston Reservoir and Upper Long Lake<sup>1</sup>

Sample Location	$^{226}\text{Ra}$ (water) pCi/l	$^{226}\text{Ra}$ (sediments) pCi/g <sup>3</sup>
Mine sluice	310 ± 12	-
Upper settling basin	240 ± 29 (8.8 ± 0.6) <sup>2</sup>	A-3131 ± 370 B- -
Lower settling basin	125 ± 39	-
Beaver dam pool	55.5 ± 0.7	A-128 ± 35. B-20.6 ± 5.1
Diversion dam	2.2 ± 0.3	A-75 ± 8 B-9 ± 3
Inlet to Ralston Reservoir	3.1 ± 1.6 (0.4 ± 0.4) <sup>2</sup>	A-32 ± 3 B-4.2 ± 0.3
Inlet to Upper Long Lake	0.5 ± 0.1	A-11 ± 3 B-2.9 ± 0.5

<sup>1</sup>Results were averaged for samples collected during 1965 and 1966 (7)

<sup>2</sup>Filtered water; all others are unfiltered. The water samples were acidified and barium carrier added to them during sample collection

<sup>3</sup>A = small particles group

B = large particles group. The author did not specify the size of each group.

Table 4.--<sup>226</sup>Ra in Mine Effluent, Ralston Creek and Ralston Reservoir, Water and Sediments<sup>1</sup>

<u>Sample Location</u>	<u>Date of Collection</u>	<u><sup>226</sup>Ra (water) pCi/l</u>	<u><sup>226</sup>Ra (sediments) pCi/g</u>
Above mine effluent	5/12/72	0.1	6
	7/20/72	0.6	-
Main mine effluent at pipe outfall upstream of sediment ponds	5/12/72	86	1230
	7/20/72	72	-
Several hundred yards downstream of mine effluent	5/12/72	3.1	188
	7/20/72	81	-
0.5 mile below mine effluent	7/21/72	22	139
1 mile below mine effluent	7/21/72	15	77
Pool behind diversion dam	5/12/72	5.6	29
	7/20/72	1.7	-
100 yards upstream of Ralston Reservoir	9/27/72	2.2	17
Ralston Reservoir	9/27/72	0.2 <sup>2</sup>	5.3 <sup>3</sup> (5.5) <sup>4</sup>

<sup>1</sup>Data obtained from reference (3)

<sup>2</sup>Average of 17 results for samples collected from different locations at Ralston Reservoir

<sup>3</sup>Average of 15 results for samples collected from different locations at Ralston Reservoir

<sup>4</sup>Average of 4 results of suspended samples collected from different locations at Ralston Reservoir

and  $4.6 \times 10^{-6}$  g/l in water containing 200 ppm sulfate. This latter concentration of radium (4.6  $\mu$ g/l) is still about six orders of magnitude greater than that permitted in drinking water (5 pCi/l) for combined  $^{226}\text{Ra} + ^{228}\text{Ra}$ . By adding barium to the radium solution in the presence of sulfate, radium can be removed nearly quantitatively from this solution by isomorphous replacement of barium in the cationic position of the crystal lattice of the barium sulfate, even though the solubility product of the radium sulfate has not been exceeded.

Radium complexes are rare in acidic solution, however in alkaline solution radium complexes with organic ligands such as EDTA, nitrilotriacetic acid and citric acid are known to occur. Complexes have found important uses in coprecipitation separations of radium. With a given ligand, the strength of the complex of the alkaline earth elements decreases in the order  $\text{Ca} > \text{Mg} > \text{Sr} > \text{Ba} > \text{Ra}$  (1). Kirby and Salutsky (8), have listed twelve complexing agents and their formation constants for radium and barium. In every case, radium was found to form 1:1 complexes with the complexing agent and the stability of radium complexes was less than that of the corresponding barium complexes.

Complexes with inorganic ligands such as bicarbonate and chloride are not reported to occur. Association of

radium with barium sulfate is known in uranium deposits (9). This association occurrence may be due to either coprecipitation or the adsorption of radium onto pre-existing barium sulfate crystals.

#### Leachability of Radium

Havlik and coworkers (10a), have cited that the leachability of radium from mill tailings waste solids (acid leaching extraction process) and sediments is highly affected by hydrogen ion concentration (pH) of the leaching medium. At a pH of 1, the largest amount of  $^{226}\text{Ra}$  is liberated (22.4%). In slightly basic solution (pH 9), the lowest amount (2.8%) of  $^{226}\text{Ra}$  is liberated whereas in a strongly basic solution (pH 13), the amount of  $^{226}\text{Ra}$  liberated increases slightly to about 5%. As a consequence, they conclude that acidic water leaching of radium might have a significance not only for surface streams but also for rain waters which in areas with high industrial emissions are of low pH and can therefore cause leaching of  $^{226}\text{Ra}$  from mine and mill dumps. Very acid media (pH 1) and very alkaline media (pH 13), never appear in normal surface waters.

In another work by Havlik and coworkers (10b), it was found that the highest amounts of  $^{226}\text{Ra}$  leached (31% from uranium ore and 100% from sediments) were obtained by using

1 N KCl as a lixiviant, and smaller recoveries (14% from the ore and 95% from the sediments) were obtained by using 1 N NaCl. The lowest amounts of  $^{226}\text{Ra}$  leached (0.3% from the uranium ore and 0.9% from the sediments) were obtained by using 1 N  $\text{BaCl}_2$  as a lixiviant. Recoveries of 0.2% from the ore and 10% from the sediments were obtained by using 1 N  $\text{SrCl}_2$ . They explain that the radium is bonded on suspended particles by adsorption forces or by ion exchange on some types of minerals. The rocks from which uranium concentrate is obtained may contain a considerable amount of clay matter which may cause adsorption of radium. It is known that some clays, e.g. illite and montmorillonite, are able to bond ions of K, Na, Ca, etc. During the contact of these minerals with water containing dissolved radium, the radium was probably bonded on the electrically active surfaces of these clays. When the clays get into surface water which is often polluted by waste waters, which contain an appreciable amount of potassium\*, radium may be displaced by potassium ions and to a lesser extent by sodium, calcium and other cations. Havlik and coworkers (10b), also explained the minimum amounts of  $^{226}\text{Ra}$  liberated in the barium chloride leaching process as follows: surface waters containing high

\*Samples collected from the tailing ponds of the works Bytiz and Najdek, Srobarova 48, Czechoslovakia

concentrations of sulfate\* normally induce precipitation of barium sulfate, the solubility of which is very low. At the same time radium coprecipitates. Consequently the dissolved radium concentration in water decreases.

An investigation was carried out by Shearer and Lee (11) on the leachability of  $^{226}\text{Ra}$  by distilled water as a function of time for samples collected from uranium mill tailings and river bottom sediments in various locations in the Colorado Plateau area. It was found that after about 15 to 30 minutes of gentle mechanical shaking, no significant additional  $^{226}\text{Ra}$  was leached up to a period of 6 days. Other workers also have found the same results (10b). Shearer and Lee (11) tested the observation by Starik (12), that diffusion of radium from the interior of ore particles, was the predominant factor governing the amount of  $^{226}\text{Ra}$  leached from natural ores. In tests run on both dry and wet samples, they found that in terms of total amounts of radium leached, there is no significant diffusion of radium from the interior of the particles. They also reported that temperature ( $3^{\circ}\text{C}$  to  $25^{\circ}\text{C}$ ) had no effect on the radium leachability.

\*Samples collected from the tailing ponds of the works Bytiz and Najdek, Srobarova 48, Czechoslovakia

### Summary of Previous Radium Leachability Studies

1. Radium in uranium ore is very weakly leachable by sulfuric acid, but is strongly leachable by hydrochloric acid and nitric acid due to the greater solubility of radium chloride and radium nitrate as compared to radium sulfate.

2. Radium in acid processing tailings is leached with EDTA, HCl, HNO<sub>3</sub> and, to a lesser extent, distilled water. The leachability of radium with distilled water is highly dependent (11) on a) the quantity of solids, and b) the liquid to solid ratio for a given quantity of solids. However, Havlik and coworkers (10a) stated that the dependency of radium leachability on the amount of salts present in the leaching solution, was found not to be justified and they relate this dependency much more to the qualitative composition of these salts.

3. Both adsorption and coprecipitation reactions may be involved in the retention of radium by the tailings. Radium may be sorbed on active sites of silicate minerals and clays (10b), as well as coprecipitated with several alkaline earth sulfates, e.g. calcium, strontium and barium sulfates. Hence radium release from tailings and stream sediments probably involves both surface desorption mechanisms as well as multi-component solubility considerations.

4. Radium can be adsorbed by using certain kinds of soils used for tailings seepage control. Beard and co-workers (13), have found that 97% of  $^{226}\text{Ra}$  is absorbed from New Mexico tailing pond solutions by using soils which were obtained from the Grants, New Mexico uranium milling areas. The major clay types in these soils are montmorillonite and kaolinite in the range of <2 to 5 percent.

5. From the data given in a report by Landa (9) based on a literature survey, the compounds listed in Table 5 are the best leaching reagents for different radium sources under the indicated leaching conditions.

Table 5.--Selected Leaching Reagents and Conditions for Leaching Radium from Different Radium Sources (9).

Source	% Leached	Leaching Conditions
Uranium ore	90	3M HCl, 85°C, 25 percent solids, 1 hr
	94	3M HNO <sub>3</sub> , 85°C, 25 percent solids, 1 hr.
Acid-leached uranium mill tailings	100	1N KCl, room temp., 10 percent solids, 6 hrs.
	95	1N NaCl, room temp., 10 percent solids, 6 hrs.
	80	0.15M EDTA, 60°C, 15 percent solids, 5 hrs.
Acid-leached uranium mill tailings (sand fraction only)	94	3M HNO <sub>3</sub> , 85°C, 25 percent solids, 1 hr.
Acid-leached uranium mill tailings (slim fraction only)	93	1M Na <sub>4</sub> EDTA, room temp., 3 percent solids, 16 hrs.
	94	1M Na <sub>2</sub> DTPA, room temp., 3 percent solids, 16 hrs.
Alkali-leached uranium mill tailings	56	0.15M EDTA, 60°C, 15 percent solids, 2 hrs.
River bottom sediments	16.5	0.015M BaCl <sub>2</sub> , 25°C, 1 percent solids, 1 hr.
	10.1-12.8	0.01M BaCl <sub>2</sub> , 25°C, 1 percent solids, 1 hr.

## METHODS OF RADIUM ANALYSIS

Several methods for radium analysis have been reported in the literature. These are:

1. Counting the alpha particles emitted by radium isotopes and their decay products (1,8,14,15,16).
2. Measurement of the alpha activity of  $^{222}\text{Rn}$  and its daughters after separation of radon from the parent  $^{226}\text{Ra}$  (deemanation method). The most commonly used deemanation method involves chemical preconcentration of radium (1,8,15,17,18,19). The direct deemanation method, without radium preconcentration has also been used (1,8,20,21,22,23,24,25). The various deemanation methods are specifically for  $^{226}\text{Ra}$  determination.
3. Isotopic radium analysis (26,27) by chemical concentration followed by separation of radium isotopes from other alpha emitters. The isotopes are determined by measuring the ingrowth rate of their daughters in the radium assay, or by extracting the daughters of the radium isotope in question and alpha counting.
4. Gamma spectrometry (1,8,13).
5. Alpha spectrometry (1,13).

## 6. Optical and x-ray spectroscopy (1,8,28).

These methods are briefly reviewed below.

### Precipitation and Alpha Counting Method

In this approach to dissolved radium determination, radium is removed from the sample solution by physical (adsorption) or chemical (ion exchange) attachment to an insoluble substance, or by coprecipitation with a carrier that is added to the solution. There are two carrier precipitation methods widely used to determine radium in water; single carrier precipitation (8,14,15,16); and double carrier precipitation (16,27). The single carrier precipitation method is simple and rapid and requires a minimum investment in equipment. This method is suitable for purposes where radium need not be determined with high precision. Interference from other alpha emitters must be absent or negligible and the isotopic nature of radium is not usually differentiated. The method is usually satisfactory for monitoring potable water. Concisely, the method is as follows: radium in a filtered sample solution is coprecipitated with barium carrier as barium sulfate. The precipitate is distributed uniformly on a membrane filter, is dried and alpha counted.

The second method (double carrier precipitation) is used whenever it is necessary to determine dissolved radium

with high accuracy. The radium is purified and concentrated from other contaminants (U, Th, Po, Pb, etc.) present in the sample solution by use of a mixed lead and barium carrier solution from which the sulfates are precipitated. The precipitate of lead, and barium, and radium sulfates is washed with 8 N nitric acid for decontamination (particularly of polonium) and then is redissolved in an EDTA-ammonia solution. Upon addition of excess acetic acid, the barium sulfate will precipitate carrying the radium, while lead remains in solution. Dissolution and reprecipitation of the barium-radium sulfate by ammoniacal EDTA-acetic acid can be repeated as often as needed for further decontamination. In all such cycles after the first, addition of sulfate is necessary to insure quantitative reprecipitation of barium. The precipitate (barium and radium sulfates) is dried and alpha counted in the same fashion as in the single-carrier precipitation method. The EDTA masking serves to purify radium from other naturally occurring alpha emitters and from the lead carrier.

#### Radium Isotope Evaluation Method

The simple method for radium isotope evaluation involves a chemical separation of radium from other naturally occurring alpha emitting nuclides (16) by a combination of

lead sulfate precipitation followed by a barium chloride precipitation. Finally the barium chloride is dissolved in dilute nitric acid, and the radium is coprecipitated with barium sulfate. The barium sulfate is collected on a membrane filter and mounted for counting. The radium isotopes are determined by measuring the growth and decay of alpha activity in the barium sulfate precipitate. However this is a crude method for radium isotope evaluation due to the interference from  $^{227}\text{Ac}$  and  $^{210}\text{Bi}$  alpha emitting daughters. Also, the reported values for radium isotopes are based on assumptions and mathematical manipulations which are not always valid.

The more accurate method for radium isotope evaluation involves the separation of radium from the sample by coprecipitation with lead sulfate followed by a specific separation of the appropriate daughter which is in equilibrium with the radium isotope and measuring the corresponding activity (16,26). The following is one of the procedures used for radium isotope estimation, for more details see reference (26). In this procedure  $^{223}\text{Ra}$  is determined by extracting its daughter  $^{211}\text{Pb}$  ( $t_{1/2} = 36.1 \text{ m}$ ) into dithizone in chloroform after the lead carrier in the radium precipitate has been removed. The organic layer is then evaporated and the residue transferred to a stainless steel planchet

and alpha counted. Interference from  $^{214}\text{Pb}$  can be minimized by boiling the solution during the three hours ingrowth time of  $^{211}\text{Pb}$ . This will volatilize the  $^{222}\text{Rn}$  ( $t_{1/2} = 3.825$  d), the precursor of  $^{214}\text{Pb}$ . If  $^{224}\text{Ra}$  is present a correction must be made for the presence of the 10.64 hr  $^{212}\text{Pb}$ . The correction is easily made by decay measurements of the separated lead activity.

Radium-224 is determined by allowing enough time (16-24 hrs) for its daughter, 10.64 hr.  $^{212}\text{Pb}$  to grow into the sample solution. The  $^{212}\text{Pb}$  is then extracted as indicated in the  $^{223}\text{Ra}$  method. The chloroform is evaporated and the residue is transferred to a planchet. 3.5 hrs. are allowed for  $^{211}\text{Pb}$  to decay before the start of counting to minimize interference.

Radium-226 can be determined precisely by the deemanation method, or roughly by subtraction of four times the  $^{223}\text{Ra}$  activity and three times the  $^{224}\text{Ra}$  activity from the gross alpha activity in the bulk precipitate containing the radium.

For  $^{228}\text{Ra}$  determination, 36 hours are allowed for ingrowth of the  $^{228}\text{Ac}$  daughter of  $^{228}\text{Ra}$  in the radium-containing solution. Actinium-228 is extracted from this solution by using di(2-ethylhexyl)phosphoric acid (EHPA). It is then stripped from the extraction reagent by shaking with two 10

ml portions of 1.5 M hydrobromic acid. The two portions are collected together and the hydrobromic layer is evaporated to dryness. The residue is transferred to a planchet and counted in a  $\beta$ -counter. For this and other procedures see also Kirby and Salutsky (8).

#### Deemanation Method

The emanation of a radioactive gas by radium salts was originally noticed by Rutherford in 1899, during his attempts at radioactive measurements of these salts. The deemanation method for radium determination is based on the emanation of the radioactive gas  $^{222}\text{Rn}$  generated by decay of the  $^{226}\text{Ra}$  isotope. This method has been employed for  $^{226}\text{Ra}$  determination at least since 1935 (20). Lucas (24), in 1957, gave the method a revolutionary step by demonstrating a low background reproducible detector apparatus (Lucas cell). Since then it has undergone only minor modifications and it has been shown by numerous scientists to be the most sensitive method, with detection limits as low as  $1 \times 10^{-14}$  Ci to  $2.1 \times 10^{-15}$  Ci (29).

#### Precipitation-Deemanation Method

In the standard deemanation method (15,19), the dissolved radium in a one liter filtered water sample is copre-

precipitated with barium sulfate using a barium carrier solution. Radium and barium are chemically so closely related to each other that they are separable only by ion exchange or fractional crystallization. Hence, the radium will substitute for barium in the barium sulfate lattice and the barium sulfate will coprecipitate virtually all the radium present in the sample solution. The barium radium sulfate is allowed to settle overnight, then the supernate is decanted and the precipitate is centrifuged and dissolved in alkaline sodium diethylenetriaminepentaacetic acid (NaDTPA) solution. The barium radium sulfate solution is then transferred into a bubbler which is used for radon ingrowth. The radium solution in the bubbler is first deemanated to make a radon-free solution by purging the solution with helium, nitrogen, or dry aged air. The bubbler is then sealed for a known period of time (2 to 20 days, depending on how much radium is present in the sample). The second deemanation is then performed to transfer the ingrown radon to the detector by purging helium gas through the aged solution. The purging gas will carry the radon with it into the detector (scintillation cell, Lucas type) (24). When the desired pressure in the cell (usually slightly less than one atmosphere to protect the cell from leaking) is reached, the purging is stopped. The cell stopcock is closed. The gas

is then aged for three to four hours before counting to allow  $^{222}\text{Rn}$  to reach a transient equilibrium with its daughters and to minimize the interference from other short-lived radon isotopes.

#### Direct Deemanation Method

In this method, the analysis for dissolved  $^{226}\text{Ra}$  is performed without any chemical preconcentration of the radium present in the sample solution as is done in the precipitation-deemanation method. The method contains the following steps: the volume of sample (typically one liter or more) which would be used in a precipitation-deemanation method is transferred to a one liter bubbler (the volume may be reduced by evaporation if necessary, prior to its transference to the bubbler). The sample solution in the bubbler is then freed of radon by purging with helium, nitrogen, or dry aged air. The bubbler is then sealed for a known period of time (typically four to seven days). It is then connected to the radon transfer system and the radon is purged and collected on an absorber. The absorber may be activated charcoal (24), silica gel (23), glass beads (18), or simply a glass U-tube (22). Liquid nitrogen (M.P. =  $-209.9^\circ\text{C}$ ) or dry ice-acetone (M.P. =  $-78^\circ\text{C}$ ) is used to cause condensation/sorption of the radon (M.P. =  $-71^\circ\text{C}$ ).

The radon is transferred to the detector scintillation cell (15,18,22,24), liquid scintillator (23), ionization chamber (20,30), or ion-counting chamber (25), by removing the liquid nitrogen and warming the absorber tube while flushing with helium gas. When liquid scintillation counting is used, the radon and absorbent (silica gel may be simply poured into the liquid scintillator contained in a counting vial (23). When an ionization chamber or ion-counting chamber is used there is no need for a liquid nitrogen trap since the radon will be transferred directly to the chamber using nitrogen as a carrier gas. By the time the pressure in the detector (scintillation cell, ionization chamber, or ion-counting chamber) gets to nearly one atmosphere about 95 to 100% of the radon has been transferred. Three to four hours are allowed for the gas in the detector to age before counting.

#### Spectrometric Methods

There are both gamma and alpha spectrometry methods for radium determination. Gamma spectrometry is rapid and non-destructive. Liquid and solid samples can be analyzed for radium by this method. Sensitivity of  $1 \times 10^{-9}$ ,  $0.5 \times 10^{-9}$  and  $2 \times 10^{-9}$  Curie for  $^{226}\text{Ra}$  in soil and  $^{222}\text{Ra}$ ,  $^{228}\text{Ra}$  in solution respectively have been reported (29). A sensitiv-

ity of  $1 \times 10^{-11}$  Curie for  $^{226}\text{Ra}$  also has been reported (1). However the sensitivity of the method is highly dependent on the sample size and type of detector used in the gamma spectrometer. Both crystal (e.g. NaI(Tl)) and semiconductors (e.g. lithium drifted germanium) detectors may be used for gamma spectrometry. The former give better counting efficiency and the latter give much better resolution. The gamma spectrum of an equilibrium sample of  $^{224}\text{Ra}$  is virtually indistinguishable from that of its parent thorium-228, the only differences are in the energies of K $\alpha$  x-ray accompanying the alpha disintegration; 0.0838 and 0.0885 MeV respectively (8). Therefore, gamma spectrometry is not a useful method for following the separation of radium-224 from thorium-228.

The rapid development of solid state alpha detectors has encouraged the use of alpha spectrometry for the analysis of mixtures of radium isotopes and other alpha emitters. However the use of alpha spectrometry imposes severe restrictions on the method of sample preparation. The most important of these are sample thickness and area. Several methods for sample preparation for alpha spectroscopy have been reported (1,8). Radium is usually electroplated to give a sufficiently thin deposit. A sensitivity of  $1 \times 10^{-14}$  Curie has been reported (29) for alpha

spectrometric determination of  $^{226}\text{Ra}$ . In a paper cited by Beard and coworkers (1980) (13) an  $\alpha$ -spectrometer was used for the determination of thorium-230 and  $^{226}\text{Ra}$ . Their samples were counted for a sufficient time to give good counting statistics.  $\pm 3\%$  error at the 95% confidence level has been accomplished.

#### Optical and X-Ray Spectroscopic Methods

These methods have not been widely used, the most sensitive lines in the emission spectrum and the common interference lines are given in reference (28). The following lines in the x-ray emission spectrum have been reported (21): 1.01A. ( $L_{\alpha_1}$ ), 0.802A. ( $L_{\beta_5}$ ), and 0.668A. ( $L_{\gamma_6}$ ). However these methods have very poor detection limits and the vaporization of the radium presents a significant hazard.

## EXPERIMENTAL

Deemanation Method for Radium

The method used in this study for  $^{226}\text{Ra}$  determination in solution was the direct deemanation method. Stream bed sediments were analyzed by decomposition followed by the deemanation procedure and also by direct gamma spectrometry.

The direct deemanation method was chosen to avoid the necessity of having to preconcentrate the radium by barium sulfate coprecipitation (see the introduction under precipitation-deemanation method). In samples of high dissolved solids and in certain other problem samples, there are potential errors in the precipitation-deemanation method due to incomplete coprecipitation of the radium or incomplete redissolution of the precipitate. The bubbler size is increased from 75 or 100 ml in the precipitation-deemanation method to one liter in the direct deemanation method, which allows the use of a larger sample volume (800 ml) instead of the 45 to 75 ml used in the former procedure. The sensitivity of the method becomes higher and this is very important for low activity samples.

## 1. Description of Radon Transfer System

The radon transfer system (Figure 3) contains the following parts: a) one liter bubbler, which is used for radon ingrowth and as a sample container, b) a glass tube packed with Drierite (anhydrous magnesium perchlorate) to remove moisture from the radon gas, c) Ascarite (NaOH on asbestos + soda-lime) to help remove acid vapors and carbon dioxide, d) an adsorber tube which contains 1.6 g of activated coconut charcoal. The adsorber tube dimensions are 0.5 cm diameter and 10 cm length, and e) manometer to indicate the pressure inside the system during the radon transfer from the bubbler to the detector and to indicate any leak in the system.

## 2. Procedure

The following paragraphs describe the experimental procedure for analysis of radium by the direct deemanation method as used in the present study.

### A. First Deemanation

800 ml of the radium sample solution is transferred to a clean one liter bubbler, and helium gas is bubbled through it at a flow rate of 120 cc/min for about 30 to 35 min to make a radon-free solution. The bubbler is then sealed and set aside for four to seven days to allow ingrowth of radon. This aging period must be accurately timed.

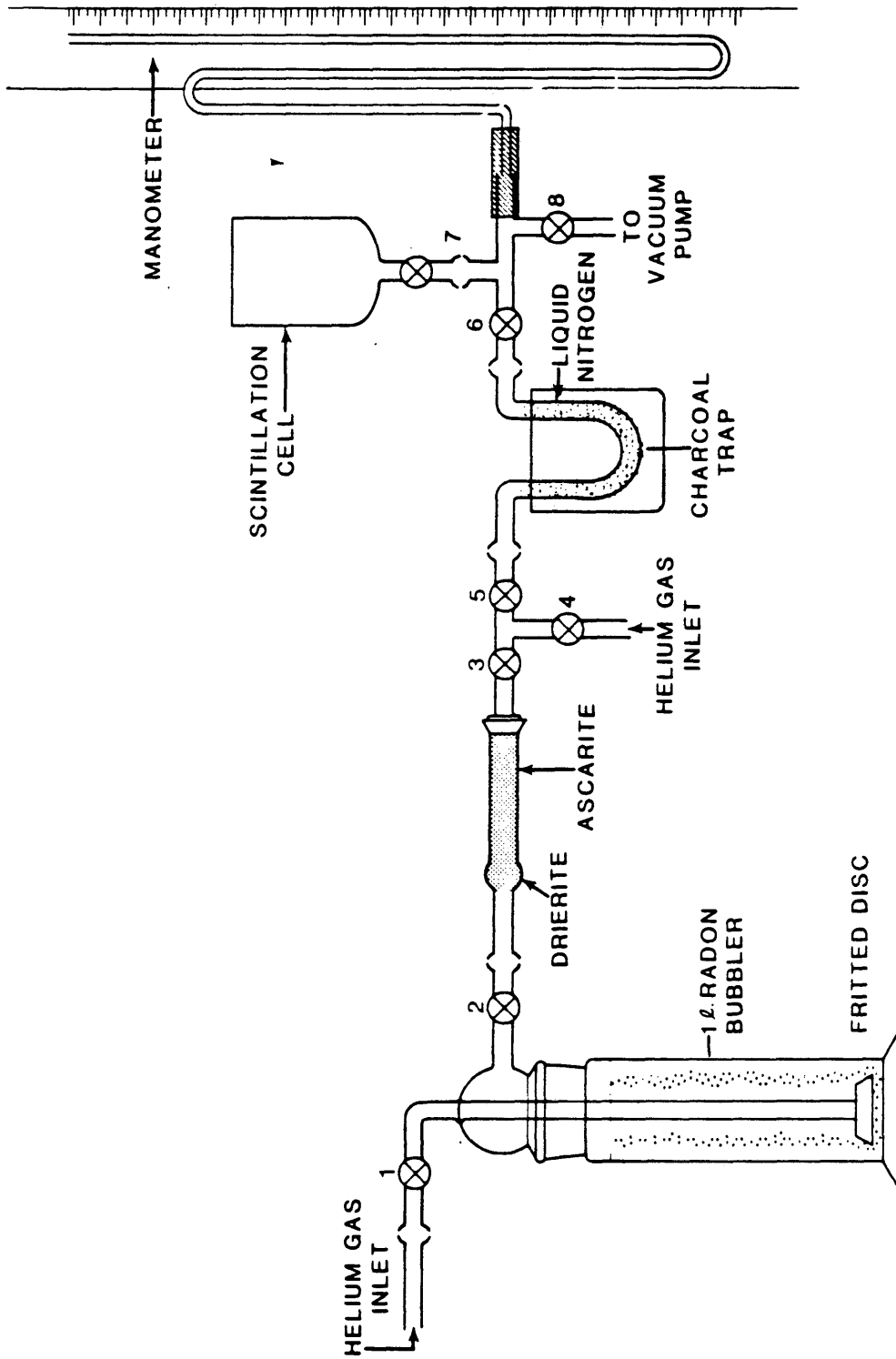


Figure 3. Radon Transfer System

### B. Second deemanation

The second deemanation is performed to transfer the ingrown radon-222, produced by the decay of  $^{226}\text{Ra}$  in the sample solution, from the bubbler (sample container) to the detector (scintillation cell). The one liter bubbler containing the radium sample solution is connected to the radon transfer system through an o-ring connection between stopcock No. 2 and the Drierite/Ascarite tube as shown in Figure 3. The helium gas inlet is connected to the bubbler through stopcock No. 1, and the helium gas outlet line (not shown in the drawing) is connected through position No. 7. An oil trap is placed in the outlet line to prevent air from coming back into the system during gas purging. Before the start of the second deemanation, stopcocks 1, 2, 4 and the gas outlet are closed. A vacuum is applied by opening stopcock No. 8, for at least 30 min. During this pumping down of the system, the charcoal tube is heated to  $250^{\circ}\text{C}$  by use of a heating tape. The vacuum stopcock, (No. 8) is then closed. Helium gas is next allowed to pass slowly through stopcock No. 4 into the system and exits through the oil trap in the gas outlet line. This gas flow is continued for 5 minutes to push out any trace of air. Stopcock No. 4 and the helium gas outlet stopcock are next closed and the system is again evacuated for five min. The vacuum stopcock

(No. 8) is closed and the system is checked for leaks by monitoring the manometer for at least 2 min. The heating tape is removed and the charcoal tube is cooled to room temperature and is then immersed in liquid nitrogen. Ten minutes are allowed for the charcoal to attain the liquid nitrogen temperature, then stopcock, No. 2 is slowly opened and the mercury level in the manometer will drop down slightly. When it reaches a stable point, stopcock, No. 1 is opened very slowly and helium is allowed to flow into the system until the internal pressure is equal to the ambient pressure, as evidenced by equal mercury levels in the manometer. When the pressures are equalized, the helium gas outlet stopcock is opened and the helium gas flow rate, as indicated by the flowmeter, is adjusted to  $120 \text{ cm}^3/\text{min}$ . Helium purging at this flow rate is continued for 35 min, then stopcocks 1, 2, 3, 5, and 6 are closed. Finally the gas outlet stopcock is closed. The scintillation cell, which has a known stable background, is then connected to position No. 7. Stopcock No. 8 is opened and the cell is evacuated and checked for leaks. The cell stopcock is then closed. Stopcock No. 6 is opened very slowly to draw out the excess helium gas. After stopcock No. 6 is closed the cell stopcock is opened to the system. After three min, the vacuum stopcock is closed and the liquid nitrogen container

is removed from the charcoal trap. The charcoal tube is allowed to warm to room temperature and then is wound with heating tape. The tube is heated to 300-350°C for 20 min, stopcock, No. 6 is then opened to the cell and the time is recorded. Stopcock No. 4 is opened and then stopcock No. 5 is opened very slowly to flush the charcoal trap with helium gas. The pressure is allowed to build up inside the cell to about 4 torr less than ambient pressure, then the cell stopcock, is closed and the time is recorded. The cell is now transferred to the counting system. Three to four hours are allowed for  $^{222}\text{Rn}$  daughters to reach secular equilibrium, then the time is recorded and sample counting is initiated. Low activity samples are normally counted for one thousand minute.

#### C. Counting System for Radon Determination

The radon counting system consisted of the following components:

Detector: A 75 ml nickel-crucible chamber internally coated with silver-activated zinc sulfide, window diameter of 2 inches

Photomultiplier: 3-inch EMI Industrial Electronic Ltd.  
(England) scintillation photomultiplier.  
Gencom, Inc. Catalog No. 9758KB.

Preamplifier: Canberra Model 2007P, connected to the photo multiplier base

Dual Scaler: Canberra Model 1774

Dual Counter/Timer: Canberra Model 1776

Power Supply: High Voltage, Canberra Model 3002

The counting efficiency of the system was in the range of 4.9 to 5.6 counts per minute per picocurie of radon with a background of 0.3 to 0.09 counts per minute.

#### Performance of the Radon System

The radon transfer system was studied to establish its performance characteristics. The first step was to find out the optimum flow rate and purging time required to transfer all the ingrown radon to the charcoal adsorbent during the second deemanation. The test was conducted using standard radium solutions of 13.1 and 25.0 pCi/l. The results obtained with helium flow rates of 70 and 120 cm<sup>3</sup>/min are shown in Table 6.

The second step of the evaluation was designed to establish the reproducibility of the system along with the counting efficiency for the detector. This study was performed by using a known concentration of <sup>226</sup>Ra solution and

Table 6.--Measured  $^{226}\text{Ra}$  as a function of stripping time for  $^{222}\text{Rn}$  daughter.<sup>1</sup>

Flow rate $\text{cm}^3/\text{min}$	Stripping time min	$^{226}\text{Ra}$ present pCi/l	$^{226}\text{Ra}$ measured	
			pCi/l <sup>2</sup>	%
70	5	13.1	$4.6 \pm 0.2$	35
	10	25.0	$15.8 \pm 0.4$	63
	15	13.1	$10.4 \pm 0.3$	79
	20	13.1	$11.6 \pm 0.2$	89
	25	25.0	$23.5 \pm 0.5$	94
	30	13.1	$13.1 \pm 0.3$	100
	35	25.0	$25.3 \pm 0.5$	101
120	5	13.1	$7.6 \pm 0.5$	58
	10	13.1	$10.7 \pm 0.5$	82
	15	13.1	$12.1 \pm 0.5$	92
	20	13.1	$12.8 \pm 0.5$	98
	25	13.1	$13.2 \pm 0.6$	101
	30	13.1	$13.4 \pm 0.6$	102

- 1) 1 liter bubbler and helium carrier gas were used.  
 2) Error terms are based on the 2 sigma counting error.

Table 7.--Reproducibility of radium analysis system.

$^{226}\text{Ra}$ conc. pCi/l	No. of analyses	Observed $^{226}\text{Ra}$ <sup>1</sup> pCi/l
5.0	4	$5.0 \pm 0.2$
10.0	4	$9.4 \pm 0.2$
13.1	3	$13.0 \pm 0.4$
25.0	4	$25.0 \pm 0.6$

- 1) Error terms are expressed at the 90% confidence level.

the optimum flow rate ( $120 \text{ cm}^3/\text{min}$ ) and purging time (30 min) obtained as described above.

The data as shown in Table 6 for radon stripping efficiency revealed that, as the flow rate of the carrier gas (helium) increases, the time required to drive out the ingrown radon decreases. This is shown in Figure 4. It was found that a helium flow rate of  $120 \text{ cm}^3/\text{min}$  for 30 min through 800 ml of radium solution in a 1 liter bubbler is efficient for stripping essentially all of the ingrown radon during the second deemanation. This flow rate and purging time were found to be reproducible within the statistical error for the method as indicated in Table 7.

As a part of the method investigation study, some of the water samples were analyzed for dissolved and suspended radium-226 by both the precipitation-deemanation and the direct deemanation methods. Results, as shown in Table 9, revealed that the radium concentration found by the precipitation-deemanation method are slightly lower than those found by the direct deemanation method. This indicated the possible loss of radium during the chemical preconcentration of radium present in the sample or in redissolving the precipitate.

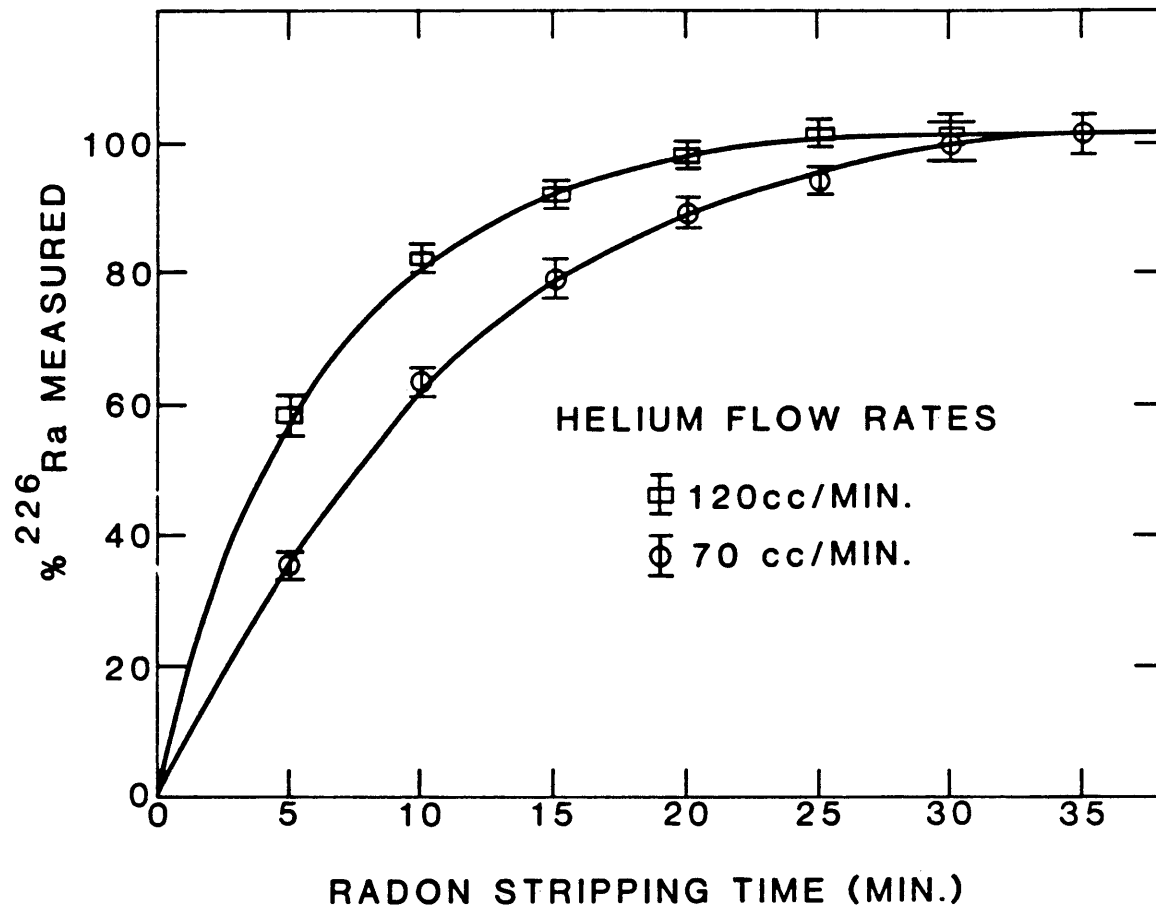


Figure 4. Radium Measured as a Function of Helium Flow Rate and Radon Stripping Time

### Gamma Spectrometric Method

Gamma spectrometry was used for analysis of stream bed sediments. The system is shown in a block diagram in Figure 5. The detector is a 3" x 3" NaI(Tl), crystal (Bicron Model 3M3) with a resolution of 6.5% for the 0.662 MeV photopeak from a  $^{137}\text{Cs}$  source. This is housed in a 2400 pound cylindrical lead shield which has a 4-inch thickness of lead on all sides. The photomultiplier of the detector is powered by an Ortec Model 456 high voltage power supply. Pulses from the scintillator are amplified by an Ortec Model 113 preamplifier and an Ortec Model 460 delay live amplifier. The output from the amplifier is fed to a Nuclear Data Model ND60A 2048 channel multichannel analyzer for conversion to a digital spectrum. 512 channels are used for accumulation of each spectrum.

Analysis for  $^{226}\text{Ra}$  is performed by allowing the sample to age for sufficient time (about 3 weeks) to allow the  $^{214}\text{Bi}$  daughter to grow into secular equilibrium. The intensity of the 1.76 MeV  $^{214}\text{Bi}$  peak is measured and related to the  $^{226}\text{Ra}$  content of the sample. Each sample was counted for 1 hr or more. Appropriate corrections were made for any thorium-series activity in the sample.

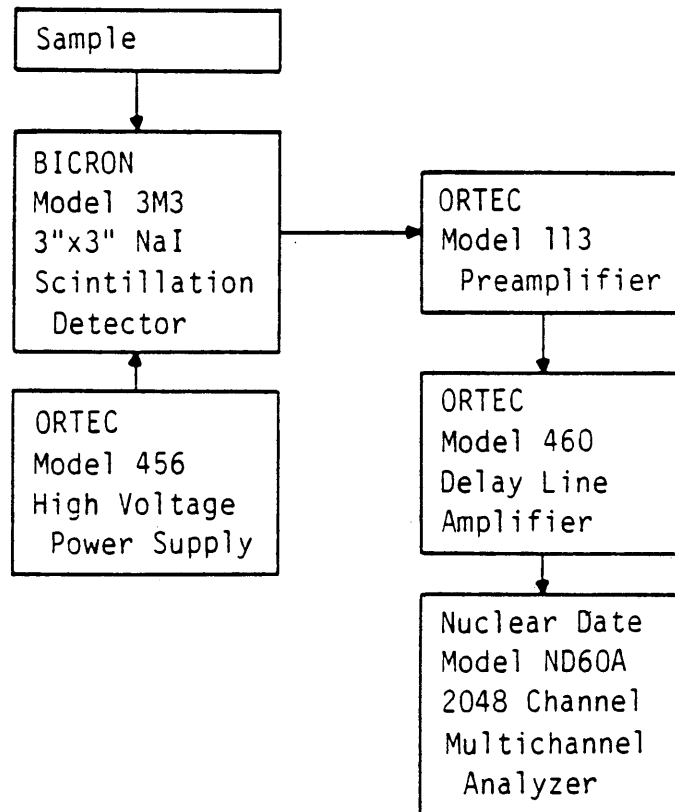


Figure 5. Block Diagram for Gamma Spectrometer.

ANALYSIS OF RALSTON CREEK AND RESERVOIR WATER  
AND SEDIMENT SAMPLES

Sample Collection

Sixteen 20 l water samples containing suspended materials, and fourteen samples of bed sediments were collected from different sites in Ralston Creek and Reservoir, during winter, 1980 and spring, 1981. Figure 2 (page 8) is a map of the area sampled and shows the sampling sites. The stream was shallow, one to three feet in depth, about 10 to 20 feet wide, and the turbulence was moderate. With this kind of stream conditions, no specialized equipment was needed for sample collection.

A. Water Samples

Water and suspended solids were collected simply by immersing a one liter plastic bottle (wide mouth) under the water surface several times at different depths. The water collected was transferred to a five gallon plastic container until the latter was filled. The samples were transferred to the laboratory as soon as possible.

B. Bed Sediments

The bed sediment samples were scooped from the upper 5 cm of the stream bottom layer as close as possible to where the water samples were collected. A plastic scoop was used

for collection and the sediment was put into a two liter wide mouth plastic bottle with a minimum amount of water and transferred to the laboratory.

### Laboratory Preparation and Analysis of Samples

#### A. Water and Suspended Solids

The water samples were filtered through a 0.45  $\mu\text{m}$  membrane filter, which had been previously weighed. Due to clogging of the filters by the suspended fine materials, it was necessary to use about seven to ten membranes for each sample to speed up the filtration. The material retained on those filters was classified as suspended solids. The filtrate was put into a plastic bottle, acidified with hydrochloric acid to pH 1 to 2 and saved for  $^{226}\text{Ra}$  analysis. 800 ml of the filtrate water for each sample was analyzed for  $^{226}\text{Ra}$  by the direct emanation method. The filter membranes for each sample were combined in a glass beaker, loosely covered, and allowed to dry at room temperature. They were then weighed again and the suspended material weight for each sample was calculated. The dry filter membranes were then ignited one at a time in a porcelain crucible covered with a watch glass. Ignition was accomplished by touching the membrane with a hot glass rod. The crucible with the residue of suspended materials was put into a

muffle furnace at 450°C to burn off any residual organic material. After three to four hours, the crucible was taken out and cooled, and then the solid residue was transferred to a teflon beaker. The crucible was washed with dilute HCl to complete the transfer. The suspended solids residue was then decomposed, using the same method as for bed sediments (see following pages). The solution from the decomposition was diluted to 800 ml with distilled water, the pH was adjusted to 1 to 2, and was then analyzed for  $^{226}\text{Ra}$  by the direct emanation method. A few milliliters from the same solution were taken for uranium analysis.

An experiment was performed to determine if the membrane filter was adsorbing any of the radium from the water samples during the filtration operation. 800 ml of water from sample site No. 10 of Ralston Creek (dissolved radium concentration was 1.11 pCi/l) was filtered through a 0.45  $\mu\text{m}$  membrane filter and then spiked with 10 pCi of  $^{226}\text{Ra}$  standard, shaken thoroughly, and then refiltered through a new membrane. The filtrate was then analyzed for  $^{226}\text{Ra}$ . The recovered  $^{226}\text{Ra}$  was  $10.53 \pm 0.33$ , or 95% of the total activity. The small difference between the amounts of radium-226 present in the spiked solution before filtration and after filtration may be due to the radium present in the suspended materials which remained in the water sample after the first

filtration and were retained by the filter membrane during the second filtration. Another test was devised to see the validity of the above explanation for the radium difference. 800 ml of distilled water was spiked within 10 pCi of  $^{226}\text{Ra}$  standard and shaken thoroughly. It was then filtered through a 0.45  $\mu\text{m}$  membrane filter and the filtrate analyzed for  $^{226}\text{Ra}$ . The recovered  $^{226}\text{Ra}$  was  $9.65 \pm 0.35$  which is equal to the spiked amount of radium within the 2 sigma statistical counting error. These two experiments have indicated that there was no significant adsorption of the dissolved radium by the filter membrane. Any radium activity found in the filter membrane is therefore attributed to the radium in suspended material which is retained by the membrane filter.

#### B. Bed Sediments

##### i) Drying and Sieving

The bed sediment for each sample was spread on aluminum foil and dried in an oven at 110°C for 24 hours, then transferred to a plastic mortar. Care was taken to break the solid cake without altering the nature of the sediment particles.

Bed sediment from sample site No. 4 (400 ft below mine outflow) was separated into ten different particle size fractions. The rest of the sediment samples were separated

into six different particle size fractions, by passing through a group of sieves. The splits from sample site No. 4 were taken for analysis by total decomposition.

ii) Decomposition

Two grams of each fraction of sample site No. 4 were treated first with 10 ml of  $H_2O_2$  (30%) to help oxidize any organic material present. This was followed by a combination of 50 ml/g HF (49%) and 10 ml/g of  $HNO_3$  (70%). The samples were then digested on a hotplate for about six to eight hours and allowed to go to dryness. This decomposition procedure was repeated four or five times. 20 ml/g of  $HNO_3$  alone was then added and heated to dryness to remove fluoride ion. 20 ml/g of conc. HCl was then added and evaporated to dryness. The yellow solid residue was dissolved in distilled water, diluted to 800 ml (pH 1-2) and transferred to a one filter bubbler for  $^{226}Ra$  analysis. A few ml of this solution were taken for uranium analysis.

The procedure described for the sediment decomposition was satisfactorily applied to both suspended materials and bed sediment. However the -270 mesh fraction was found to be difficult to totally decompose. Because of the small amount of undecomposed residue (23.5 mg compared to the original 2 g of sediment), it was thought that the amount of  $^{226}Ra$  which might still be associated with the residue is

probably small. To check this prediction, the undecomposed solid was transferred with the solution to the bubbler and analyzed by the emanation procedure. Because of the small particle size of the residue, it was thought to be likely that a substantial fraction of the radon produced therein will escape into the solution and be measured in the analysis. On analysis of this solution the radium content was found to be 67.4 pCi per gram of the original sediment. The solution was then filtered through a 0.45  $\mu\text{m}$  membrane filter and the weight of undecomposed solid was determined to be 23.5 mg (about 1% of the original 2 gram sample).

The filtrate was analyzed again for  $^{226}\text{Ra}$ , and a slightly lower result (62.2 pCi/g) of  $^{226}\text{Ra}$  was found. The residue was then decomposed and added to the filtrate in the bubbler and reanalyzed for  $^{226}\text{Ra}$ . A much higher result (175 pCi/g) was observed this time. This value fits into the sequence of the results of  $^{226}\text{Ra}$  in the other fractions.

These experiments have shown that a large fraction of the radium can be held by a small amount of solid residue during sediment decomposition. The amount of radon which is emanated from solid material containing radium is also a small fraction, in this instance, of the amount which will be released if the solid material is totally decomposed. Consequently it is concluded that during sediment decomposi-

tion, the solid material must be totally decomposed. For total radium per liter (dissolved and suspended), the analysis for radium should be done separately on the water and suspended solids. Otherwise the reported result may be in serious error.

#### C. Preparation for Gamma Spectrometry

The creek bed sediment samples after being dried as described earlier, were separated into six different particle size fractions, by passing through a group of sieves. Each sample fraction was packaged for gamma spectrometry analysis in cylindrical steel cans. One, two and four ounce cans were used for sample sizes in the range of 30 to 200 grams, depending on the amount of each fraction available for packaging.

#### D. Preparation for Leaching Studies

An experiment was designed to establish the best lixiviant for leaching radium from the bed sediment. HCl, EDTA, BaCl<sub>2</sub>, and KCl were selected for study. Three grams of bed sediment sample from site No. 4 (-42 + 60 mesh fraction) containing 51.6 pCi/g of <sup>226</sup>Ra and 83.7 µg/g of natural uranium, were put into a 500 ml conical flask. 200 ml of the leaching solution were added, and the flask was stoppered and put on a mechanical shaker adjusted to 80 impact/min. The tests were conducted at room temperature,

for different periods of time and different reagent concentrations as shown in Table 13 (page 78). After the specified time for shaking has elapsed, the leaching solution was filtered through a 0.45  $\mu\text{m}$  membrane filter, and the filtrate was diluted to 800 ml (pH 1 to 2) and put into a one liter bubbler for  $^{226}\text{Ra}$  analysis. A few milliliters of this solution were taken for uranium analysis. The sediment residue which remained on the membrane filter for each leaching reagent was dried and weighed again. The following weight percents of the sediments for each leaching reagent were found to be decomposed during the leaching process.

Table 8. Percent of sediment decomposed during the leaching process

<u>Leaching Reagent</u>	<u>% wt. of the sediment decomposed</u>
2 $\underline{\text{N}}$ HCl	5.2
0.1 $\underline{\text{M}}$ $\text{Na}_2\text{EDTA}$ (pH=10)	2.5
1 $\underline{\text{N}}$ KCl	0.6
1 $\underline{\text{N}}$ $\text{BaCl}_2$	0.3

A small amount of a colorless gas (probably  $\text{CO}_2$ ) was evolved during the hydrochloric acid leaching process and the leaching solution color changed to a light yellowish color. No gas was evolved during the  $\text{Na}_2\text{EDTA}$  leaching process, and the leaching solution became a light yellowish-brown

color. Nothing unusual was noticed in the  $\text{BaCl}_2$  and KCl leaching process.

From the above preliminary leaching study, 200 ml of 2 N HCl was selected as a lixiviant and leaching conditions of 1 hr shaking (80 impact/min) at room temperature were used for conducting the leaching study on other bed sediment samples.

i) Sediment Samples Above Mine Outflow (400 ft)

The  $^{226}\text{Ra}$  concentration in most above-mine fractions was quite low as shown in Table 12 (page 75). In order to get reproducible results, only the two smallest particle-size fractions (-115 + 270 and -270 mesh) were selected for the leach study (Table 10, page 70).

ii) Sediment Sample Below Mine Outflow (400 ft)

Three grams each of the ten fractions of this sample were taken for the leach study (Table 10).

iii) Sediment Samples From Ralston Reservoir Inlet

The leaching study of this sample was performed on 24 grams of the bulk sediments (Table 10).

Another test was devised to determine the leaching action of hydrochloric acid for  $^{226}\text{Ra}$  for high barium (radium) sulfate content in a real sample. It has been proposed that the suspended materials in the mine outflow to Ralston Creek must be of high barium (radium) sulfate

content, since barium sulfate is used as a decontaminant agent for radium by the mine waste treatment plant. 36 mg of suspended material collected on 9/10/1981 from the mine outflow to Ralston Creek were leached by using 2 N HCl with 1 hr shaking (80 impact/min), at room temperature. The leaching solution was then filtered and the filtrate was analyzed for radium-226. The percent of  $^{226}\text{Ra}$  leached is shown in Table 10.

## RESULTS AND DISCUSSION

Dissolved Radium-226

The concentrations of dissolved  $^{226}\text{Ra}$  in Ralston Creek and Reservoir water were determined on samples filtered through 0.45  $\mu\text{m}$  membrane filters. Results for all sampling sites are shown in Table 9.

The data revealed that  $^{226}\text{Ra}$  concentration in creek water 400 ft above the mine (dissolved  $^{226}\text{Ra}$  background in the creek) was very low, 0.13 pCi/l. Previous study has indicated a concentration range of 0.1 to 0.6 pCi/l for  $^{226}\text{Ra}$  in water samples collected from sites above the mine during 1972, see Table 4. The mine water outflow to Ralston Creek was found to contain 0.58 to 1.03 pCi/l on the three dates sampled. Therefore the mine contribution to the dissolved radium concentration in the creek water was fairly low. The  $^{226}\text{Ra}$  concentration in the creek water below the mine was significantly higher at all sampling stations between the mine and the reservoir. Although significant differences in radium concentration with sampling date occurred, in all cases but one the  $^{226}\text{Ra}$  content in the stream water was found to be higher than in treated discharge water from the mine which was entering the stream. This increase in radium content of the stream is probably due, in large part, to

Table 9.--Concentration of  $^{226}\text{Ra}$  in solution and in suspended materials of Ralston Creek and Reservoir water.

Collection Date	Site no.	Sample Location	Dissolved $^{226}\text{Ra}$ $^{2,3}$ pCi/l	Suspended $^{226}\text{Ra}$ $^{2,3}$ pCi/g	pH
1/15/81	1	400 ft above mine outflow to Ralston Creek	0.13±0.02*	68± 14 (66.7)	7.5
1/15/81	2	Mine outflow to Ralston Creek (0 ft)	0.58±0.19 (0.52)	1290±220	8.1
5/ 5/81	2	"	0.67±0.04*	---	---
9/10/81	2	"	1.03±0.07 (0.87)	---	---
1/15/81	3	200 ft <sup>1</sup>	1.43±0.06	578± 7	8.3
1/15/81	4	400 ft	1.13±0.06	209± 1	8.2
9/10/81	4	400 ft	1.26±0.05	---	---
11/ 5/80	5	0.2 mi	1.18±0.19	547± 23	8.3
8/17/81	5	0.2 mi	2.22±0.08*	---	---
11/ 5/80	6	0.4 mi	1.09±0.04	332±121	8.3
9/10/81	6	0.4 mi	1.63±0.06*	---	---
11/ 5/80	7	0.6 mi	1.19±0.23	275± 28	8.2
9/10/81	7	0.6 mi	1.69±0.06	---	---
11/ 5/80	8	0.8 mi	1.35±0.25	320± 16	8.3
11/ 5/80	9	1 mi	1.35±0.39	261± 46	8.3

Table 9.--Continued

Collection Date	Site no.	Sample Location	Dissolved $^{226}\text{Ra}^{2,3}$ pCi/l	Suspended $^{226}\text{Ra}^3$ pCi/g	pH
11/ 5/80	10	1.4 mi	1.11±0.12	249±64	8.3
11/ 5/80	11	1.5 mi	1.27±0.06*	203±57	8.2
11/ 5/80	12	Long Lake ditch directly below diversion dam	1.19±0.17	—	8.4
11/ 5/80	13	2.4 mi	0.82±0.03* (0.79)	34± 3	8.1
11/ 5/80	14	Long Lake ditch near upper end of Ralston Reservoir	1.17±0.07	—	8.4
5/ 5/81	15	Ralston Reservoir inlet	0.46±0.03*	22±10	7.8
5/ 5/81	16	Ralston Reservoir outlet	0.24±0.02	12± 1	7.4

- 1) Locations shown are distances from mine outflow into Ralston Creek to sample site downstream.
- 2) Errors indicated with (\*) are the 2 sigma counting error for samples on which a single measurement was made, while others are based on reproducibility of replicate measurements and expressed at the 90% confidence level.
- 3) Numbers in parentheses are for  $^{226}\text{Ra}$  determined by precipitation-deemanation method. Others are by direct deemanation method.

rapid leaching and/or redissolution of the freshly precipitated  $Ba(Ra)SO_4$  when some of it enters the stream as suspended and colloidal particles. In the treatment plant an excess of sulfate ion is used to assure fairly complete coprecipitation of the radium. Because of dilution on entering the stream, the sulfate concentration may drop significantly. The common ion effect which was utilized in effecting nearly complete precipitation of the barium and radium in the plant is partly offset by dilution on entering the stream. Partial redissolution of some of the surface radium and barium in suspended particles may then be expected to occur. The larger  $Ba(Ra)SO_4$  particles containing the bulk of the radium are recovered within the plant. The fine particles with high surface area may be discharged into the stream. As can be seen later, the suspended solids in the discharge water are very high in radium (1290 pCi/g).

It is also possible that some leaching of stream bed sediments is occurring. In the early days of the mine, discharge water was not treated to remove radium. Much larger amounts of radium were probably entering the stream in the forms of uranium-ore particles and dissolved radium. Some of this uranium ore may have deposited in the stream bed. Some dissolved radium may have been absorbed by reacting with clays or oxide, carbonate, or sulfate miner-

als. Leaching of this older radium may be expected to occur rather slowly and is probably a minor source of dissolved radium. A final possibility of the apparent increase in radium concentration as the discharge water enters the stream is that changes in the discharge water prior to analysis cause low results to be obtained. The residence time of treated water in the plant is relatively short and it is likely that true equilibrium is not attained. Between the time of collection and laboratory filtration, it is possible that significant crystal growth may occur. Colloidal ( $<0.45 \mu\text{m}$ ) particles which will pass the filter membranes used may increase in size after collection and prior to filtration to a point where a significantly enhanced retention of the particles occurs. The effect of such an occurrence would be to give lower results for "dissolved" radium than would be obtained if immediate filtration were carried out. The assumption is made that the colloidal  $\text{Ba}(\text{Ra})\text{SO}_4$  which passes through the filter shows up as dissolved radium in the analysis. Discharge of water entering the stream is diluted and crystal growth of the  $\text{Ba}(\text{Ra})\text{SO}_4$  would not be expected to occur. On the contrary, some colloidal particles may go back into true solution.

Dissolved  $^{226}\text{Ra}$  concentrations at various distances below the mine were very close to each other (Figure 6) for

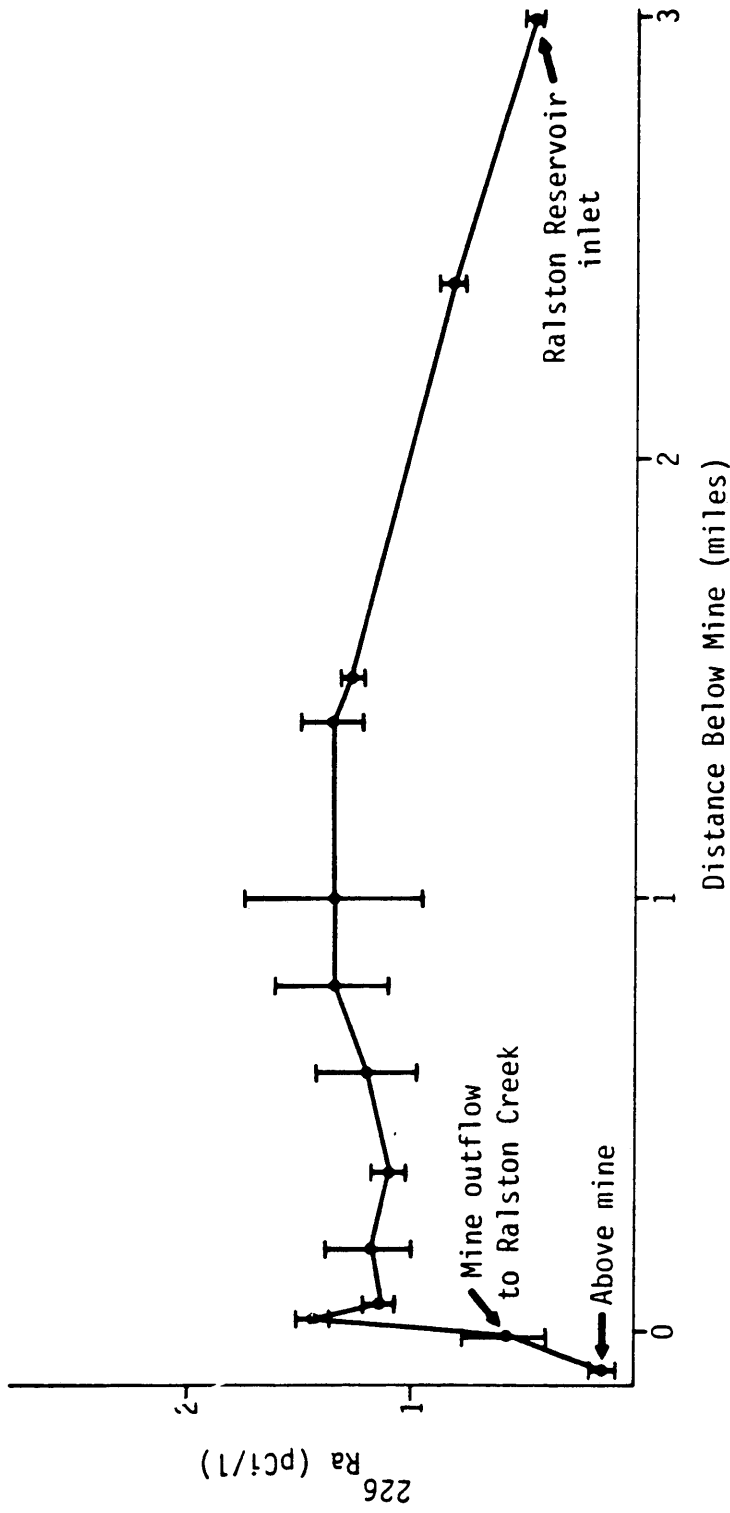


Figure 6.--Dissolved <sup>226</sup>Ra in Ralston Creek

about one and a half miles downstream, with an average of 1.23 pCi/l. The 0.82 pCi/l  $^{226}\text{Ra}$  concentration for sample site No. 13, was lower than the radium concentration in the sample above this site. At the time of collection of this sample, the diversion dam valve was closed, causing the bulk of the stream water to be diverted to Long Lake ditch and only a very small amount was flowing in the stream bed at the sample site. There was a small stream entering Ralston Creek at a point just above sample site No. 13 which may have diluted the concentration of the radium in the creek water at this point.

The  $^{226}\text{Ra}$  concentration at Ralston Reservoir inlet (sample site No. 15) was a 0.46 pCi/l and the outlet (sample site No. 16) was 0.24 pCi/l. This drop in the  $^{226}\text{Ra}$  concentration of the reservoir sample sites is probably due to the dilution by the large amount of reservoir water. The major part of this water comes from the western slope of the Continental Divide through the Moffat Tunnel and enters the reservoir's extreme northeast part, at a point not far from the reservoir outlet.

Seasonal variation is probably responsible for the slight change in  $^{226}\text{Ra}$  concentration for sample sites No. 2 through No. 7.

Other studies for dissolved  $^{226}\text{Ra}$  concentration in Ralston Creek and mine effluent indicated that,  $^{226}\text{Ra}$  concentration in samples collected from the Mine inflow to the sedimentation ponds (Table 4) in May and July, 1972, were 86 pCi/l and 72 pCi/l respectively (3). No sample was collected from this location in the present study. Lammering (3) in his report has indicated that, for water samples collected in July 20 and 21, 1972 from Ralston Creek. The maximum  $^{226}\text{Ra}$  concentration in these samples (81 pCi/l) was found in a sample collected at several hundred yards down stream of mine effluent. This  $^{226}\text{Ra}$  concentration then drops down to 1.7 pCi/l for a sample collected from the pool behind the diversion dam. This high  $^{226}\text{Ra}$  concentration in the creek water compared to the concentration found in the present report is probably related to the high amount of dissolved  $^{226}\text{Ra}$  discharged to the creek during 1972 in contrast to the amount discharged during the years 1980 and 1981. The mine waste treatment operation was started in Oct., 1972 (3). Samples collected before this date would therefore be likely to contain higher levels of radium. Parsont (7) reported an average of  $2.24 \pm 0.29$  pCi/l of  $^{226}\text{Ra}$  concentration for samples collected from Ralston Creek diversion dam, and  $3.1 \pm 1.6$  pCi/l in samples collected from the inlet to Ralston Reservoir (Table 3). These samples were collected during

the years 1965 and 1966. These results are higher than the corresponding results in the present study. However, all Parsont's water samples were acidified and a barium carrier added to them during the sample collections. The analyses for  $^{226}\text{Ra}$  in these samples were performed without filtration. Therefore the results do not accurately reflect the dissolved radium-226 concentration in the water samples. The major part of  $^{226}\text{Ra}$  in all these results might come from the suspended sediment which has been reported as a concentration per liter. On the other hand the  $^{226}\text{Ra}$  present in the suspended solids can not be measured accurately by the direct deemanation method, unless the suspended solids are totally decomposed prior to the analysis. Consequently the  $^{226}\text{Ra}$  concentration in this case will depend on the amount of suspended solids collected along with the water sample during the sample collection. The error in the reported data is clearly seen from the analysis of  $^{226}\text{Ra}$  (same report) for filtered and unfiltered water samples collected from the upper settling basin and the inlet to Ralston Reservoir (Table 3).

#### Suspended Radium-226

The material retained by the 0.45  $\mu\text{m}$  membrane filters during filtration of the water samples collected from

Ralston Creek and Reservoir were classified as suspended solids. The suspended  $^{226}\text{Ra}$  concentrations are shown in Table 9. The suspended  $^{226}\text{Ra}$  in the mine outflow to Ralston Creek was 1290 pCi/g. The suspended material load for this sample was 6 mg/l during the sample collection. The total  $^{226}\text{Ra}$  per liter (dissolved and suspended) in the mine outflow was then calculated to be 8.3 pCi/l. Assuming a daily average of 800,000 gallons of the mine outflow to Ralston Creek, this will give about 25  $\mu\text{Ci/d}$  (microcuries per day) being discharged to the creek. The suspended  $^{226}\text{Ra/l}$  in the mine outflow was 7.74 pCi/l, compared to the dissolved  $^{226}\text{Ra}$  of a 0.58 pCi/l, in the same sample. Thus, the radium contamination of Ralston Creek by Schwartzwalder mine outflow is mainly from radium associated with the suspended materials. The suspended  $^{226}\text{Ra}$  concentration was found to decrease as the distance below the mine increases (Figure 7). At one mile below the mine,  $^{226}\text{Ra}$  concentration drops to about one fifth (261 pCi/g) of the mine outflow, and to one fortieth (34 pCi/g) at a distance of 2.4 miles below the mine. This drop in concentration of the suspended  $^{226}\text{Ra}$  is probably due to the settling of suspended  $\text{Ba}(\text{Ra})\text{SO}_4$ . This may be enhanced by varying stream temperatures, turbulence and interaction with bed sediments. To a lesser extent

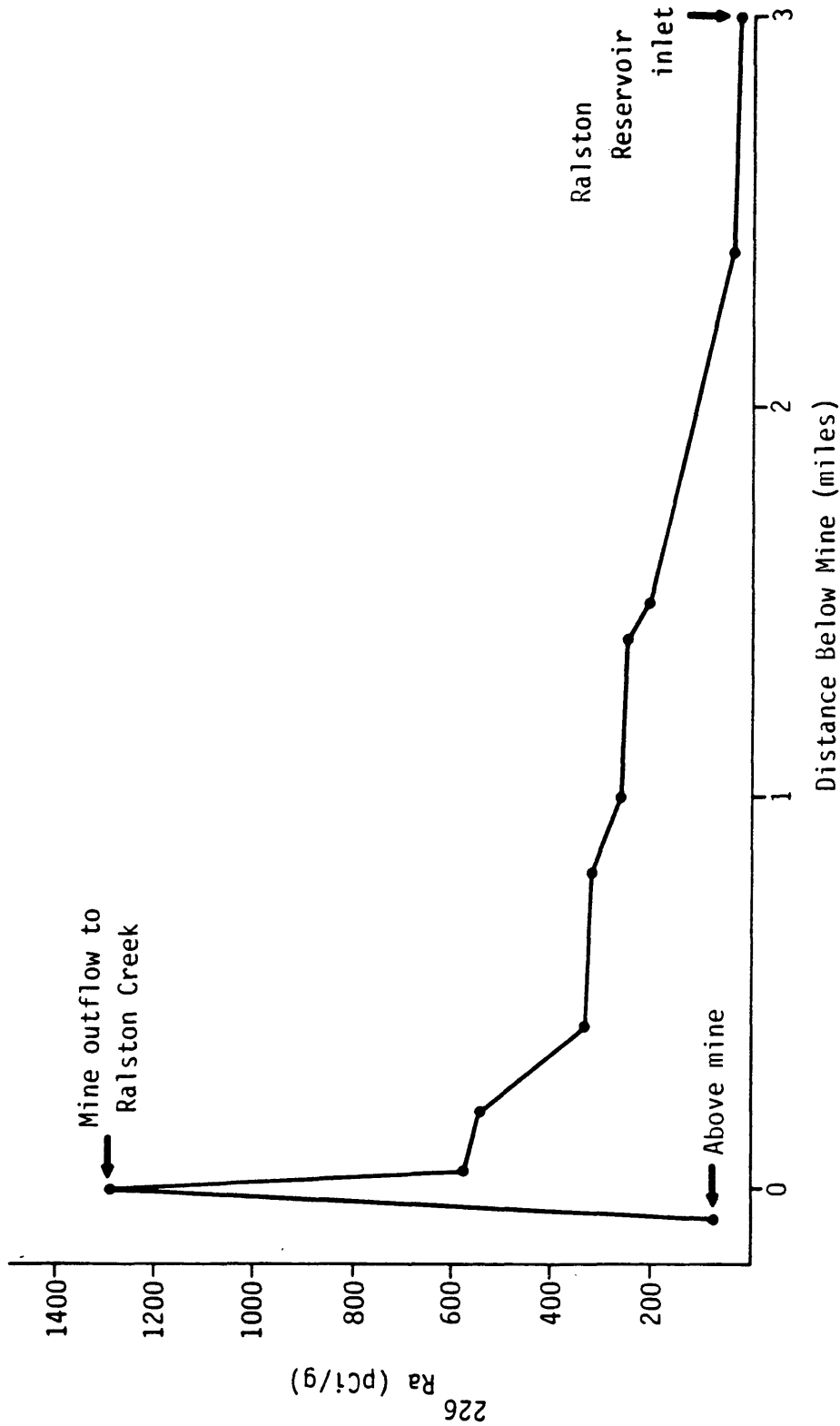


Figure 7.--Suspended <sup>226</sup>Ra in Ralston Creek

radium might be leached from the suspended materials by the creek water action.

Most of the radium associated with the suspended solids in the mine outflow is probably in the form of barium (radium) sulfate. The barium sulfate is used as a decontaminant for radium by the mine water treatment plant. The hydronium ion concentration (pH) in the creek water was about 8.3 (Table 9). This stream medium is not likely to enhance the leach of radium by the creek water, especially from the suspended materials.

The dilution of the high content  $^{226}\text{Ra}$  suspended materials by the lower  $^{226}\text{Ra}$  content during the suspended movement by the stream water, introduced another possible reason for the remarkable drop in the  $^{226}\text{Ra}$  suspended concentration below the mine. The concentration of  $^{226}\text{Ra}$  above the mine outflow (68 pCi/g), was not as low as was expected. 400 ft above mine outflow may not be far enough to represent the true background concentration of the suspended  $^{226}\text{Ra}$  in Ralston Creek. It is possible that uranium ore might have been transported from the mine area to the sampling point above the mine by weathering means, e.g. by wind and water erosion during rainfall or snowmelt.

The creek flows in a valley surrounded by the foothills of Colorado's front range, where the uranium background in the area is moderately high.

The minimum concentrations of suspended  $^{226}\text{Ra}$  were found in samples collected from the inlet and the outlet of Ralston Reservoir. Those are  $22 \pm 10$  pCi/g and  $12 \pm 1$  pCi/g respectively. Previous measurements for  $^{226}\text{Ra}$  concentration in the suspended material for samples collected at different locations of Ralston reservoir, were in the range of 12 pCi/g to 2.1 pCi/g (3).

#### Distribution of $^{226}\text{Ra}$ in Different Particle Sizes

This study was performed on the bed sediment of sample site No. 4. The  $^{226}\text{Ra}$  concentrations in different particle sizes of this sample were determined by total decomposition of each fraction followed by analyses for  $^{226}\text{Ra}$  by the direct emanation method. The results of these analyses are shown in Table 10.

In general, the concentration of  $^{226}\text{Ra}$  in the bed sediments varies inversely with particle size (Figure 8), this might indicate the adsorption of radium by the particle surfaces. However, the extent of radium sorption is related to the total available sites on the surface of the adsorbing particles. The concentration of the adsorbing sites varies

Table 10.-Distribution and leaching efficiency of  $^{226}\text{Ra}$  in different particle sizes of Ralston Creek and Reservoir sediments.

Particle size (mesh)	% by weight	Total $^{226}\text{Ra}$ <sup>2</sup> pCi/g	Leached $^{226}\text{Ra}$ <sup>1</sup>	
			pCi/g <sup>2</sup>	%
1-Above Mine (400 ft)				
-115+270	6	9.23 <sup>3</sup>	1.61±0.98	17
-270	2	7.25 <sup>3</sup>	3.13±1.89	42
2-Below Mine (400 ft)				
- 10+20	28	—	—	—
- 20+28	15	47.3±5.1	30.7±2.5	65
- 28+42	21	43.2±2.6	34.7±4.6	80
- 42+60	13	51.6±1.6	43.5±3.0	84
- 60+80	10	61.5±2.0	49.6±3.3	81
- 80+100	3	75.5±8.4	62.5±3.0	83
-100+115	1	80.4±1.9	69.3±4.4	86
-115+150	3	82.3±6.3	71.7±12.0	87
-150+170	1	112.3±2.3	80.2±8.2	71
-170+270	2	121.9±4.9	90.7±1.2	74
-270	3	175.2±7.2	114.2±8.8	65
	<u>100</u>			
3-Mine outflow (suspended)		1290±220	208.9±16.1	16
4-Reservoir <sup>4</sup>	—	3.29 <sup>3</sup>	2.03±1.2	62

- 1) Leaching conditions are 2N, HCl, 1 hr shaking at room temperature.
- 2) Errors terms are expressed at the 90% confidence level.
- 3)  $^{226}\text{Ra}$  determined by gamma spectrometry; all others are by direct deemanation method.
- 4) Unfractionated (total) sediment.

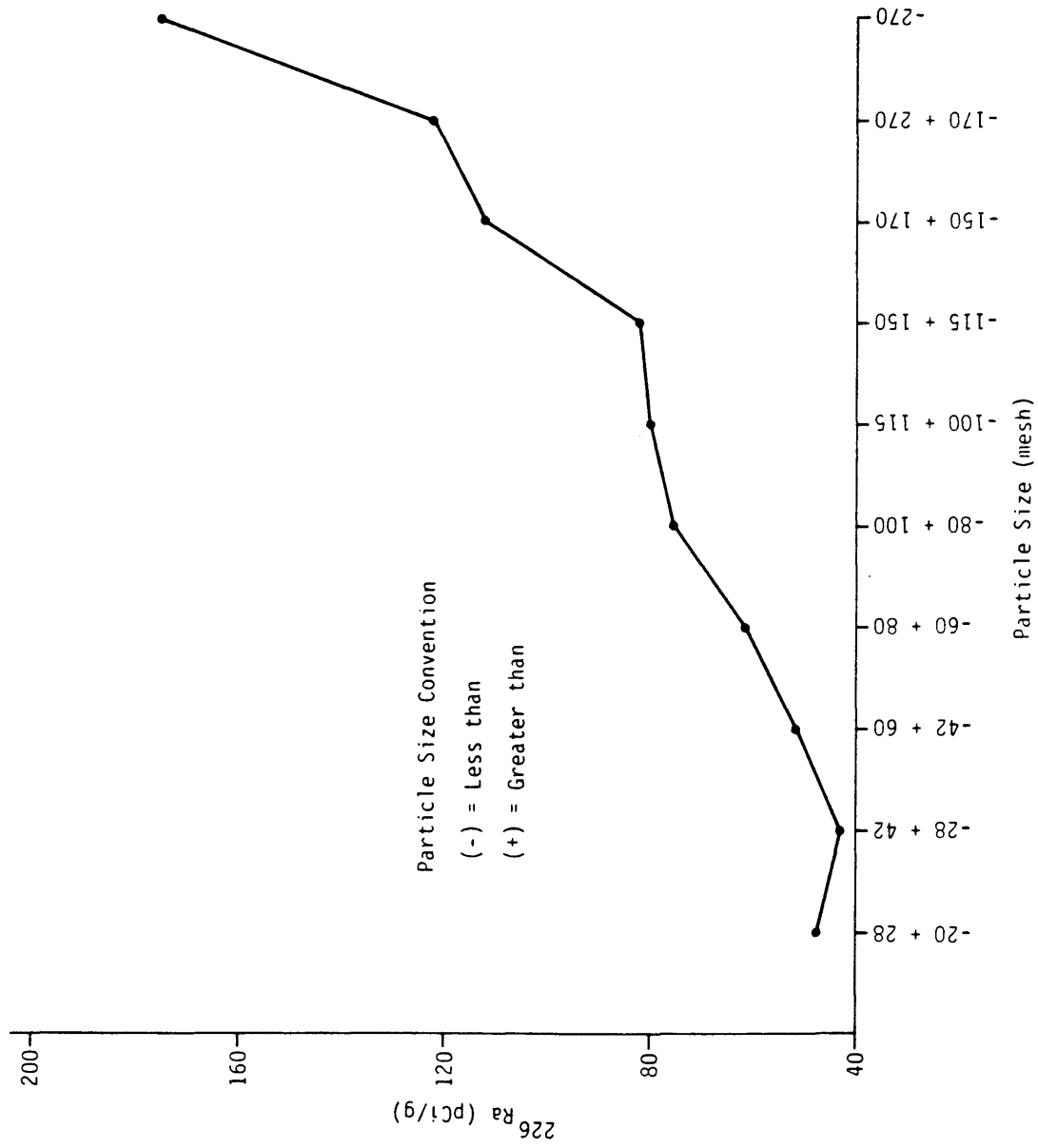


Figure 8 .--Distribution of  $^{226}\text{Ra}$  as a function of particle size in Ralston Creek bed sediments.

inversely with particle size. The concentration of adsorbing sites and the distribution constants for radium on these sites is highly dependent on the mineralogy of the sediments and the water chemistry. Since no mineralogic studies were performed on the sediments, the concentration, exchange capacity and chemical composition of ion exchange and adsorption sites are unknown.

The sediment fractions of the sample collected above the mine showed much lower radium content than the corresponding fractions immediately below the mine. This is consistent with the radium above the mine being from the native uranium mineralization rather than coming from treated waste.

#### Comparison Study for Radium-226 Analyses by the Direct De-emanation and Gamma Spectrometry Methods

This study was conducted on Ralston Creek bed sediments from sample site No. 4, for the particle size fractions shown in Table 11. Two grams of each fraction were decomposed (see the bed sediment decomposition method) and analyzed for  $^{226}\text{Ra}$  by the direct deemanation method. The same fractions were packaged for  $^{226}\text{Ra}$  determination by the gamma spectrometric method. Results produced by the two methods are shown in Table 11.

Table 11.-Comparison of  $^{226}\text{Ra}$  analyses of Ralston Creek sediment by deemanation and gamma spectrometric methods<sup>1</sup>

Fraction (mesh)	Deemanation method $^{226}\text{Ra}$ (pCi/g)	Gamma spectrometry method $^{226}\text{Ra}$ (pCi/g)
-20+28	47.3±5.1 <sup>2</sup>	38±2 <sup>3</sup>
-28+42	43.2±2.6	50±2
-42+60	51.6±1.6	57±2
-60+80	61.5±2.0	66±2

- 1) Sample collected from Site No. 4 (400 ft below mine).
- 2) Errors are expressed at the 90% confidence level.
- 3) Error terms based on the 2 sigma counting error.

The analysis of  $^{226}\text{Ra}$  by gamma spectrometry was used to support the accuracy of the data generated by the direct deemanation method and the latter to insure confidence in the results produced by the gamma spectrometric method.

The data as shown in Table 11 revealed that generally, results produced by gamma spectrometry are slightly higher than those obtained by the direct deemanation method. This systematic difference may be resulted from the internal calibration differences in the two methods or may be due to the sample size differences used by the two methods. The sample size used for the gamma spectrometric analysis was in the range of 30g to 200g. This large sample size is probably more representative of the bed sediment than the sample size (2 grams) which was used in the direct deemanation method.

#### Distribution of Radium as a Function of Particle Size and Distance Below Mine

In this study, the analysis for  $^{226}\text{Ra}$  concentration in the bed sediment was carried out by using gamma spectrometric analysis. Results are shown in Table 12.

Generally  $^{226}\text{Ra}$  concentration in the bed sediment increases as the particle size decreases and as the distance below the mine outflow decreases. This relation is shown

Table 12.-Distribution of  $^{226}\text{Ra}$  in different particle sizes and at different locations of Ralston Creek, Ralston Reservoir and Long Lake ditch sediments.

Sample location	Site no.	Particle size (mesh)					
		-10+20	-20+28	-28+60	-60+115	-115+270	-270
400 ft above mine <sup>1</sup> 0.2 mi <sup>2</sup>	1	0.44	0.69	0.86	2.4	9.2	7.3
	5	11 (20) <sup>1</sup>	16 (15)	24 (15)	29 (24)	43 (40)	88 (96)
	6	41 (14)	38 (11)	40 (11)	38 (21)	51 (31)	127 (95)
0.6 mi 0.8 mi 1 mi 1.4 mi 1.5 mi	7	20	29	37	76	105	154
	8	19	17	13	15	21	50
	9	20	9	16	27	41	69
	10	12	11	12	21	28	42
	11	4.1	4.4	4.1	4.5	6.8	12
Long Lake ditch directly below diversion dam	12	2.1	3.4	3.1	5.5	9.6	23
	13	3.1	2.4	3.8	---	---	---
2.4 mi <sup>2</sup>	14	1.4	1.4	1.7	1.4	2.1	31
Long Lake ditch near upper end of Ralston Reservoir	15	2.7	3.4	3.1	3.4	4.1	25
Ralston Reservoir inlet <sup>1</sup>							

- 1) Samples collected on 5/5/81, along with the results between parenthesis. The rest of the samples collected on 11/5/80.
- 2) Locations shown are distances below mine.
- 3) All results are produced by gamma spectrometry.

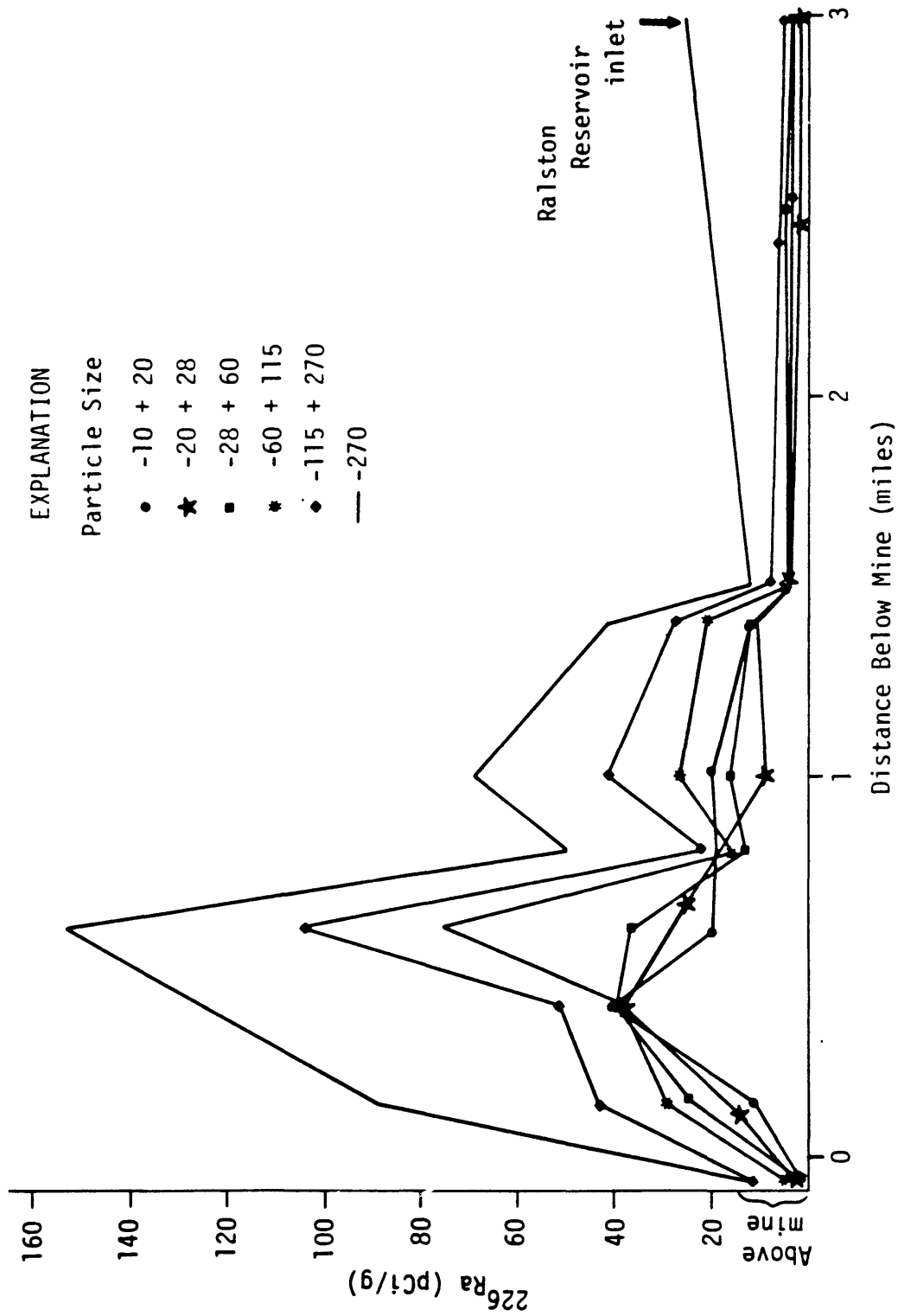


Figure 9.--Distribution of 226Ra in Ralston Creek bed sediments as a function of particle size and distance below mine.

graphically in Figure 9. There was a regularity of the maximum and the minimum of the radium concentration in the bed sediments for all samples as shown in Fig. 9. This may indicate mine-discharge uranium ore particles are present in the sediment from the early days of the mine operation. The uranium ore particles apparently have been accumulated in certain stream zones due to the stream condition or high activity spillout from the mine during the history of the mining operation. Suspended particles of  $Ba(Ra)SO_4$  from the mine discharge pipe probably also settled out in these regions and contribute to the high radium contents of the fine particle sizes. The drop in the radium concentration at a distance beyond 1.5 mile below the mine outflow probably indicates that most of the suspended materials and uranium ore bearing sediment have settled out before these sample points.

#### Leachability of Radium-226 by Using Different Leaching Reagents

The data shown in Table 13 reveal that generally, the leachable amount of  $^{226}Ra$  from Ralston Creek bed sediment is dependent upon the concentration of the leaching solution. 83 to 84 percent of  $^{226}Ra$  was liberated from the sediments by using 1 N and 2 N HCl as lixiviants respectively, whereas

Table 13.-Leachability of  $^{226}\text{Ra}$  from Ralston Creek bed sediment.  
(-42+60 mesh fraction)<sup>1</sup>

Leaching Reagent <sup>2</sup>	No. of analyses	Leached $^{226}\text{Ra}$	
		pCi/g <sup>3</sup>	% <sup>4</sup>
HCl, 2N	4	43.6 ±5.9	84
HCl, 2N (2hr)	4	43.0 ±0.7	83
HCl, 1N	2	43.2 ±4.9	84
HCl, 0.0001N	2	0.22±0.04	0.4
KCl, 1N	2	15.4 ±0.5	30
KCl, 0.1N	3	4.8 ±0.3	9
KCl, 0.01N	4	1.5 ±0.4	3
BaCl <sub>2</sub> , 1N	4	5.2 ±0.6	10
BaCl <sub>2</sub> , 0.1N	2	3.2 ±1.0	6
BaCl <sub>2</sub> , 0.01N	2	3.6 ±0.5	7
Na <sub>2</sub> EDTA, 0.1M (pH=10)	2	34.0 ±3.9	66
Na <sub>2</sub> EDTA, 0.1M (2hr) (pH=10)	2	33.4 ±8.4	65
Na <sub>2</sub> EDTA, 0.25M (pH=10)	2	35.4 ±8.9	67
Na <sub>2</sub> EDTA, 0.1M (pH=4.5)	2	17.0 ±2.5	33

- 1) Sample collected from Site No. 4 (400 ft below mine).
- 2) Leaching carried out at room temperature for 1 hr (unless otherwise indicated) with shaking, using 200 ml of lixiviant and 3g of sediment.
- 3) Error terms are based on reproducibility of replicate measurements and expressed at the 90% confidence level.
- 4) % extracted based on 51.6 pCi/g found on total decomposition of this sediment fraction.

at lower HCl concentration (pH 4), the amount of  $^{226}\text{Ra}$  liberated was very low (0.4%). Increasing the shaking time of the leach beyond one hour, did not effect the amount of  $^{226}\text{Ra}$  liberated. Under the same leaching conditions, when potassium chloride (KCl) and barium chloride ( $\text{BaCl}_2$ ) are used as lixiviants, it was found that, in both cases, the amounts of  $^{226}\text{Ra}$  leached were significantly lower than the amounts leached by hydrochloric acid or  $\text{Na}_2\text{EDTA}$ . The  $^{226}\text{Ra}$  liberated by 0.1 N and 1 N KCl solutions is greater than by barium chloride solutions of the same concentrations. However at lower concentration (less than 0.1 N KCl or  $\text{BaCl}_2$ ), the amount of  $^{226}\text{Ra}$  leached by  $\text{BaCl}_2$  solution exceeded the amount leached by KCl solution. The leaching action of  $\text{Na}_2\text{EDTA}$  at pH 10 and concentrations of 0.1 M and 0.25 M with shaking time of 1 hr and 2 hr were approximately 66% leached in all cases, whereas at pH 4.5, the amount of  $^{226}\text{Ra}$  liberated by 0.1 M  $\text{Na}_2\text{EDTA}$  was reduced to 33%. For all lixiviants used in the tests under the same experimental conditions, it was found that the leaching power decreases in the order:  $\text{HCl} > \text{Na}_2\text{EDTA} > \text{KCl} > \text{BaCl}_2$ .

The percent weights of the sediment loss during the leaching process (Table 8, page 54) increases as the amounts of radium leached increases. This finding indicates that most of the radium released to the leaching solution was by

breaking up the sediment particles and not by a displacement reaction on the particle surfaces, i.e. the large part of radium is not adsorped on the particle surfaces, it is rather inside the sediment matrices.

#### Leachability of Radium as a Function of the Bed Sediment Particle Size

From the above leaching studies it is clear that the best lixiviant and leaching conditions for the creek sediments were 2 N HCl and 1 hr shaking time (80 impact/min) at room temperature. This leaching reagent and leaching conditions were adopted to the study of the leachability of radium as a function of the particle sizes. Results are shown in Table 10 (page 70).

The amount of  $^{226}\text{Ra}$  extracted from the fine particles (-270 mesh) of the sample above the mine outflow (400 ft) appears to exceed the amount extracted from the coarser particles (-115 + 270 mesh). This is probably due to the larger surface area exposed to the leaching reagent in the fine particles as compared to the coarser sample. The relatively large uncertainty in these concentrations make this a tenuous conclusion, however.

The fraction of  $^{226}\text{Ra}$  extracted from the -20 + 28 mesh of sample site No. 4 (400 ft below mine outflow) was 65%,

and for particles smaller than 28 mesh and larger than 150 mesh, the amounts extracted were about 84% and showed little variation between them. This probably indicates that the major part of radium in those particle sizes is present on the particle surfaces. This is supported by the finding that the total radium content of these particle size fractions increases as the particle gets smaller. The percentage of  $^{226}\text{Ra}$  leached from all the fractions smaller than 150 mesh drops down gradually to 65% for the finest particle size fraction (-270 mesh). In these fractions the radium associated with the sediment particles, is not necessarily by adsorption on the surface, but may be associated with certain minerals or in the form of radium sulfate discharged from mine, which can not be leached by the hydrochloric acid. The abundance of these radium bearing materials apparently increases in the bed sediment fine particles. Radium also might be present in the sediment matrices to a lesser extent.

The idea that radium is associated with the bed sediment particles by an adsorption mechanism is not firmly established by the leaching study. If radium is present in clay minerals it would probably be readily leachable by barium and potassium ions. The fact that  $\text{BaCl}_2$  and  $\text{KCl}$  solutions extracted less of radium than the  $\text{HCl}$  and  $\text{Na}_2\text{EDTA}$

imply that radium may be associated with the uranium ores which are easily attacked by the acid or strong chelating agent. The percent loss of the sediment during the hydrochloric acid or  $\text{Na}_2\text{EDTA}$  leaching process was greater than the percent loss during the  $\text{KCl}$  and  $\text{BaCl}_2$ . Therefore, we believe that the major part of radium present in the bed sediment below the mine outflow is associated with the uranium ore particles and radium is released to the leaching solution by chemical attack of the sediment or at least those components of the sediment which contain most of the radium. It was noticed that a colorless gas was evolved during the hydrochloric acid leaching process. This gas was probably the carbon dioxide generated by the decomposition of some carbonate minerals present in the sediment. This fact supports our prediction that radium probably is associated with carbonate minerals of uranium ore. Radium may also be partially trapped inside the colloidal hydroxides of iron and magnesium. Hydrochloric acid would effectively break up those hydroxides and the  $\text{Na}_2\text{EDTA}$  can complex with the metal ions, thereby releasing the radium to the solution.

Barium sulfate is produced in the mine waste treatment plant for radium decontamination. Consequently radium might

also be present in the bed sediment in the form of barium (radium) sulfate.

Since barium (radium) sulfate forms as a fine crystalline material which will be concentrated in the finest particle fraction of the bed sediment, e.g. the -270 mesh of sample site No. 4. This is evidenced by the highest total  $^{226}\text{Ra}$  content of the finest fractions (Table 10, see also Figs. 8 and 9) and the lower percentage of  $^{226}\text{Ra}$  extracted (Table 10) from these fractions. The very low yield of  $^{226}\text{Ra}$  extracted from the suspended material of mine outflow water (Table 10), which is likely to be high in barium (radium) sulfate content, also indicates the likelihood of radium in the bed sediment as a barium (radium) sulfate form. This is because the barium (radium) sulfate is less likely to be leached by  $\text{KCl}$ ,  $\text{BaCl}_2$  or  $\text{HCl}$  except the alkaline  $\text{Na}_2\text{EDTA}$  due to its strong complexing capability.

## SUMMARY AND CONCLUSION

Water and bed sediment samples were collected from Ralston Creek and Ralston Reservoir during fall 1980 and spring 1981. These samples were analyzed for  $^{226}\text{Ra}$  by the direct deemanation method. The bed sediments were also analyzed for  $^{226}\text{Ra}$  by gamma spectrometry. The direct deemanation method was efficiently applicable to radium determination in solution without the sample preparation difficulties associated in some cases with the precipitation-deemanation method.

The dissolved radium-226 in the mine outflow and in Ralston Creek were below the acceptable level of dissolved  $^{226}\text{Ra}$  in drinking water (3 pCi/l). The suspended  $^{226}\text{Ra}$  in the mine outflow was very high,  $1290 \pm 220$  pCi/g. The suspended solids load in the mine outflow was approximately 6 mg/l. The suspended  $^{226}\text{Ra}$  in the mine outflow is believed to be in the form of  $\text{Ba}(\text{Ra})\text{SO}_4$ . The contamination of Ralston Creek by the mine waste is mainly due to  $^{226}\text{Ra}$  associated with the suspended solids discharged to the creek. This study has shown an elevated radioactivity in Ralston Creek bed sediment as  $^{226}\text{Ra}$  which constitutes a long term contamination problem for this environment.  $^{226}\text{Ra}$  was fairly leachable from Ralston Creek bed sediments by using

either 1 N or 2 N HCl with one hour shaking at room temperature. The highest portion of radium-226 was found to be associated with the fine particles of the bed sediments.

Most of the  $^{226}\text{Ra}$  radioactivity in Ralston Creek, dissolved, suspended and in the bed sediments, was found to decrease greatly before it reaches to Ralston Reservoir.

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