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A RAPID, SIMPLE METHOD FOR THE DETERMINATION
OF THE RADON CONTENT OF WATER

by

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Health Instrument Divisions

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A RAPID, SIMPLE METHOD FOR THE DETERMINATION
OF THE RADON CONTENT OF WATER

INTRODUCTION:

The historical approach to the separation of radon from water is liberation of the radon from the sample by boiling under vacuum in the presence of a strong acid; flushing the liberated radon, with an inert gas, into an ionization chamber or an alpha proportional counter, and measuring the collected activity.^{1,2,3} Such an analysis requires a manipulation time of approximately one hour, a waiting period of two to three hours before measurement to allow transitory equilibrium to be reached, and finally a measurement time, resulting in 4 to 6 hours for one analysis. In addition, specialized equipment including a vacuum train is required. If it is desired to count the alpha particles from radon and its daughters in a proportional counter, absorption trains to remove all oxygen, a poor counting gas, are required.

The method presented herein requires only 20-25 minutes for a complete analysis and except for the beta counter utilizes standard laboratory equipment.

DISCUSSION:

For review the natural radioactive uranium decay series is presented below. The symbols in parenthesis indicate the isotopic element in the formalized nomenclature. The type of decay, excluding γ and the half lives are also shown.

In their natural state, and if no preferential leaching occurs by the ground water, these products should exist in secular equilibrium down to the gaseous member (radon) and this portion of the series will decay with the half-life of UI; 4.56×10^9 years. As the ground water flows through formations containing uranium, a portion of the radon (released from chemical combination in the ground) will dissolve in the water. The amount of radon is dependent upon the rate of flow of the ground water, the nature of the uranium bearing deposit as well as the extent of the bed and the absolute activity. Other variables such as temperature will also affect the amount of radon dissolved.

As this separated radon decays, secular equilibrium is reached with its daughters. From the decay scheme it may be seen that radon decays to RaA with a 3.05 min half-life, by alpha emission to RaB with a 26.8 min half-life, and by beta decay to RaC with a 19.7 min half life. Here the chain splits with 99.96% of the decay going to RaC¹ with a beta emission and 0.04% of the decay going to RaC¹¹ with an alpha emission. Both of these branch daughters decay relatively rapidly to RaD with a 22 yr half life. Because of the long half life of radium D the chain is effectively broken; small amounts of radon forming undetectable amounts of RaD.

The rate of decay of this shortened series will be governed by the half-life of the radon because of its relatively long half-life (compared to the detectable daughters) and again secular equilibrium for practical purposes will be reached. This equilibrium may be expressed⁽⁴⁾ as:

$$\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3$$

where λ = decay constant (fraction decaying in a given time period)

N = No. of atoms

Thus for each disintegration of radon there is one disintegration from each daughter and by separating the daughters and measuring the associated activity the amount of radon may be determined.

RaB and RaD are isotopes of lead, RaC is an isotope of Bi; therefore these daughters should be easily separated chemically in a form suitable for beta counting.

Because of the short half lives of these daughters, the time required for the chemical separation must be short and the decay during this time should be accurately expressed.

An expression for the total decay of the two beta emitting daughters may be obtained by summing the three components: (1) the direct decay of the RaB; (2) the

direct decay of the RaC precipitated; and (3) the decay of the RaC formed from the RaB decaying after the precipitation. These expressions may be calculated from the well-known radioactive decay relationships in the following manner. (4)

Let $N = d/m \text{ of Rn} = d/m \text{ of RaB} = d/m \text{ of RaC at time 0}$

$$(1). \quad d/m \text{ of RaB at time } t = N e^{-\lambda \beta t}$$

$$(2). \quad d/m \text{ of RaC at time } t = N e^{-\lambda c t}$$

$$(3). \quad d/m \text{ of RaC at time } t$$

$$\text{from RaB decay} = N \frac{\lambda c}{\lambda \beta} \cdot \frac{\lambda \beta}{\lambda c - \lambda \beta} (e^{-\lambda \beta t} - e^{-\lambda c t})^*$$

$$(4). \quad \text{Total } d/m \text{ at } t = N e^{-\lambda \beta t} + N e^{-\lambda c t} + \frac{N \lambda c}{\lambda c - \lambda \beta} (e^{-\lambda \beta t} - e^{-\lambda c t})$$

A plot of this decay is shown in Figure I. For comparison a decay curve of a separated sample has been imposed on the curve. As may be seen they are comparable. It should also be noted that considerable time is allowed for analysis before the decay correction factor becomes exorbitant.

The problem then is to precipitate these daughters as rapidly as possible in a quantitative manner from as large a sample as possible. Values of 10^{-10} to 10^{-7} (5) curies of radon/l in water have been reported indicating the need of large samples for sensitivity.

*This relationship is usually given in terms of number of atoms. Dividing N by $\lambda \beta$ converts N into atoms of RaB. Multiplying by λc then converts the answer into disintegrations per minute of RaC.

EXPERIMENTAL:

Equipment used during the developmental work consisted of a 2000 ml heavy wall filtering flask connected to the house vacuum (approximately 25 cm), a size 0 buchner funnel, filter paper and a 2 liter beaker. Test solutions were prepared from aliquots of standardized radium solution diluted to 1 liter and allowed to stand for 30 days so that equilibrium between the Rn and the parent Ra was obtained. After standing, the standards were transferred to the two liter beakers, precipitating reagents added, and the mixture filtered with vacuum. The sample was then rapidly dried with acetone and air and counted.

Because the mass of these isotopes present in a sample is small (on the order of 10^{-16} to 10^{-17} gms), 20 mg. of lead nitrate was added to each sample to act as a carrier.

Variables tested in the experiment included precipitating agents, type of filter paper, and type of filter aid.

Precipitation as the sulfide, the chromate, the sulfate and the molybdate were all tried and tested for ease of filtration by visual inspection of the filtrate and by observed counting yield. Of the four reagents tried ammonium polysulfide gave the highest yields and the clearest supernate. Whatman filter papers No. 1, 2, 5, 40, 41 and 42 were tested for speed by timing and completeness of filtration by visual observation of the supernate. Results of these tests indicated Whatman No. 40 filter paper to be the fastest and as quantitative as any. Using ammonium sulfide and Whatman #40 paper the effect of macerated filter paper, Johns Manvilles filter aid, "Hyflo super cell," and Fuller's earth were tested for speed and completeness. Of the three Hyflo super cell was most effective, cutting filtering time from about 30-35 minutes to 10 to 15 minutes.

These tests indicate the use of ammonium sulfide, Whatman No. 40 filter paper and hyflo super cell filtering aid.

The procedure then, consisted of transferring a liter sample to a 2 liter beaker, adding 20 mg of lead nitrate as carrier, 10 cc of ammonium sulfide and 10 cc

of filter aid (prepared by adding 1 gram of Hyflo super cell to 100 cc of water) filtering through a Whatman #40 filter paper, (through which 5 cc of filter aid had been poured to speed filtration) and finally drying the collected filtrate with about 5 cc of acetone followed with 30 seconds of air flushing. The filter paper was then removed, placed on a counting mount and counted. Time required for this operation, excluding counting time is approximately 15 minutes.

Counting was done with a mica-end window GM tube filled with alcohol-argon operated by a Higgenbotham scaler. Samples were positioned 0.33 cm from the face of the tube and counted for 5 three minute periods.

The counts were corrected for decay to zero time and the average value reported.

To find the disintegration rate of the sample, corrections for counter geometry, window and air absorption, self-absorption, backscatter and source size must be applied. Absolute geometry was determined from a calibrated Bureau of Standards RaD source. Window and air absorption was determined from the absorption coefficient obtained from an aluminum absorption curve which was corrected for decay by alternating counts with and without the absorber. Backscatter corrections were obtained by counting a high specific activity precipitate on a 0.3 mg/cm^2 nylon film, backing the sample with filter paper and filter aid and noting the increase in counting rate. Source size corrections were obtained by counting a point source at different positions across the diameter of the tube, weighting the values for the annular areas concerned, and graphically integrating the curve. Self absorption was measured by adding weighed amounts of carrier to a source and noting any decrease in activity. The correction factors used are:

Geometry - - - - -	23%
Source Size- - - - -	0.590
*Window and Air Absorption-	0.932
Self Absorption- - - - -	1.00
Backscatter- - - - -	1.04

*Absorption coefficient of $0.0175 \text{ cm}^2/\text{mg}$

These individual factors give a total correction of 7.62. The value must further be corrected for decay by the use of equation (4) which automatically accounts for the particles from both RaB and RaC.

RESULTS:

Results of six standard solutions indicate an average yield of $99\% \pm 7\%$. Later, eight samples from a well in Benton City were analyzed to confirm reproducibility. The standard deviation for these eight samples was 6.9%. It should be noted that these samples showed a 4% standard deviation in counting results indicating a laboratory error of 6%.

The sensitivity of the method is a function of the statistical fluctuations occurring in nuclear phenomena. The mica window counters in use have backgrounds on the order of 17 c/m. The minimum counting rate detectable above such a background may be estimated by calculating the intersection points of the distribution curve of counting rates around the background and the sensitivity limit at the desired confidence level. Thus, with a three minute measurement and a three minute background, the minimum significant activity on a 90% confidence level would be 9 c/m. For nine minute measurements, the minimum activity would be about 5 c/m. These calculations are made assuming a normal distribution of counting results with the standard deviation given by the square root of the total number of counts measured.

This gives a minimum value of approximately 25 d/m of radon per liter (approximately 1×10^{-5} μ c/liter). The previously mentioned method of measuring radon has a sensitivity of approximately 2×10^{-6} μ c/liter, a factor of five better than the method presented,⁽³⁾ and with special methods and extremely long counting rates, values of 10^{-7} μ c/liter may be obtained.

It would be possible to increase the sensitivity of this method by sandwiching the sample between two Geiger Muller tubes, effecting nearly 100% geometry. However, the majority of samples are well above the quoted detectable range and the need for greater sensitivity has not been felt.

It should be noted that the daughters of thoron, if present, will also carry through the separation giving a falsely high counting rate. Corrections may be made, however, by observing the total decay of the separated products to determine the amount of thoron daughters ($1/2$ life = 10.6 hr) and subtracting from the counting rate at zero time.

Results of samples from various locations in the northwest are presented in Table 1.

Table 1

RESULTS OF ANALYSES

<u>Sample Location</u>	<u>Type</u>	<u>d/n/l</u>	<u>λ_c/l</u>
Kiona, Washington	Tap Water	180	8.3×10^{-5}
Benton City, Washington	Tap Water	220	1.0×10^{-4}
Yakima, Washington	Tap Water	< 25	$< 1.1 \times 10^{-5}$
Moxee City, Washington	Tap Water	270	1.2×10^{-4}
Cranger, Washington	Tap Water	410	1.9×10^{-4}
Ellensburg, Washington	Tap Water	240	1.1×10^{-4}
Sunnyside, Washington	Tap Water	340	1.5×10^{-4}
Mandan, North Dakota	Tap Water	< 35	$< 1.6 \times 10^{-5}$
Miles City, Montana	Tap Water	< 30	$< 1.4 \times 10^{-5}$
Billings, Montana	Tap Water	46	2.1×10^{-5}
Columbus, Montana	Tap Water	14.0	6.4×10^{-5}
Livingston, Montana	Tap Water	< 30	$< 1.4 \times 10^{-5}$
Bozeman	Tap Water	50	2.3×10^{-5}
Butte, Montana	Tap Water	75	3.4×10^{-5}
Diamond, Montana	Tap Water	1310	6.0×10^{-4}
Missoula, Montana	Tap Water	45	2.0×10^{-5}
Wallace, Idaho	Tap Water	57	2.6×10^{-5}
Kellog, Idaho	Tap Water	38	1.7×10^{-5}
Couer d'Alene, Idaho	Tap Water	< 24	$< 1.1 \times 10^{-5}$
North Bend, Washington	Spring	140	6.1×10^{-5}
Benton City, Washington	Spring	1700	7.8×10^{-4}
N.W. Rattlesnake Mountain	Spring	75	3.3×10^{-5}
Rattlesnake Mountain	Spring	90	4.1×10^{-5}
Forsyth, Montana	Spring	1750	8.0×10^{-4}
Pipestone Pass (Continental Divide)	Spring	12,360	5.6×10^{-3}
Osborne, Idaho	Well	41	1.9×10^{-5}
Yakima River near Richland, Washington	River	30	1.4×10^{-5}
Columbia River near Richland, Washington	River	< 25	$< 1.1 \times 10^{-5}$
Mississippi River Minnesota-Wisconsin border	River	< 37	$< 1.7 \times 10^{-5}$
West Gallatin near Bozeman, Montana	River	4	1.9×10^{-5}
Yellowstone River near Bozeman, Montana	River	< 26	$< 1.2 \times 10^{-5}$

Table 1 (continued)RESULTS OF ANALYSES

<u>Sample Location</u>	<u>Type</u>	<u>d/m/l</u>	<u>$\mu\text{Ci/l}$</u>
Mill Creek, Anaconda, Montana	River	<28	$< 1.3 \times 10^{-5}$
Blue Creek near mountain Couer d'Alene, Idaho	River	338	1.5×10^{-4}

The samples taken from tap water may not be significant of the amount of radon in the underground water supply of these cities. Two variables, the amount of time in the pipes and the amount of radon release by change in water pressure as the sample is drawn, effect the true value. The low values found in river water is to be expected as the radon escapes during the turbulent flow.

It is hoped to extend this survey for general radioactive background information in the Pacific Northwest.

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FIG 1
RADON DAUGHTERS
BETA DECAY

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