DETERMINATION OF ^{226}Ra IN NATURAL SAMPLES

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Abstract—The natural content of ^{226}Ra in environmental samples was determined by the emanation technique. The reliability and sensitivity of the method made measurements possible at a very low level. Analyses of human teeth could, for instance, be performed satisfactorily and the concentrations obtained, ranging from 0.008 to 0.138 pCi/g ash, are in agreement with the literature data. The highest ^{226}Ra contents found are of the order of 1, 2 and 6 pCi per gram of calcined material.

The chemical preparation of the different samples such as milk, bones, teeth and minerals are described. Detailed description of the apparatus with schematic diagram and of the measurement technique is also given. The equation used for the calculation of the activity expressed in pCi ^{226}Ra/g ash or pCi ^{226}Ra/l., is shown.

INTRODUCTION

The natural radiation background may vary greatly from locality to locality. In order to know the differences in population exposure it is, therefore, necessary to monitor as many areas as possible. The aim of the present study is to provide data on levels of radioactivity due to natural radium in human environment. Numerous samples such as water, milk, animal bones and teeth, bovine flesh and soil, were collected for the determination of ^{226}Ra content. When available, human teeth from the monitored areas were also analyzed in order to have an indication of local skeletal burdens. (1)

MATERIAL AND METHODS

1. *Preparation of Samples*

The methods used to prepare the samples for the ^{226}Ra analysis by the emanation technique, varied with the nature of the material collected.

1.1. *Water.* Water samples from fountains, springs and rivers received pre-analysis treatment only by the addition of 2 ml of concentrated HNO_3 to keep the radium in solution and also to avoid the formation of algae. In case of presence of suspended matter, a filtration, followed by a separate analysis of the filter content, was performed. 500 ml were generally used for the measurements. For low activities it was advisable to use larger volumes reduced by evaporation to 500 ml.

1.2. *Milk.* Milk samples were slowly evaporated to dryness in large beakers. The dry residues were then ashed in a muffle at 600°C for 8–10 hr. Amounts ranging from 5 to 10 g of the powdered milk ashes were dissolved in the minimum volume of concentrated HNO_3 in a 50 ml centrifuge tube by using an electric stirrer, and the clear solutions brought to a final volume of 500 ml with 1 N HNO_3.

1.3. *Animal bones and teeth.* A more complex procedure was followed for the preparation of bone and teeth solutions. The samples, sawn into small pieces (2–3 cm of length), were scraped, and cleansed from residues of blood and soft tissue by boiling them several times in ethylene diamine and then in distilled water. After drying in an oven at 120°C the bones were ashed at 600°C, whereas a temperature of

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950°C was required for the ashing of teeth. The ashes, ground in an agate mortar, were dissolved in concentrated HNO_3 and solutions of ~ 500 ml were obtained by diluting with 1 N HNO_3.

1.4. *Bovine flesh.* The ashing of soft tissues is somehow more delicate than for other samples. It was performed in a platinum dish by increasing the temperature of a muffle furnace in steps of ~ 25°C so that the organic matter burned gradually without sudden outburst and consequent loss of substance. The final temperature of 600°C was maintained for about 10 hr. A residue of only 1% of the fresh weight was generally obtained, therefore it was necessary to use considerable amounts of material if a few grams of ashes were desired. The nitric solutions were prepared as for the other samples.

1.5. *Mineral samples.* Suspended matter from water samples, soil, and muds were analyzed not only to obtain information concerning a specific type of environment, but also to establish a suitable routine procedure for the radium determination of ores, silts, river muds and dry food items.

Dissolution of the mineral substances was preferred to leaching with inorganic reagents in order to assure the passage into solution of all the radium. The dry samples, finely ground in a porcelain mortar, were calcined at ~ 600°C for the elimination of any organic matter present. H_2SO_4 and HF (2 : 1) were added, with 50 mg of Ba^{++} as carrier, to a weighed amount (1–5 g) of ashes in a Pt crucible. A slow evaporation on a steam bath was then performed with complete elimination of white fumes of SO_3 until dryness. For material with high silica content the treatment with H_2SO_4 and HF was repeated several times. An extra addition of HF was occasionally necessary. H_3PO_4 was then added to the residue and the crucible heated over a burner. When a clear fused mass was obtained, it was allowed to cool and then dissolved in concentrated HNO_3 and the excess of acid evaporated. A final solution of ~ 500 ml was prepared diluting with 1 N HNO_3. Instead of the acid treatment a fusion of the samples with an alkaline flux followed by a dissolution of the melt in acids[8] may be performed.

Samples of suspended matter from river water received a different treatment. After the filtration the dry filter was burnt in a Pt crucible, HNO_3 and HF (1 : 2) were added to the residue and the crucible heated on a sand bath at 200°C until dryness. The acid treatment was repeated and, after elimination of fumes of HF, a clear nitric solution obtained. Dilution to ~ 500 ml was then performed with 1 N HNO_3. This procedure may be followed for samples of known low silica content.

1.6. *Human teeth.* Because of their low radioactive content human teeth need to be handled with special care to avoid contamination. Pt crucibles and glassware require very thorough cleaning by repeated washing with warm decontaminating solutions or warm diluted HNO_3. The crucibles must previously be cleaned with purified sea sand. Samples having blood residues were boiled, as were bovine teeth, in ethylene diamine and distilled water. Metallic fillings, when present, were removed before the ashing at 950°C. The ground ashes, always 73–75% of the fresh weight, were then dissolved in nitric acid and final solutions of ~ 500 ml were prepared by diluting with 1 N HNO_3.

2. *Technique of radon measurements*

All the solutions prepared by the different procedures described in the previous paragraphs, were transferred into emanation flasks and flushed for about 20 min with nitrogen for complete removal of radon. The flasks were then sealed and the time recorded (t_1, beginning of radon ingrowth). According to the levels of radioactivity the solutions were allowed to stand for a minimum of 5 days to a maximum of 30; at the latter time radium and radon are in equilibrium and no further build-up of the gas takes place. The accumulated Rn was then transferred to a trap containing charcoal and from this to the detector for counting.

The scheme of the emanation technique apparatus* set up for this study is shown in

* Apiezon grease, type M, AEI (Manchester) Ltd., England, is used to connect the spherical joints; type T to seal the flasks. Silicone grease is used for the stopcocks.

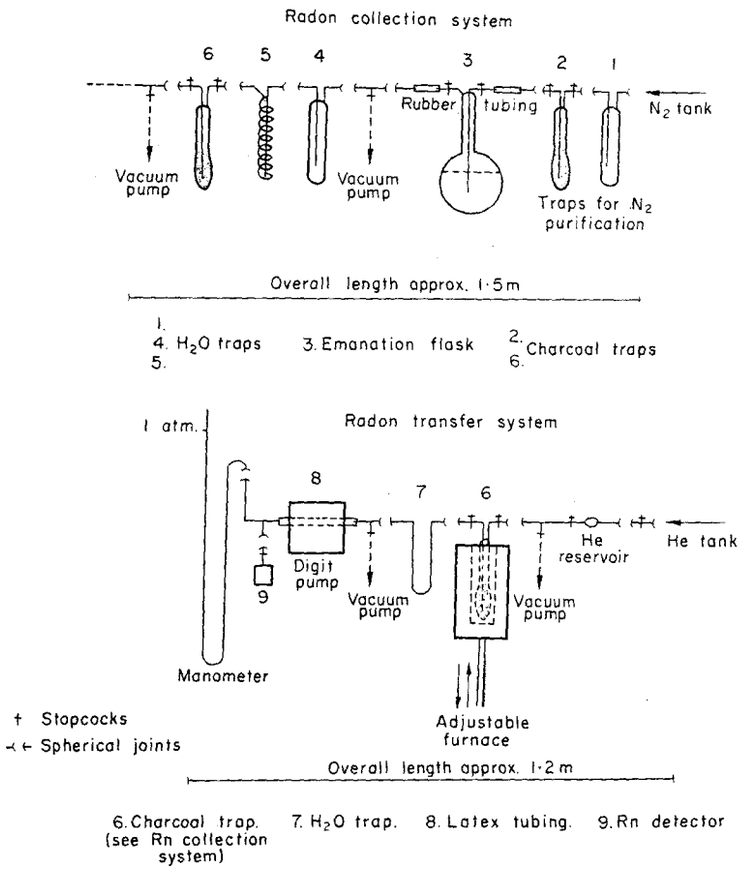

FIG. 1. Apparatus for emanation technique (scheme).

Fig. 1. The nitrogen used for the removal of radon from the flasks during the measurements was dried and purified (radium in the tank steel may cause contamination) by means of a water trap and a charcoal trap cooled to $\sim -80°C$ with dry-ice and acetone and allowed to bubble in the solution contained in the emanation flask (Fig. 2) for 12 min at a flow rate of 45 l/hr. The randon removed by the nitrogen passing through two cooled water traps was absorbed on activated charcoal* also cooled to $\sim -80°C$.

The model of the trap containing a weighed amount (always 7 g) of degassed charcoal, used for the purification of nitrogen and for the absorption of radon, is shown in Fig. 3. When de-emanation was complete the flask was sealed again and the time recorded (t_2, beginning of decay of removed radon and also beginning of a new radon ingrowth in the flask). The charcoal trap on which the gas had been absorbed was evacuated, while still at low temperature, without removing it from the system. The trap placed then in the second section of the apparatus shown in Fig. 1, was heated at 500°C by means of a cylindrical furnace which could be raised and lowered. The Rn liberated from the charcoal, passing through a cooled water trap, was transferred to the detector, a cell with a scintillating layer of ZnS at the interior. Helium was used as carrier gas at a continuous slow flow obtained with two needle

* Activated coconut charcoal. 6–14 mesh. Burrell Corporation, Pittsburgh, U.S.A.

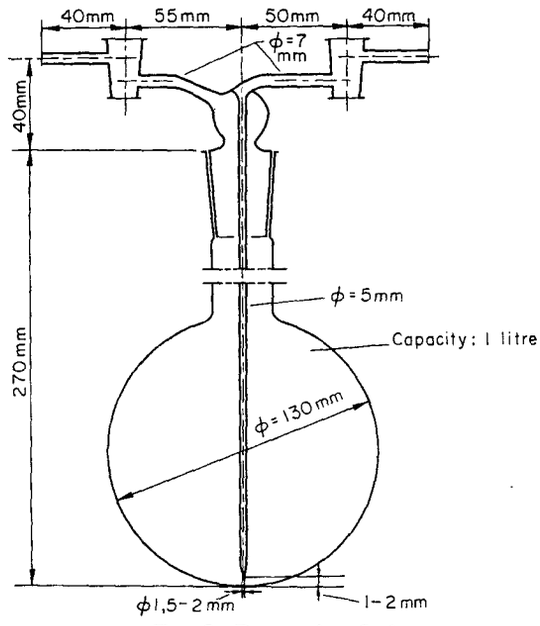

FIG. 2. Emanation flask.

valves* at the exit of the tank. A digit pump† facilitated the filling of the detector until atmospheric pressure was reached, usually in about 8 min. The latex tubing‡ used with the pump (see Fig. 1) was replaced after high counting rate measurements. By means of mechanical pumps the vacuum ($\sim 2 \times 10^{-2}$ Torr) could be obtained in each section of the apparatus, radon collection system and radon transfer system, before the passage of the nitrogen and of the helium, in order to avoid any contamination due to air from the exterior. After the complete transfer of the Rn to the detector the charcoal traps were evacuated, while still heated at 500°C, before using them again. Except when promptly re-used they were evacuated and heated again at the moment of a new analysis. The detectors containing the radon were counted four hours after the end of the de-emanation of the solution, when equilibrium between Rn and its daughters (^{218}Po and ^{214}Po) was reached. Counting times differed according to the radioactivity which had to be detected. For low levels, the samples were usually counted for not less than 16 hr.

Two types of scintillation detectors were used for the present study. One made of stainless steel with quartz window[3] for activities $\geq 10^{-13}$ Ci of ^{226}Ra and one of lucite, which has been described elsewhere,[4] for levels of the order of 10^{-14} Ci. The calibration of the system was performed with the metallic and the plastic detectors measuring the radon from standard solutions of 11.1×10^{-12} and 1.57×10^{-12} Ci of ^{226}Ra. Over-all efficiencies of 80 and 75 $\pm$ 2% were obtained. The decay of the radon emanated from each standard solution was followed observing the counting rates given by the two different detectors during 2 weeks; a half life of 3.8 days was found. Therefore no radon diffusion, suspected especially for the porous lucite, occurred through the detector walls.

CALCULATIONS

The radium content of the samples analyzed was calculated by means of the equation:

$$A\ (^{226}\mathrm{Ra}) = \frac{\frac{N_s}{t_s} - \frac{N_b}{t_b}}{C_1 \times C_2 \times R \times Q \times 3.7 \times 10^{-2} \times 3}$$

pCi/g ash or pCi/l.

where A (^{226}Ra) = activity expressed in picocuries of ^{226}Ra per gram of ash or per liter;

N_s = total counts obtained for the sample;

N_b = total counts obtained for the background;

t_s, t_b = counting times in seconds for samples and for background;

C_1 = radon growth coefficient (fraction of radioactive equilibrium): $1 - e^{\lambda t_g}$; t_g = days elapsed from beginning of radon in growth to de-emanation $(t_2 - t_1)$;

C_2 = radon decay coefficient: $e^{-\lambda t_d}$; t_d = time elapsed from de-emanation to the half of the counting interval;

R = over-all efficiency: 0.80 or 0.75;

* Model Osid; Edward High Vacuum Ltd., England.

† Model T-6S; Sigmamotor, Inc. Middleport, N.Y., U.S.A.

‡ Latex Surgical Tubing 0.5 cm ID., 0.25 cm Wall Amber; Rubber Latex Products, Inc., Cuyahoga Falls, Ohio, U.S.A.

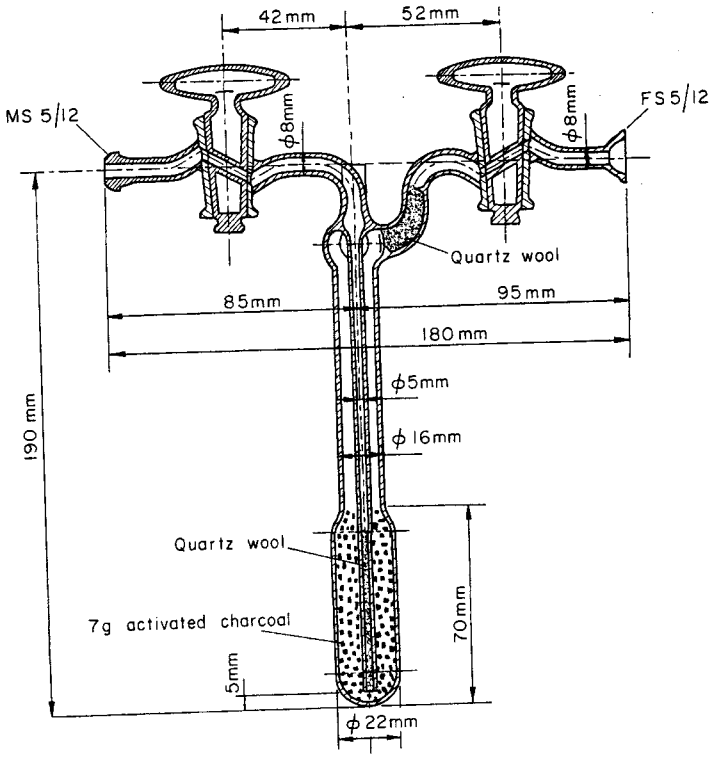

FIG. 3. Charcoal trap.

Q = weight of ashes in grams or volume of sample in liters;
3.7×10^{-2} = conversion factor to picocuries;
3 = correction due to the fact that at equilibrium for each radon disintegration three α-particles are detected, one from Rn, the others from its two daughters ^{218}Po and ^{214}Po.

RESULTS

Tables 1 and 2 show results obtained for water, milk, animal samples and minerals. Since the present paper is concerned mainly with the description of the method of analysis, it was considered unnecessary to list all the numerous samples analyzed and their radium content. The data contained in the tables are sufficient to show the different levels of natural radioactivity due to ^{226}Ra observed in the course of the work, even in samples of the same nature. Radium concentrations of human teeth from normal environments are summarized in Table 3. The values given in the three tables are averages of two analyses on the same solution, in agreement within the statistical counting error which is at maximum $\sim 15\%$. Blank determinations were regularly performed analyzing reagents and distilled water, especially before measurements at very low level. The counting rates obtained, ranging from 0.0015 to 0.0035 counts/sec were always subtracted from the counting rates given by the samples. The high sensitivity of the method permitted the determination of the radium content even of a single human tooth. Nevertheless a pool of teeth of the same origin and same formation time should be made, if possible, for better statistical results.

The analyses of the two bovine mandibles complete with teeth confirmed the results obtained in the course of a previous research.[5] A good agreement exists between the radium

Table 1. *^{226}Ra in Water, Milk and Minerals*

Sample identification and origin	Type of sample	Volume (in l.)	Ash weight (in g)	pCi/l. or pCi/g ash
E 178 Belgium	river water	0.500	—	0.440
E 182 ,,	,, ,,	,,	—	0.783
A 1 ,,	drinking water	,,	—	1.459
Is 1 Italy	,, ,,	0.230	—	0.011
Is 2 ,,	,, ,,	,,	—	0.036
Is 3 ,,	thermomineral water	0.300	—	0.037
Is 4 ,,	,,	0.600	—	0.345
64 Belgium	milk	0.980	6.539	0.017
65 ,,	,,	1.000	6.635	0.025
22 ,,	,,	1.200	7.356	0.032
69 ,,	,,	1.302	9.377	0.049
21 ,,	,,	1.080	7.572	0.073
14 ,,	,,	1.410	10.080	0.190
R 1 ,,	mineral	—	1.108	0.763
R 2 ,,	,,	—	1.053	1.088
B 4 ,,	river mud	—	1.000	2.238
Is 10 Italy	thermal mud*	—	1.288	0.669

Range of estimated error = ±0.015—0.185 pCi/l. or pCi/g ash.
* Collected near the spring of sample Is 3.

Table 2. *^{226}Ra in Animal Bones and Teeth*

Sample identification and origin	Type of sample	Fresh weight (in g)	Ash weight (in g)	pCi/g ash
65 Belgium	rabbit bone	1.055	0.633	0.154
84 ,,	,, ,,	6.829	4.097	6.493
1 B ,,	cow bone	11.725	7.841	0.184
1 B ,,	cow tooth I_4*	2.022	1.410	0.177
1 B ,,	,, ,, P_1	2.589	1.961	0.255
1 B ,,	,, ,, P_3	10.799	8.188	0.240
2 B ,,	cow bone	11.626	7.769	0.318
2 B ,,	cow tooth I_4	5.088	3.822	0.311
2 B ,,	,, ,, P_1	2.264	1.683	0.265
2 B ,,	,, ,, P_2	7.605	5.772	0.255
2 B ,,	bovine flesh	144.130	1.423	0.378
2 C† U.S.A.	cow bone	1.502	0.982	0.171
23 C† U.S.A.	,, ,,	4.790	3.066	2.381

Range of estimated error = ±0.020—0.250 pCi/g ash.
* I_4 = fourth incisor; P_1, P_2, P_3 = first, second, third premolar.
† Samples analyzed also at ANL (see ref. 5).

Table 3. ^{226}Ra in Human Teeth

Sample identification and origin	Type of sample	Fresh weight (in g)	Ash weight (in g)	pCi/g ash
208 Belgium	2 premolars	1.847	1.681	0.0093
236 „	„	1.514	1.396	0.0098
154 „	3 incisors	2.884	2.535	0.0141
144 „	1 molar	2.331	1.939	0.0142
1 K „	1 incisor	1.051	0.771	0.0153
2 K „	1 „	0.505	0.373	0.0183
153 „	4 premolars	3.767	3.348	0.0187
225 „	2 „	1.863	1.685	0.0198
304 „	3 incisors	3.496	2.483	0.0285
303 „	1 molar	1.786	1.460	0.0451
305 Italy	1 „	1.935	1.560	0.0082
309 „	1 „	2.067	1.630	0.0102
312 „	1 „	1.952	1.520	0.0132
302 „	1 „	0.703	0.614	0.0138
310 „	1 premolar	0.739	0.553	0.0148
307 „	1 molar	1.077	0.779	0.0234
313 „	1 „	1.663	1.335	0.0246
311 „	1 premolar	0.559	0.409	0.0449
308 „	1 molar	1.855	1.340	0.1380

Range of estimated error = $\pm 0.0020 - 0.0150$ pCi/g ash.

concentrations in bone and teeth, especially those with late formation time. This fact justifies again the use of teeth to estimate skeletal burdens when bone samples are not available.

The concentrations found in human teeth, despite their different origin, are very close to those found in teeth or bones from normal environment by several authors and among others by Walton *et al.*,[6] by Lucas,[1] Hursh and Lovaas,[7] Holtzman,[8] Owers and Parker.[9] Hence, since the skeletel radium content is due to the radium ingested with drinking water and food,[1] whenever a systematic abnormal Ra intake is suspected, intensive determinations of body burdens (through analyses of bones and teeth) could be very useful for the study of possible cumulative effects of low level radiations over long periods of time.

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REFERENCES

1. H. F. Lucas. Correlation of the natural radioactivity of the human body to that of its environment. ANL-6297, pp. 55–56 (1960).
2. D. E. Rushing, W. J. Garcia and D. A. Clark. The analysis of effluents and environmental samples from uranium mills and of biological samples for radium, polonium and uranium. *Radiological health and safety in mining and milling of nuclear material.* I.A.E.A., Vol. II, pp. 187–230 (1964).

3. H. F. Lucas. *Rev. Sci. Instr.* **28,** 680 (1957).
4. E. R. di Ferrante, E. Gourski and R. R. Boulenger. Detector for radon measurement at very low level. *The Natural Radiation Environment,* Ed. Adams & Lowder, Chicago Press, pp. 353–357 (1964).
5. E. R. di Ferrante. *Health Physics* **10,** 259 (1964).
6. A. Walton, R. Kologrivov and J. L. Kulp. *Health Physics* **1,** 409 (1959).
7. J. B. Hursh and A. Lovaas. *Nature* **198,** 265 (1963).
8. R. B. Holtzman. *Health Physics* **9,** 385 (1963).
9. M. J. Owers and A. Parker. Radioactivities in human and animal bones. AERE-R 4466 (1964).