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The paper

TRANSLOCATION OF THORIUM DAUGHTERS TO BONE

L. D. Marinelli and H. F. Lucas, Jr., Argonne National
Laboratory

will appear in Proceedings of the Symposium on Some Aspects of Internal
Irradiation, Heber, Utah, May 8-11, 1961, Pergamon Press.

The following papers were presented at the meeting, but were not available
for inclusion in the proceedings:

COMPARATIVE RETENTION AND DISTRIBUTION OF RADIOCERIUM
AND RADIOCESIUM IN DOGS

T. W. Speckman, Argonne National Laboratory

RADIOACTIVITY IN AIR

P. F. Gustafson, Argonne National Laboratory

ANALYTICAL PROBLEMS ASSOCIATED WITH THE SL-1 INCIDENT

C. W. Sill, Health & Safety Division, USAEC, Idaho Falls

BIOCHEMICAL STUDIES ASSOCIATED WITH CRITICALITY
INCIDENTS

D. F. Petersen, Los Alamos Scientific Laboratory

THE POWER FUNCTION AS A DESCRIPTION OF ISOTOPE
METABOLISM

W. P. Norris, Argonne National Laboratory

FLUOROMETRIC DETERMINATION OF SUBMICROGRAM QUANTI-
TIES OF THORIUM

C. W. Sill and C. P. Willis, Health & Safety Division, Idaho Falls

The latter paper has been published in Analytical Chemistry, 34, 954 (1962).

INTRODUCTION

The Seventh Annual Meeting of the Bio-Assay and Analytical Chemistry group was held October 12 and 13, 1961, at Argonne National Laboratory. The meeting was sponsored by the Industrial Hygiene and Safety Division of the Laboratory. Similar meetings, sponsored by other organizations, have been held each year since 1955. The proceedings of previous meetings have been issued as reports NCLO-595, WASH-736, WASH-1023, TID-7591, and TID-7616. No proceedings were issued for the meeting held in 1957.

The primary objective of these meetings is to provide an opportunity for those working in this field of health protection (sometimes called bio-assay, health radiochemistry, occupational biochemistry, or radiation hygiene chemistry) to exchange information and discuss problems of mutual interest.

INFLUENCE OF PHYSICAL STATE ON THE REMOVAL OF HYDROLYZABLE RADIOELEMENTS BY CHELATION

by

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The distribution and ease of removal of certain radioelements that are readily hydrolyzable is, other things being equal, a property of the physical and chemical states in which such substances are introduced into the body. Among the elements of interest are the members of the transition series, such as the iron, transuranic, and the rare earth series. In general, the members of these series form polyvalent cations, whose salts readily hydrolyze in aqueous solution at pH 7 or below. These quickly become insoluble due to polymer formation by means of oxygen bridges between the molecules. The resultant solution is colloidal in nature, consisting of fairly large particles.

However, if these salts are placed in solution in the presence of a complexing agent for which the cation has a relatively high affinity, the hydroxide ions and the anion of the complexing agent compete for the cation, and the tendency toward polymerization is reduced. A solution prepared in this manner is less colloidal in nature and consists of smaller particles. A complexing agent frequently used is sodium citrate.

These two different types of solutions differ markedly in their uptake after intravenous injection. A colloidal solution is cleared from the circulation rapidly, largely through the process of intracellular uptake by the macrophages of the liver, spleen, and bone marrow. Some extracellular deposits also occur in the form of insoluble polymerized molecules. An ionic solution leaves the circulation much more slowly, and deposition is largely in the form of a protein-metal complex on cellular surfaces.

The most effective chelating agent for the removal of the transuranium elements and the rare earths is a member of the polyamino acid group known as DTPA (diethylenetriaminepentaacetic acid). This compound has a high stability constant for the metals in question and promotes their excretion by the formation of soluble, stable complexes. Foreman studied the metabolism of this compound and showed that it was largely extracellular in its distribution, as indicated by the fact that 90% of a parenterally administered dose was excreted in the urine within 24 hr and only about 5% was retained in the soft tissues.⁽¹⁾

One would expect that the efficiency with which such an extracellular agent could remove deposits of a radioactive metal would be diminished if these deposits were intracellular and relatively insoluble. Two experiments were performed to evaluate the extent of this effect. The radioelements chosen for study were thorium-234 and plutonium-239. In the first experiment, thorium was prepared in two ways: (1) as the nitrate at pH 2.7 with a small amount of added carrier thorium, and (2) as the citrate at pH 5.0 with no added carrier. The nitrate solution was visibly colloidal with a marked Tyndall beam, and the citrate was largely ionic. These solutions were injected intravenously into Sprague-Dawley female rats at $0.6 \mu\text{c}$ per rat, with three rats in each control and treated group. CaDTPA was administered intraperitoneally in a series of four injections, beginning on the third day after thorium administration and ending on the seventh day, when the animals were sacrificed. Saline was given intraperitoneally to the controls.

The results⁽²⁾ showed that deposition of the colloidal thorium was largely in the liver (63% of the injected dose) with only a small amount (6%) in the skeleton. Treatment with CaDTPA at 370 mg/kg/injection had little or no effect on this distribution and promoted only a slight increase in the urinary excretion of thorium (3% in the treated urines as compared with 0.2% in the controls). In another group in which the treatment was increased to near-toxic levels of CaDTPA (1330 mg/kg/day), the thorium content of the liver was reduced by only 13% of the injected dose (i.d.) with a corresponding promotion of the urinary excretion to 11% i.d. The distribution of the ionic thorium was markedly different, with 60% of the injected dose going to the skeleton and only 3% in the liver. Treatment with DTPA at 370 mg/kg/injection reduced this skeletal burden to 43% i.d. and promoted a corresponding increase in the urinary excretion (34% i.d. in treated vs 12% i.d. in controls).

The patterns of urinary excretion of the two types of thorium were notably different (Figure 1). The amount of excretion of ionic thorium

Fig. 1
Effect of CaDTPA administration on thorium excretion in the urine of rats.

promoted by the treatment injections decreased with each succeeding injection, whereas the percentage of colloidal thorium in the urine increased with each succeeding injection of CaDTPA. This increase reflects the slow depolymerizing action of DTPA on the insoluble deposits of thorium, which makes them available for excretion as molecules of thorium-DTPA chelate.

In the second experiment,⁽³⁾ two solutions of plutonium were compared in the same manner. Both were prepared as citrate solutions of $\text{Pu}(\text{NO}_3)_2$ at pH 5.5, but ultrafilterability tests with the two solutions showed that one was over 93% ultrafilterable and the other only about 70%, indicating that the latter contained particles of larger size. The reason for this was that the latter had been prepared from a dried solution of $\text{Pu}(\text{NO}_3)_2$ which had developed a significant amount of insoluble plutonium oxide on standing for a long period of time.

A total of 140 CF No. 1 female mice were injected intravenously with one or the other of the two forms of plutonium (ionic and colloidal)

Fig. 2. Removal of ionic plutonium with daily CaDTPA therapy.

at a level of $3.3 \mu\text{c/kg}$ for the ionic and of $2.6 \mu\text{c/kg}$ for the colloidal. DTPA therapy, begun three days later, consisted of twelve daily intraperitoneal injections at 500 mg/kg each. Saline solution was given to the controls. The results of the tissue analysis are shown in Figures 2 and 3. Three days after plutonium administration, the total amount of retained plutonium was about the same in both cases (65% of the injected dose), but the partition between liver and bone differed markedly. The ionic plutonium was divided almost evenly between the two tissues, whereas the amount of colloidal plutonium in the liver was over twice that in the bone. The

spleens of the mice receiving ionic plutonium contained only 0.1% i.d., whereas those receiving the colloidal form contained 1.3% i.d. The plutonium in the livers of untreated mice decreased steadily in the 15-day period after injection of the ionic form; the route of this excretion was fecal. In contrast, after injection of the colloidal form of plutonium, there was little change in the liver during this period. In the animals receiving DTPA therapy, ionic plutonium was almost completely removed from the liver in three days, whereas in those receiving colloidal plutonium, the liver still retained almost two-thirds of its initial burden after the

entire treatment period was over. For both forms of plutonium, bone levels were stable in the controls and the effect of DTPA therapy was about the same (50% reduction). In summary, the total reduction of body burden brought about by DTPA therapy was considerably greater in those animals receiving ionic plutonium (75% reduction) than in those receiving the colloidal form (40% reduction). This is due mainly to the difference in response of the two types of plutonium in the liver and suggests a difference in their location and solubility in this organ.

Fig. 3

Removal of colloidal plutonium with daily CaDTPA therapy.

The results outlined here demonstrate that the distribution and ease of removal of a given radioelement can vary markedly with its chemical preparation. The implications of these findings for the clinician and the bioassayist are apparent. Information regarding the physical and chemical state of a hydrolyzable radioelement is as necessary as that regarding the route of entry and time of intake for proper evaluation of the extent of the body burden and the advisability of chelating agent therapy.

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LONG-TERM EFFECTS OF THERAPEUTIC REMOVAL OF INTERNALLY DEPOSITED PLUTONIUM

by

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The chronic toxicity of internally retained radioactive substances has been recognized since the appearance of bone abnormalities and tumors in the radium dial painters who had licked the tips of their brushes. Following the tremendous increase in both volume and variety of radioactive metals handled after 1941, therapeutic means for the removal of these substances from the body have been sought. This search has been increasingly successful for the hydrolyzable radioelements such as plutonium. Treatment with sodium citrate was the first therapy tested. Then, the metal carriers such as zirconium were employed to pick up circulating radioelements and remove them from the body. Most recently, the polyamino acid chelating agents have been used to increase the solubility and excretion of radioelements. Diethylenetriaminepentaacetic acid (DTPA), the most effective of these chelating agents yet developed for the removal of plutonium and related metals, can remove almost all of the radioelement from the body when it is administered without delay. More importantly from a practical standpoint, DTPA can reduce long-standing deposits in bone, as well as in soft tissues, by one-half or more. In view of these developments, it is surprising that only recently has any detailed attempt been made to answer the question as to whether or not this removal has any significant long-term beneficial effect on chronic radiation injury, especially the development of tumors.

The experiment summarized here was designed to correlate tumor incidence with degree of removal of plutonium from the bone and selected soft tissues of the mouse, and also to relate tumor reduction with any microscopic redistribution of the plutonium, determined from autoradiographs. Experimental details and preliminary results have appeared,^(1,2) and the final results and analyses will be published in the open literature.

Mice were treated once a day with an intraperitoneal injection of CaDTPA (500 mg/kg) or saline. Therapy was initiated three days after administration of 2.6 $\mu\text{C/kg}$ of a polymeric form of plutonium and given for 1 to 12 days. The mice were allowed to live until moribund, when they were sacrificed and autopsied, and roentgenograms were taken of their skeletons. Other mice, used for analysis of plutonium content and autoradiograms, were sacrificed serially. The amount of plutonium in the

bone was reduced by about one-half and that in the liver by about one-third in mice receiving optimal DTPA therapy (for 12 days). Correlated with this removal of plutonium from the skeleton, bone-tumor incidence was also reduced by one-half, using as an index the proportion of mice in each group to develop bone tumors (Figure 1). In addition, the survival of the plutonium-poisoned mice was significantly increased by DTPA therapy for 8 to 12 days. For example, the mean survival time in these two combined groups was increased by 54 days to 450.2 ± 8.5 days in comparison with that in controls, which was 396.5 ± 8.5 days.

Fig. 1

Reduction of bone-tumor incidence and plutonium levels in bone in plutonium-injected mice by DTPA therapy. In the left-hand figure, the solid sections of the bars represent mice with bone tumors that had outgrown the normal outline of the bone as seen on the roentgenogram. The hatched sections represent additional mice found to have bone tumors after histological examination of selected skeletal areas (from Ref. 2).

These preliminary results are encouraging with regard to the long-term benefits to be expected following radioelement removal. Life expectancy has been increased and bone-tumor incidence significantly decreased in spite of the use of a polymeric form of plutonium that is relatively refractory to removal,^(3,4) and in spite of the fact that the radioelement had become deposited in the tissues during the three-day delay before therapy was initiated.

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THE ESTIMATION OF A BODY BURDEN OF Pu FROM URINALYSIS DATA

by

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W. H. Langham has studied the excretion of Pu^{239} by adult humans over a period of 140 days following intravenous injection. By study of cases of occupational exposure, he has extended the period of study to as much as 5 to 6 years and shown that the excretion data may be fitted approximately by power functions. Specifically, he has given the functions

$$Y_u(t) = 0.0023 t^{-0.77} ; \quad (1)$$

$$Y_f(t) = 0.0063 t^{-1.09} ; \quad (2)$$

$$Y_{u+f}(t) = 0.0079 t^{-0.94} \quad (3)$$

to approximate the urinary excretion, the fecal excretion, and the total excretion on the t^{th} day following an intravenous injection of unit amount into the blood.⁽¹⁻³⁾ Using these formulae and his extensive experience with exposure to plutonium, Langham has developed methods of predicting the body burden** of an individual on the basis of the urinary excretion data.

J. N. P. Lawrence has developed a computer code for the IBM 704 which embodies the principal features of Langham's method and gives results in general agreement with Langham's personal estimates. This paper develops an alternative method of treating the data and gives a preliminary discussion of the accuracy of the two methods. The influence of spurious data points or of insufficient data is indicated also.

Equations (1), (2), and (3) presuppose a single injection. In order to treat the more general case of continuous exposure, it is necessary to consider the continuous case as the integral of the discrete case. This has been justified for a few elements in several studies. Although no such study involving plutonium is known, this procedure is that generally used in estimating body burdens and seems a necessary one in the present state

*Operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

**More specifically, the bone burden, since the method probably underestimates the lung burden.

of our knowledge. With this assumption, the urinary excretion on the t^{th} day of an exposure period beginning at time $t = 0$ is given by

$$U(t) = \int_0^t d\tau I(\tau) a(t-\tau)^{-\alpha} \quad , \quad (4)$$

where $I(\tau)$ is the intake to blood on the τ^{th} day, $a = 0.0023$, and $\alpha = 0.77$, in accordance with (1). The units of I may conveniently be taken as d/m/day and for $U(t)$ as d/m/24-hr sample.

Fractional retention of plutonium on the t^{th} day following a single intravenous injection has been given⁽⁴⁾ by

$$r(t) = bt^{-\beta} \quad (5)$$

with $b = 0.99$ and $\beta = 0.01$. Applying the same principle of integrating the single-dose formula to obtain the continuous case, one obtains the body burden $q(t)$, or retention, on the t^{th} day following the beginning of exposure:

$$q(t) = \int_0^t d\tau I(\tau) b(t-\tau)^{-\beta} \quad . \quad (6)$$

With the above choice of units for I , q will be given in d/m.

Alternatively, one may express the retention following a single intravenous injection as the difference of the intake and the total excretion. Using (3), one obtains

$$r(t) = 1 - \frac{C}{1-\gamma} t^{1-\gamma} \quad , \quad (5')$$

with $C = 0.0079$ and $\gamma = 0.94$. Then the body burden $q(t)$ on the t^{th} day following the beginning of a period of continuous exposure is given by

$$q(t) = \int_0^t d\tau I(\tau) \left[1 - \frac{C}{1-\gamma} (t-\tau)^{1-\gamma} \right] \quad . \quad (6')$$

Equations (4) and (6), or alternatively Eqs. (4) and (6'), involve the functions q and I , which must be assumed to be largely unknown in most cases of exposure, and the function U , which is known in part, i.e., U is known to the extent that urinalysis data are available. The mathematical problem consists in expressing the unknown functions q and I in terms of the known or partially known function U .

The mathematical solution for q and I can be obtained elegantly by the use of the Laplace transform. Using a bar over a function to designate the transform of the function, the application of the Laplace transform to Eqs. (4), (6), and (6') yields⁽⁵⁾

$$\bar{U}(s) = \bar{I}(s) a \Gamma(1 - \alpha) s^{\alpha-1} ; \quad (4^*)$$

$$\bar{q}(s) = \bar{I}(s) b \Gamma(1 - \beta) s^{\beta-1} ; \quad (6^*)$$

$$\bar{q}(s) = \bar{I}(s) \left[s^{-1} - \frac{b \Gamma(2 - \beta) s^{\beta-2}}{(1 - \beta)} \right] , \quad (6'^*)$$

where Γ denotes the gamma function. Solving for $\bar{q}$ and $\bar{I}$, one obtains

$$\bar{q}(s) = \bar{U}(s) b \Gamma(1 - \beta) s^{\beta-\alpha} / a \Gamma(1 - \alpha) ; \quad (7^*)$$

$$\bar{q}(s) = \bar{U}(s) \left[s^{-\alpha} - \frac{b \Gamma(2 - \beta) s^{\beta-\alpha-1}}{1 - \beta} \right] / a \Gamma(1 - \alpha) ; \quad (7'^*)$$

$$\bar{I}(s) = \bar{U}(s) s^{1-\alpha} / a \Gamma(1 - \alpha) . \quad (8^*)$$

If the inverse transforms are formed, there are obtained

$$q(t) = \frac{b \Gamma(1 - \beta)}{a \Gamma(1 - \alpha) \Gamma(\alpha - \beta)} \int_0^t d\tau U(\tau) (t - \tau)^{\alpha - \beta - 1} ; \quad (7)$$

$$q(t) = \frac{1}{a \Gamma(1 - \alpha) \Gamma(\alpha)} \int_0^t d\tau U(\tau) (t - \tau)^{\alpha-1} - \frac{b \Gamma(2 - \beta)}{a(1 - \beta) \Gamma(1 - \alpha) \Gamma(\alpha - \beta + 1)} \int_0^t d\tau U(\tau) (t - \tau)^{\alpha - \beta} d\tau ; \quad (7')$$

$$\int_0^t d\tau I(\tau) = \frac{1}{a \Gamma(1 - \alpha) \Gamma(\alpha)} \int_0^t d\tau U(\tau) (t - \tau)^{\alpha-1} . \quad (8)$$

It will be noted that the solution for I does not yield an explicit formula for I but rather for its integral. The function I can then be recovered by differentiation, but for most practical purposes the accumulated intake may be of equal interest.

Formulae (7), (7'), and (8) require that U be given as a continuous function of the time. In practice, the urinalysis data will be available only at certain discrete times when the individual submitted a sample. Thus the actual urinalysis data must be regarded as a sampling of the values of the function U , and in computing formulae (7), (7'), and (8) it is necessary to interpolate the values of U from the urinalysis data of the individual. There are many ways of doing this, and some methods may be more appropriate than others in certain cases. For example, if an individual is known to have a high exposure on a certain date, the data should not be

"smoothed" or averaged to remove a sharp increase in urinary output. However, it might be useful to smooth the data over periods where sporadic intakes of large amounts are not considered likely. Clearly, any decision to alter or treat the data must be based on a close study of the exposure situation.

Codes for the IBM 7090 have been prepared which calculate the formulae (7), (7'), and (8). The input consists of the sample dates (day, month, year) and the sample values (d/m/24-hr sample), as well as identification of the case and the time when the body burden is to be estimated. The code converts the dates into days following the beginning of the exposure period, taking the first sample date as 0. Thus, the data are converted into the form (t_i, C_i) , $i = 1, 2, \dots, n$, where n is the number of sample values, t_i is the number of days following the beginning of the sample record when the sample value C_i was observed, and t is the day on which the body burden or total intake is required. The code uses linear interpolation to estimate U for values between successive sample dates. Thus,

$$C = C_i + m_i (\tau - t_i)$$

for

$$t_i \leq \tau \leq t_{i+1}$$

with

$$m_i = (C_{i+1} - C_i) / (t_{i+1} - t_i) \quad .$$

Equation (7) then becomes

$$q(t) = \frac{b\Gamma(1-\beta)}{a\Gamma(1-\alpha)\Gamma(\alpha-\beta)} \sum_{j=1}^{n-1} \frac{C_j t_{j+1} - C_{j+1} t_j + (C_{j+1} - C_j) t}{t_{j+1} - t_j} \left[\frac{(t - t_j)^{\alpha-\beta} - (t - t_{j+1})^{\alpha-\beta}}{\alpha - \beta} \right] - \frac{b\Gamma(1-\beta)}{a\Gamma(1-\alpha)\Gamma(\alpha-\beta)} \times \sum_{j=1}^{n-1} m_j \left[\frac{(t - t_j)^{\alpha-\beta+1} - (t - t_{j+1})^{\alpha-\beta+1}}{\alpha - \beta + 1} \right] ,$$

and analogous expressions for (7') and (8) may be written down directly by substitution for U . These are the expressions which have been coded for the IBM 7090.

Unfortunately, there is little in the way of precise data which can be used as a check on the accuracy of the method. Figure 1 illustrates the

effect of truncation on the data. Urinalysis data corresponding to a hypothetical case of a single intake at time $t = 35$ days were computed for 200 additional days. The accumulated intake was computed by taking data points at intervals of 30 days, 20 days, 10 days, and 5 days. Ideally, the accumulated intake should be zero before day 35 and one thereafter, and the various approximations illustrate the effect of truncation on the data. Figure 2 illustrates the same effect, but the unit single intake has been placed at day 30 so as to coincide with one of the sample dates. Figures 3 and 4 show the estimated body burdens at various times for these two cases as compared with the theoretical body burden predicted by 4. It will be noted that the position between sample dates of a single intake may have considerable effect on the result. The reason for this can be inferred from Figures 5 and 6. The dotted lines show the data used by the computer. This differs considerably, in some cases, from the solid curves, which represent the hypothetical case from which the sample values were selected. This effect and a remedial programming technique are under study also. Finally, it should be borne in mind that this is only a check on the mathematical treatment of the problem and does not test the validity of the biological assumptions.

Fig. 1
Effect of truncation on estimated intake

Fig. 2
Effect of truncation on estimated intake

Fig. 3
Effect of truncation on
estimated body burden

Fig. 4
Effect of truncation on
estimated body burden

Fig. 5
Excretion data and truncation
for input to code

Fig. 6
Excretion data and truncation
for input to code

Table I contains estimates of body burden for 26 individuals* by Langham, by the PUQFUA code, and by PUQUAP and PUQUAE. Since PUQFUA postulates a single intake 15 days prior to the first sample date, the PUQUAP and PUQUAE estimates are shown with and without this assumption. When this assumption is made, the first actual datum point has been extrapolated back by formula (1) to obtain a datum point for this first day. As will be noted, there is broad agreement of the estimates. The last entry, E822, is the case reported by Langham,(6) and in this case the additional estimate is from the autopsy data.

Table I
COMPARISON OF PLUTONIUM BODY-BURDEN ESTIMATES

Code	Langham	PUQFUA	PUQFUA Invalidated Samples	PUQUAP ¹	PUQUAP ²	PUQUAE ¹	PUQUAE ²
C135	0.08	0.1382	16	0.0882	0.1002	0.0758	0.0861
D334	0.07	0.1336	2	0.1002	0.1058	0.0872	0.0921
D711	0.07	0.1375	1	0.0901	0.1312	0.0785	0.1142
G717	0.06	0.0732	2	0.1340	0.1488	0.1168	0.1297
D63	0.06	0.1137	0	0.0702	0.0769	0.0611	0.0670
E36	0.06	0.0797	1	0.0739	0.0784	0.0644	0.0683
C397	0.05	0.0294	5	0.0454	0.0456	0.0390	0.0391
D501	0.04	0.0552	2	0.0376	0.0407	0.0328	0.0355
F664	0.04	0.0934	0	0.0511	0.0540	0.0445	0.0471
G716	0.04	0.0350	1	0.0242	0.0407	0.0211	0.0355
E742	0.03	0.0579	2	0.0490	0.0539	0.0427	0.0469
D775	0.02	0.0250	5	0.0231	0.0284	0.0201	0.0246
D182	0.02	0.0233	1	0.0179	0.0296	0.0156	0.0258
G524	0.02	0.0227	2	0.0177	0.0254	0.0154	0.0221
E629	0.02	0.0277	1	0.0165	0.0256	0.0144	0.0223
E390	0.02	0.0174	1	0.0173	0.0201	0.0151	0.0175
D791	0.02	0.0278	2	0.0205	0.0230	0.0178	0.0200
D591	0.02	0.0398	1	0.0213	0.0235	0.0186	0.0205
D205	0.02	0.0397	0	0.0156	0.0192	0.0136	0.0168
C137	0.02	0.0286	17	0.0350	0.0350	0.0300	0.0300
F634	0.01	0.0418	0	0.0478	0.0478	0.0413	0.0413
E252	0.01	0.0233	2	0.0173	0.0174	0.0150	0.0151
F412	0.006	0.0112	2	0.0103	0.0119	0.0090	0.0104
D670	0.006	0.0020	2	0.0179	0.0219	0.0156	0.0191
C365	0.006	0.0114	10	0.0090	0.0157	0.0077	0.0135
E822	0.032	0.0186	20	0.0296	0.0299	0.0255	0.0257
E822	0.0175*						

¹Assumes exposure begins on date of first sample.

²Assumes exposure begins 15 days before date of first sample with urine count predicted by excretion formula.

*Body burden estimate from autopsy.

*Langham selected these cases as being some for which the body burden is considered to be best known.

Since case E822 is the only case for which the body burden was determined by autopsy, a special study of the data was made in an effort to understand why PUQUAP and PUQUAE gave larger estimates than the

Fig. 7. Urinalysis data of case E822

autopsy value might indicate, while PUQFUA gave an estimate in close agreement. The urinalysis data of case E822 are shown in Figure 7, and the connecting lines indicate the interpolated data used by PUQUAP and PUQUAE. It is evident that two of the highest values occurred after periods of 230 and 233 days during which no other sample was taken. The linear-interpolation results in attributing high

urinary excretion values over an extended period in each case. In actuality, no data are available for this period. To test the influence of this assumption of linearity on the estimate, the code was rerun after insertion of two additional fictitious data points at days 2062 and 2522, attributing to these the excretion values 0.701 and 0 in line with the preceding sample value. By means of this modification, the estimated body burden of E822 was 0.0206 by PUQUAP and 0.0177 by PUQUAE. These are well in line with the actual value. Figure 8 shows the accumulated growth of body burden as estimated by PUQUAP and PUQUAE without any modification of the data. Figure 9 shows the effect of the modification for PUQUAE. This in no sense justifies the use of such a procedure* but does indicate that the higher estimates were due to the effect of the linear-interpolation scheme applied over such an extended period and not to the high values themselves. It was found on examination that PUQFUA

Fig. 8. Estimated growth of body burden of case E822

also rejected these data points. This example indicates the great importance of adequate urinalysis data, because such extensive periods where some assumptions must be made may introduce a large uncertainty in the estimate.

*In subsequent discussion with Lawrence, he has indicated that, after study of the working record, he feels there may be some justification for the assumption that the urinary excretion of E822 was not high for most of these two periods of time.

Fig. 9. Two estimates of body burden case E822

provide interpretation of this phenomenon. In fact, it seems important that the methodology used in these codes be thoroughly explored and that similar methods be developed for other isotopes if this is feasible.

There are many aspects of the problem which call for further exploration. It is evident that $I(\tau)$ represents the intake into the blood and not ingestion or inhalation of the material. Thus, there is no apparent inconsistency in $I(\tau)$ being positive, even though the individual is not currently exposed. The material may be feeding into the blood from the lung or from other body tissues. This phenomenon of a rather high rate of urinary excretion of an individual removed from exposure is frequently observed in cases of occupational exposure. It would be valuable to have carefully controlled animal experiments which would

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THE DETERMINATION OF GROSS BETA AND GROSS ALPHA ACTIVITY IN URINE

by

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General Dynamics/Fort Worth operates two semimobile research reactors, each capable of operating at 3-Mw power levels, for a variety of experimental programs and investigations; one other low-power reactor is used in fuel-element verification and in experimental studies of core configurations. Also in use are two linear accelerators of nominal 100- and 150-kv potentials, and nearly three hundred sources of various types, solid and liquid, sealed and unsealed, ranging from tritium to plutonium, with activities of from a few disintegrations per second to the kilocurie level. About one hundred people are routinely actively engaged in operations in conjunction with one or more of these sources of radioactive materials, while another three hundred or more are less frequently or rarely involved directly in such operations.

Along with the other phases of our radiological protection services, the Health Physics Group of the Medical Section at General Dynamics performs routine urinalyses as a part of the personnel-monitoring program. Twenty-four-hour urine samples are collected at regular intervals, usually monthly, from employees engaged in operations in which potential exposures to loose radioactive materials might occur. These samples are analyzed to aid in the detection of individual internal depositions of radioactive materials and as a quality-control check on exposure-prevention methods and techniques. Specimens are also collected, either annually or semi-annually from other people in our nuclear programs who are not generally subject to potential exposures. These samples are analyzed as random or "spot" checks and to serve as background baselines.

Because of the diverse nature of the experimental nuclear work at General Dynamics, the Health Physics Group rarely knows in advance which radionuclides any specific individual may be excreting. Although a urine sample can be systematically analyzed for each radioisotope which the employee might conceivably be excreting, the cost of doing such becomes exponentially astronomical. Considerations of time and economy prohibit successive specific analyses of this type on a widespread routine basis.

Since our experimental activities involve a great variety of radionuclides, so that specific analyses are neither practical nor satisfactory

in general, a rapid and reliable procedure for the accurate estimation of gross excreted activity offers an economical compromise between what is desirable and what is practically obtainable; this procedure also provides an effective means of screening routine urine samples. Gross procedures lack specificity and obviously cannot be precisely interpreted in terms of internal dose or body burden. However, samples showing high gross activity levels may be subjected to specific identification techniques without appreciable loss of additional time.

Gross techniques suffer from two serious complications:

1. the presence of naturally radioactive potassium-40 in the urine, generally ranging, we find, from 2,000 to 5,000 disintegrations per minute per liter, thereby effectively masking the levels of beta activity in which we are primarily interested; and
2. the self-absorption of emitted radiation in the urine solids, causing a reduction in detection sensitivity and a low estimation of activity actually present.

The first problem is resolved by a carrier precipitation of the urine activity, which leaves the alkali earths in solution. The second disadvantage is minimized by wet-ashing the raw urine to reduce the mass to inorganic salts and by making self-absorption corrections based on the mass present.

Fission products and activation products arising from the operation of three nuclear reactors are the radionuclides of primary interest in our particular case. Consequently, the procedure was designed to yield satisfactory results for these activities, and may therefore be applied to urinalysis problems at any installation at which fission and activation products are the principal sources of potential internal contamination.

The urine sample as received is thoroughly agitated to ensure homogeneity. A 100-ml aliquot of the raw urine is wet-ashed with concentrated nitric acid and dried without boiling. The warm residue is dissolved in 5 ml of 3 N hydrochloric acid. The resulting solution is diluted with 30 ml distilled water. (Occasionally, complete dissolution does not occur until the distilled water is added. On rare instances, some solids remain after dilution. These are collected in the precipitate and tend to give a conservative result. Filtration and analyses of these solids at this point have always yielded negative results.) The pH is adjusted to one with ammonium hydroxide (and hydrochloric acid, if required) to prevent premature precipitation of the carrier, the urine calcium and the urine magnesium. Five ml of the cerium and strontium carrier are added.* The

*The carrier is prepared by dissolving 3.0998 gm $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 3.0496 gm $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ in distilled water, and diluting to one liter with distilled water.

solution is heated almost to boiling and 4 ml of 0.1 M hydrated barium chloride are added to precipitate the urine sulfates and phosphates. Five ml of a 0.67 M ammonium hydroxide and 1.17 M ammonium carbonate solution are added to the hot solution to precipitate the insoluble carbonates and hydroxides. (The containers are agitated gently during these precipitations.) The final pH after the addition of the precipitating agent is slightly basic. Experimental data have established that the final pH is not critical so long as the solution is basic. The solution is then cooled to room temperature and vacuum filtered onto an HA millipore filter. The precipitate is dried and transferred to a weighed stainless steel planchet. The final mass of the precipitate usually varies from 200 to 300 mg.

The dried precipitate is counted for alpha and beta activity in an internal flow proportional counter. (The filtrate is not discarded until the precipitate is counted and the results are deemed negative.) Counter efficiency, background, and self-absorption corrections are made, and the data are recorded as disintegrations per minute per 24-hr sample. Gamma scintillation studies may be made if necessary, and the precipitates may be retained in a desiccator for decay or other appropriate studies if desired.

Verification of theoretical predictions encompassed two types of experiments. The first consisted of adding known amounts of various radionuclides to urine samples and then subjecting the samples to the procedure just outlined. Samples containing the added activity were compared to control samples, and the percent recoveries were calculated. The results of this study are shown in Table I.

Table I

Isotope(s)	Beta Recovery %	Alpha Recovery %	Gamma Recovery %
Mn ⁵⁴	20 ± 2	-	95 ± 2
Co ⁶⁰	43 ± 4	-	70 ± 7
Sr ⁹⁰ -Y ⁹⁰	78 ± 9	-	-
Zr ⁹⁵ -Nb ⁹⁵	34 ± 5	-	95 ± 4
Ru ¹⁰³ -Rh ^{103m} Ru ¹⁰⁶ -Rh ¹⁰⁶	42 ± 8	-	51 ± 5
Cs ¹³⁷ -Ba ^{137m}	1	-	1
Ba ¹⁴⁰ -La ¹⁴⁰	88 ± 4	-	-
Ce ¹⁴¹ Ce ¹⁴⁴ -Pr ¹⁴⁴	96 ± 3	-	-
U + dtrs	67 ± 7	55 ± 7	-
Th + dtrs	49 ± 5	53 ± 3	-
Mixed Fission Products	58 ± 5	-	-

The recoveries are presented according to the type of emission observed, i.e., alpha, beta, or gamma. The apparent discrepancy between the beta recovery and the gamma recovery for some of the isotopes (Mn^{54} , Co^{60} , the Zr^{95} - Nb^{95} duet) is attributed to the use of a beta self-absorption correction factor derived from Tl^{204} . This isotope emits beta particles having a maximum energy of 0.765 Mev. Factors derived from studies with Tl^{204} are used for all beta corrections, since thallium has an energy representative of the average energy of most beta emitters which are expected. For isotopes with lower beta energies, such as those mentioned, the self-absorption factor is low, and for those having greater beta energies, the self-absorption correction is high. Since the beta energy of possible urine contaminants will obviously be unknown in advance, the use of an average-energy beta correction factor is justifiable on a routine basis. Therefore, although the evident removal of low-energy beta emitters appears unsatisfactory on the basis of beta-counting data, the actual removal is much better, as evidenced by gamma scintillation studies.

The second phase of experimental work was the analyses of a series of urine samples "spiked" with known amounts of either a conglomerate of fission and activation products, natural thorium, and its daughters, or natural uranium and its daughters. These samples were analyzed under pseudoroutine conditions, since the analyst did not know which of the samples were spiked; controls were also analyzed for comparative purposes. The analyst did not know the amount or type of spike added. The results of this study are presented in Table II.

Table II

Series	Average Alpha Control (dpm/L)	Number	Average Beta Control (dpm/L)	Number	Average Alpha Error (%)	Number	Average Beta Error-Alpha Spikes-(%)	Number	Average Beta Error-Beta Spikes-(%)	Number
A	61	9	673	3	28.9	6	40.9	6	30.7	6
B	113	9	671	3	13.4	6	18.6	6	35.8	6
C	170	9	407	3	43.0	6	31.5	6	27.1	6
D	98	9	327	3	38.5	5	25.2	5	23.4	6
E	193	9	602	3	25.7	6	18.5	6	43.5	6
F	119	9	791	3	41.7	6	32.4	6	47.1	6
G	12	9	0	3	13.7	6	27.2	6	41.8	6
H	10	9	0	3	19.1	6	33.4	6	55.2	6
Avg.	97	72	434	24	28.0	47	23.5	47	38.1	48

The overall effectiveness of the procedure is presented in Figure 1 in the form of a shaded periodic table. The different shadings represent the sensitivity of the procedure for that particular element and the evidence upon which the conclusion is based. Satisfactory results were obtained experimentally for those elements in the cross-hatched squares. Satisfactory results on the basis of the chemical similarity of the element to an element on which direct measurements were made are predicted for those elements indicated by squares with the dot pattern. For example, satisfactory recovery of lanthanum, cerium, and praseodymium is extrapolated to include the other twelve rare earths. A square with a

diagonal pattern is used for those elements for which no recovery was expected, and in particular for those elements of atomic number 95 through 102 which are not expected to be encountered and for those elements which do not have a known isotope of appreciable half-life. Elements in the unshaded squares are in the area of uncertain behavior. (Some daughter elements of thorium and uranium are multishaded since they were not tested explicitly, but recoveries were obviously made in conjunction with tests on the parent.)

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
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Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mv	No
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Fig. 1

Although the absolute sensitivity of the procedure has not been established experimentally, numbers of the observations were made at various activity concentrations for some of the isotopes. The range of activity concentrations studied is given in Table III along with a theoretical calculation of the sensitivity, derived on the assumption that the detection limit is twice the standard deviation of the background determination. For comparative purposes, the maximum permissible excretion rate per day, based on a chronic exposure to the maximum permissible air concentration for each isotope, is presented in column four of Table III.

The cost of performing these analyses is relatively modest. On a routine basis, operating supplies (including reagents), carrier solutions, pH adjustments, glassware breakage, etc., will average about forty to fifty cents per sample processed. On a volume basis of approximately twenty or more samples per week, each analysis will require approximately one man-hour of labor. Laboratory installation requirements are not stringent, hoods and adequate counters being the major items.

On the basis of experimental evidence obtained, we conclude that the ammonium carbonate-hydroxide procedure will yield satisfactory results at a competitive price when fission and activation products are the

primary source of contamination. The procedure could also be advantageous in some cases of operations limited to work with one or two isotopes in the determination or "screening" of samples to be analyzed for specific isotopes.

Table III

Isotope(s)	Experimental Activity Conc, dpm/L	Theoretical Sensitivity, dpm/L	Maximum Permissible Excretion Rate, dpm/24-hr
Mn ⁵⁴	476 to 9,120	400	1.2×10^6
Co ⁶⁰	97,080	200	1.6×10^7
Sr ⁹⁰ -Y ⁹⁰	442 to 14,640	110	390
Zr ⁹⁵ -Nb ⁹⁵	224 to 3,584	250	1.5×10^5
Ru ¹⁰³ -Rh ^{103m} Ru ¹⁰⁶ -Rh ¹⁰⁶	6,130 to 245,000	300	10^7
Cs ¹³⁷ -Ba ^{137m}	294,520	-	6.6×10^5
Ba ¹⁴⁰ -La ¹⁴⁰	549,720	100	3.6×10^5
Ce ¹⁴¹ Ce ¹⁴⁴ -Pr ¹⁴⁴	646 to 14,212	90	1.7×10^5
U + dtrs	13,800 alpha 23,000 beta	40 alpha 130 beta	500 alpha + beta
Th + dtrs	14,700 alpha 22,840 beta	35 alpha 120 beta	1,000 alpha + beta
Mixed Fission Products	1,036 to 12,950	150	-

THE DETERMINATION OF β -EMITTING RADIONUCLIDES IN AQUEOUS FORMAMIDE SOLUTIONS

by

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The assay of carbon-14 in formamide solutions has been discussed in previous publications.^(1,2) The ease with which these determinations can be made led to the extension of this method to other radionuclides. Attempts were made to count P^{32} from "infinitely thick" solutions. Although this method was useful, the depths of the liquid, of the order of 9 mm, was such that the solution frequently slopped over as the counter was slid into place. It was subsequently found that infinitely thick solutions were unnecessary, and that the planchets used for carbon-14 could be used provided that exact counters were pipetted into the sample holder. The amount used was 1 ml, which did not quite fill the planchet. With the exception of gold-198, all the beta or beta-gamma emitters available in the laboratory were successfully counted by means of the formamide technique.

Procedure

A suitable carrier, 10 mg of the appropriate acid or salt, i.e., phosphoric acid for P^{32} , sodium chloride for sodium-22 or -24, is weighed into a 10-ml volumetric flask. One-tenth to 1 ml of an aqueous solution of the radionuclide to be counted is added to the carrier, the flask and the solution then being made up to volume with purified formamide.⁽²⁾ If the activity is too high for counting, 1 ml of this solution is added to 10 mg of carrier in a second flask and made up to volume with formamide. If a windowless flow proportional counter such as the one used in this laboratory* is available, a sample containing an activity of up to 500,000 cpm may be counted.

The detection equipment is calibrated by counting a known solution previously calibrated by an absolute counting technique, such as 4π counting or β - γ coincidence. This gives a counting efficiency for the particular nuclide under the conditions to be used in future determinations. Once the counter has been calibrated, the calibration remains constant for years.

*PC3A - Nuclear Measurements Corporation, Indianapolis, Indiana

In our laboratory, the counter as calibrated by a uranium oxide specimen remained constant to better than 1% over a period of eleven years.

In order to check the performance of the detection system, a reference sample such as mentioned above may be made by mixing a suitable amount of uranium oxide with either Ward's bioplastic or epoxy resin and pouring the mixture into a planchet of exactly the same size as the one used in subsequent determinations. The planchet is covered with sufficient aluminum foil, approximately 10 mg/cm², to absorb the alpha particles. It might be advisable to use two reference samples, one of uranium and another of carbon-14 in the form of a wafer of conducting plastic. The use of two reference samples, one with high-energy and the other with low-energy beta rays, is to insure that there is no discrimination in the efficiency of the detector against low-energy beta rays.

Table 1 gives the efficiency which has been found for various radionuclides using this technique. Table 2 shows the reproducibility when 1-ml aliquots are pipetted into the counting planchet at different times and counted.

Table 1

Radionuclide	Carrier (10 mg)	% Efficiency
Na ²²	NaCl	11.6 ₁
Na ²⁴	NaCl	31.2 ₁
P ³²	H ₃ PO ₄	35.7 ₃
S ³⁵	Na ₂ SO ₄	1.14 ₅
K ⁴²	KCl	49.9 ₄
Fe ⁵⁹	FeCl ₃	4.97
Co ⁶⁰	CoCl ₂	4.22 ₅
Sr ⁹⁰ -Y ⁹⁰	SrCl ₂ YCl ₃	24.7 ₉
Cs ¹³⁷	CsCl	10.5 ₄
Pm ¹⁴⁷	NdCl ₃ - 10 mg Citric Acid-300 mg	1.66
Hg ²⁰³	Hg(C ₂ H ₃ O ₂) ₂	3.55
Tl ²⁰⁴	Tl(NO ₃) ₃	12.4 ₃

Table 2

REPRODUCIBILITY

1-ml aliquots of P^{32} solution.
Decay corrected to 1430-4/6/59

1.	208,300
2.	206,800
3.	208,100
4.	206,400
5.	207,700
6.	208,400
7.	208,200
8.	208,800
9.	208,200
Average 207.9	
Standard Deviation = 0.8	

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INITIAL TWO-YEAR EXPERIENCE WITH THE
SAVANNAH RIVER PLANT PLUTONIUM
URINALYSIS PROCEDURE*

by

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Introduction

The first analytical procedure used for plutonium urinalysis at the Savannah River Plant (SRP) was adapted from techniques used at Hanford Atomic Products Operations and Oak Ridge National Laboratory. Development work, started in 1956 at SRP by S. C. Leidt and S. M. Sanders, resulted in a new and more sensitive procedure. This procedure requires a smaller urine sample and decreases the number of operations and the analysis time.

The new procedure was presented at the fifth meeting on Bio-Assay and Analytical Chemistry in October 1959. The method consists of wet ashing the urine, purification of the plutonium by anion exchange, elution by sulfurous acid, and electrodeposition in nitrate media on a stainless steel disc. The disc is autoradiographed on nuclear track emulsion plates, and the resulting tracks are magnified and counted by a microprojector.

With some exceptions the new procedure (which was put into routine use in May 1959) proved to be as advantageous as claimed⁽¹⁾ by Leidt and Sanders; the two-year accumulation of data further substantiated the statements and analytical results described in their procedure.

This paper describes problems that arose and procedural modifications adopted, outlines development work associated with the analysis, and summarizes the statistical data accumulated during the initial two-year experience with the procedure.

*The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

Discussion

Difficulties and Procedure Modifications

Problems which arose during routine application of the new plutonium urinalysis procedure resulted in several modifications.

Dissolution of Inorganic Residue. Soon after the method of analysis was placed in use, it was noted that the inorganic solids remaining in many routine samples after the wet ashing step were not completely dissolved by the 8N nitric acid solvent. These solids caused the ion exchange column to clog and thus decreased the flow rate. Apparently, some of the nitrates would not dissolve in the small volumes of nitric acid specified in the procedure. This was overcome by first adding distilled water, warming, and dissolving as much of the solid material as possible. Small portions of concentrated nitric acid were then added, with gentle warming between each addition. The total volume of concentrated acid equalled the volume of water; thus, the solvent gradually was concentrated to 8N. Some finely divided particles, which proved to be phosphates, did not dissolve in water, but were eventually solubilized as the acid concentration was increased.

Allowing the solution to stand overnight and increasing the volume of solvent from 25 to 40 ml aided in complete dissolution of solids. After it was determined that these changes had no adverse effect on plutonium recovery, they were incorporated in the routine procedure. The column reservoir was modified to contain the entire 40 ml of solvent solution.

Evaluation of Uranium Decontamination Factors. Leidt and Sanders reported the decontamination factor for uranium to be greater than 60 for the ion exchange step. Forty-six spikes, containing from 0.3 to 65.5 d/m uranium per 1.5 liters of blank urine, were analyzed by this procedure to further evaluate the uranium decontamination factors. Results are listed in Table 1. Not enough uranium was recovered to be reported as a positive

Table 1

URANIUM DECONTAMINATION FACTORS

Spike Value, d/m/1.5 l	Number of Samples	Average Recovery, d/m/1.5 l	Average DF
65.5	2	0.035	2000
32.8	4	0.022	1500
6.0	10	0.003	2000
3.0	10	0.003	1000
0.6	10	0.006	100
0.3	10	0.002	150

plutonium result (greater than 0.05 d/m per 1.5 l) except in two instances. Even in these few exceptions, it was not conclusive that the tracks were due to the uranium spike since the total number of tracks were within the statistical extremes shown by urine blanks.

Autoradiography. Occasional fogging of the nuclear track emulsion slides used in the autoradiography step was eliminated by substitution of hydrogen peroxide for chromic acid as a track eradicator. The slides were exposed to the vapors of a 0.0075 percent hydrogen peroxide solution in a dessicator for 16 hr prior to use in the autoradiographic cameras. Difficulties were encountered with the Lucite indexing block component of the brass autoradiographic cameras. Frequent realignment of the microprojector staging was necessary because the camera disc positions were not uniform. A standard slide with inked circles indicating the correct disc position was prepared, and those indexing blocks which failed to match the slide were discarded. A slide with intersecting lines at the center of each reading position was also prepared for periodic alignment of the microprojector.

Reagent Contamination. Reagent contamination caused one of the most annoying problems which arose during the first two-years of experience with this procedure. During the latter part of July 1960, the urine blank and low-level spike data moved considerably out of control limits. The contamination was eventually traced to the sulfurous acid used to elute plutonium from the anion exchange resin. The contaminant was identified as radium-226 and its daughters.

The procedure requires 5 ml of sulfurous acid per sample and the contaminated lot contained 0.2 d/m alpha contamination in this volume of acid. Since radium and its alpha-emitting daughters were not completely electrodeposited under the conditions of this procedure, the resulting alpha activity on the discs was quite variable and caused erratic answers, especially in the blank urine and low level spike samples.

Development Work

Efforts to improve the analysis covered nearly all the procedural steps and are enumerated in the succeeding paragraphs.

Ion Exchange. Current studies are directed toward improvements of the ion exchange step of the analysis. A resin was desired which would allow a faster flow rate than the Amberlite CG-400, type 2 currently used, but would continue to provide good absorption. Additionally, an eluting agent was desired that would yield better recovery of plutonium from the ion column than sulfurous acid.

Table 2 shows the results of anion resin evaluations. Dowex 21K, 50 to 100 mesh resin exhibits the same retention characteristics for plutonium in 8N nitric acid as the Amberlite CG-400, type 2 resin, but provides an increase in flow rate by a factor of 10.

Table 2

EVALUATION OF ANION RESINS

Resin	Plutonium in Effluent,* %	Approx Flow Time, min
Dowex 1, 50-100 mesh	5	20
Dowex 1, 100-200 mesh	8	25
Amberlite CG-45, Type 1	25	20
Amberlite CG-400, Type 2	3	60
Dowex 21K, 50-100 mesh	1 to 4	6

*Solution volume was 15 to 20 ml of 8N HNO₃.

As shown in Figure 1, plutonium concentration in the column effluent increases when the volume of 8N nitric acid is increased. Use of longer columns is under investigation to take advantage of the improved resin. The effect of inorganic salts, in the quantity found in wet ashed urine, on column behavior is also under investigation.

Figure 1. Effect of solution volume on the retention of Pu on Dowex 21K resin.

As noted in Table 3, procedural recovery of the 0.84 d/m/1.5 liters spike averages 70 percent. It is believed that the largest part of plutonium loss is due to incomplete elution by sulfurous acid. Based on data presented by Wish and Rowell,⁽²⁾ hydrochloric acid was evaluated as a replacement for sulfurous acid as an elutrient.

Table 3
SPIKE RECOVERY

Spike Value, d/m/1.5 l	Period	Mean Recovery, %	Precision, % (95% CI)
0.042	May 1959 through Jul 1960	53	29
0.042	Jan 1961 through Jun 1961	62	42
0.084	May 1959 through Jul 1960	51	30
0.084	Jan 1961 through Jun 1961	70	36
0.84	May 1959 through Jul 1960	65	30
0.84	Jan 1961 through Jun 1961	74	34

The most effective concentration evaluated was 2N HCl. Using Dowex 21K resin, 95 to 100% of the plutonium was eluted with 10 ml of 2N HCl. Using Amberlite CG-400, type 2 resin, comparable recovery was obtained only when elutrient volume was increased to 20 ml. Since 20 ml is too large a volume for use with the electrodeposition cells and an additional evaporation step is not desired, hydrochloric acid will not be employed until the problems concerning the use of Dowex 21K resin are solved.

Electrodeposition and Autoradiography. An adaptation of the electrodeposition of plutonium from chloride media devised by R. F. Mitchell⁽³⁾ was evaluated for use in connection with the ion exchange improvements. This approach was found to be successful only when the cathode area was greater than 0.64 cm². The area in present use is 0.1 cm². The increased plating area will be advantageous if the use of solid-state counters proves feasible.

If the area of the nuclear track emulsion slide, which is exposed to the electrodeposited plutonium, could be magnified and photographed, the resulting picture would afford a better method of track counting than the microprojector technique. The electrodeposited area should be no larger than 0.5 mm², in order to obtain a satisfactory picture. Efforts to deposit plutonium on the polished end of a platinum wire were begun by S. C. Leidt and continued by the author.

Various techniques employed to ensure that deposition was confined to the end of the wire included: (1) encapsulment in a ceramic holder, (2) coating the wire with Krylon, and (3) use of several different types of plastic holders. None of these were entirely satisfactory, but imbedding the wire in a Lucite holder sufficed for preliminary studies.

Several electrolytes were evaluated for depositing plutonium on the small-area cathode. The best results were obtained with a nitric acid-ammonium oxalate solution. Analysis of the electrolyte after deposition showed less than ten percent plutonium remaining in solution. However, the formation of a carbonaceous deposit on the electrode interfered severely with the counting of the plutonium deposited.

Efforts to avoid the formation of the black deposit included: (1) the use of oxidizing agents, lower currents, and different metals for the cathode, and (2) flaming the end of the wire. These were either unsuccessful or resulted in no plutonium deposition. No development work is being conducted on this portion of the procedure at present.

Silicon solid-state counters are being evaluated for possible replacement of the autoradiography portion of this procedure. These counters exhibit very low backgrounds, some with less than one count per day. The units with backgrounds this low are exceptions, and, thus far, such very low background detectors cannot be constructed consistently enough for routine use in the plutonium procedures. These counters were recommended for routine use in the enriched uranium urinalysis, where higher backgrounds can be tolerated.

Statistics

Figures 2 through 7 show a two-year summary of the monthly data compiled in connection with routine plutonium urinalyses. The arithmetic mean number of tracks is plotted for spikes and urine blanks and the precision at the 95% confidence interval is shown. The same data are presented for slide background as a verification of track eradication efficiency and for tracks caused by a 5-min exposure to a plutonium source. The latter serves as a control of slide quality. Table 3 shows average percent plutonium recovery for each of the three spikes over a two-year period.

Five "standard slides" were prepared by exposing the nuclear track emulsion slides in the source position for varying times to a plutonium source. This was done to evaluate the fraction of total procedural error that is due to track counting errors. These slides were then read daily in random order and the resulting track counts analyzed. Data compiled are presented in Table 4. Comparison of these results with the 0.84-d/m/1.5 liters spike data shows that about one-third of the total error is due to track counting.

Figure 2. Data for urine blank samples.

Figure 3. Data for the 0.042-d/m spike.

Figure 4. Data for the 0.084-d/m spike.

Figure 5. Data for the 0.84-d/m spike.

Figure 6. Slide background data.

Figure 7. Source data.

Table 4

STANDARD SLIDE COUNTS

Source Number	Number of Times Read	Average Number of Tracks	Deviation, % (95% CI)
1	7	342.6	2.0
2	7	322.1	2.0
3	9	250.7	10.3
4	9	234.9	5.3
5	10	413.5	9.1
6	10	455.2	4.9
7	14	153.0	11.4
8	14	170.9	11.9

The analysis of fourteen "audit" samples containing a known amount of plutonium from 0.05 to 1.68 d/m/1.5 liters of urine averaged 91 percent of the correct value, with a standard deviation of 25 percent.

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CRITICALITY AND CRITICALITY CONTROL

by

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Introduction

During the past few years unique kinds of industrial operations, previously carried out only in the large government-owned plants operated for the Atomic Energy Commission, have been undertaken also in commercial plants. These plants, although supported in part or whole by government funds, often are privately owned buildings located near urban areas. These operations are unique from the safety viewpoint because the hazards cannot be detected beforehand, as in the case of radiation, toxic fumes, and industrial dusts. Rather, off-standard safety conditions in fissionable material-processing plants might, or might not, result in a serious nuclear incident. Although thermal energy might damage nearby equipment, the importance of such an incident lies in the production of lethal radiations to workers and possible radioactive contamination in the vicinity. One must, therefore, understand the conditions which could initiate this energy burst, i.e., the conditions for criticality, and how such conditions may be controlled by equipment or procedure design to achieve nuclear safety. It should be pointed out that criticality control or nuclear safety is often not an exact science; nuclear safety is partly an art.

What, then, is criticality and criticality control; what is the fission process?

In general, there are three forms of stored, natural energy available to man, namely:

1. potential energy in the form of falling water;
2. chemical energy liberated during the rearrangement of molecules, as in the burning of coal; and
3. nuclear energy which results from the rearrangement of certain atomic nuclei, such as during fission.

The difference between nuclear energy and the other energy sources is in the process used to free the energy. Potential energy is freed as water goes from one level to another in rivers and mechanisms are interposed

which divert some of the energy for use. The second way is to rearrange the molecular structure by converting material from a less to a more stable form, thereby producing heat, as in the burning of coal, or electricity, as in a battery. The third method involves nuclear reactions in which the atomic nuclei are changed.

In drawing on these three kinds of energy storage, we are really exploiting three kinds of physical force fields: gravitational, electric, and nuclear. We know of other kinds of fields (i.e., neutrino, higher order meson) but these are apparently very weakly interacting with common matter, and so do not seem to provide any practical means for storing energy.

It has sometimes been pointed out that in nuclear fission man has found power which has not come from the sun. The water in rivers was once rain and before that was evaporated from the ocean by the sun's heat. The coal which is mined from under the earth was living matter in the carboniferous age, about 200,000,000 years ago, and the energy was put there by photosynthesis which also drew on the sun's heat. The energy from fission has, however, existed in potential form as long as matter has been in its present state. When the elements were first formed, they had a mass distribution with a large amount of associated free energy. The sun and stars have been feeding on this supply ever since and now we have found a way of getting at some of the same vast resources.¹

The fission process, then, is the fundamental reaction in nuclear reactors or chain-reacting piles. Isotopes whose nuclei undergo fission are U^{233} , U^{235} , and Pu^{239} . Although other nuclei are also fissionable, their use in reactors is impractical for various reasons.

The large energy release in the fission process and the associated production of radiations and radioactive fission products constitute the hazards of criticality and of nuclear reactors. Good reactor design, in addition to the achieving of an economic reactor core, consists in:

1. Safely removing the energy, which is manifested largely as heat. If the heat were not removed, the fuel and its associated materials might melt or burn, and disperse the toxic fission products and fuel outside the reactor proper.
2. Containing the fission products. Most reactor fuels are clad or canned in a nonfissile metal. Large reactors are also contained inside large metallic spheres.
3. Attenuating the radiations to safe levels by massive shields, usually made of water, concrete and/or iron.

¹Unpublished Reactor Physics Lecture, H. Kouts, BNL

In nuclear safety, on the other hand, one is concerned only with the prevention of criticality.

Principles of Nuclear Safety

Problems of nuclear safety can be divided into two major categories. The first involves the prevention of criticality in systems normally sub-critical; the second involves the prevention of supercriticality in systems normally critical. In other words, the first category is nuclear safety as we will discuss it here, and the second deals with reactor safety.

In general, the assurance of nuclear safety is a three-step problem. First, there are the scientific considerations having to do with the measurement of basic nuclear properties, the subsequent calculation of critical parameters, and a comparison of these parameters with the results of critical experiments. The next step involves the engineering problems, wherein one determines that the contemplated disposition and configuration of fissionable material in the design of a fabrication or process conforms to nuclearly safe values. This safety of design must not be alterable by off-standard conditions, such as human or equipment failure. The third step in assuring nuclear safety is administrative in nature in that controls must be set up or modified to offset possible equipment and personnel failure. This step should also involve an independent check of the proposed process, for example, by examining the technical details of a proposed AEC contract or license application. However, the nuclear energy business has expanded so that there are not enough persons available to resolve adequately the daily problems of nuclear safety. This is especially true in the case of small plant or commercial-type fabrications, where the services of a full-time criticality engineer cannot usually be justified. Hence, the independent analysis by the AEC is very important. The Health and Safety Laboratory (HASL) has been concerned with the prevention of unwanted criticality in the processing of unirradiated fissionable material for about seven years. In general, it is a requirement of the New York Operations Office (NYOO) to require its S. S. Accountability Stations to devise a nuclear safety plan acceptable to the HASL, which supplies technical staff assistance to the NYOO.

The conditions sought in nuclear safety are quite opposite to those desired in nuclear reactor design. In the latter case, good neutron economy is essential, while, when striving for nuclear safety, the loss of neutrons by leakage from the fissionable material and by absorption in nonfissionable materials ought to be as great as feasible.

First, consider what good neutron economy is by examining an idealized, critical thermal-neutron system. Starting with a representative 100 thermal or slow neutrons, we can follow the neutron balance established

at criticality. In Figure 1, a total of 43 neutrons are captured and absorbed, but do not produce fission. Fifty-seven thermal neutrons are captured by U^{235} nuclei and cause fission, producing 139 new neutrons, which are fast (have high energies). Fission by fast neutrons produces additional neutrons for a grand total of 143 fast neutrons. These fast neutrons are then slowed down or thermalized by any moderating material present. During this slowing down, 16 neutrons are absorbed and 26 leak out of the system. Hence, a total of 101 thermal neutrons result from this idealized chain. If a further neutron leaks out of the system, we have a perfect balance, 100 neutrons put into the system resulting in 100 neutrons out. Such a cycle is a "chain." If the last thermal neutron did not leak out, but eventually produced a fission, there would have been a neutron excess. Hence, the former system is critical, whereas the latter is supercritical, in which neutrons would be multiplied ad infinitum. If there had been an output of less than 100 neutrons, the system would have been subcritical.

Fig. 1. Neutron cycle in critical thermal system

It is clear, then, that nuclear safety involves the assurance that either or both of neutron leakage from the system and absorption not leading to fission be maximized in some way.

In discussing criticality in simple terms, as above, I have ignored the possibility of preventing criticality simply by excluding neutrons from the system. This possibility is extremely impracticable, since appreciable quantities of neutrons exist at all times. To provide an adequate neutron shield, one which would remove all neutrons, is virtually impossible. Remember that, given a critical or supercritical system, all one needs is

a single neutron to initiate the chain. Thus, dependence on nuclear safety is placed on adjusting the system so that a high fraction of the neutrons released by any chance fission either undergo parasitic capture or escape from the system so that, on the average, fewer fissions occur in later generations or cycles than in the earlier ones.

In fabrication and processing plants, though the background neutron level, i.e., the background fission rate, cannot be made zero, extremely low levels do exist, since neutron sources are not placed in these plants. This low neutron background permits a significant time delay between the establishment of a supercritical configuration and the initiation of a chain reaction by a chance neutron. For example, the Godiva I assembly was operated at Los Alamos without the use of a neutron source, and the time delays were measured. The observed delay times ranged from 2 to 10 sec for the case of one-dollar reactivity addition.² It was found that the delay time is a function of the reactivity addition and the background fission rates. The delay time becomes important when a large amount of reactivity is available and the addition rate is large. In such a circumstance, one could conceivably add all of the reactivity, if in a low neutron background, before a chance neutron begins the reaction. In other words, one can achieve a greatly supercritical assembly and, therefore, a greater energy burst, in this case.

The potential for uncontrolled criticality, coupled with another aspect of fabrication or processing plants, summarizes the seriousness of assuring that adequate provision for nuclear safety exists in these plants. These plants are operated in much the same manner as any small metallurgical shop or chemical plant. The workers often carry out the process steps directly and, hence, would be afforded little or no protection from the prompt radiations produced in the event of uncontrolled criticality. Further, there are no shutdown mechanisms specifically provided. Termination of the chain reaction, or at least of the initial pulses, would be accomplished by destruction or distortion of the system in question. Conceivably, one could have a chain reaction lasting indefinitely, similar to that in the Y-12 accident.³ It is clear, then, that a nuclear incident in one of these plants would be extremely serious, though more localized than a reactor accident.

At this point, one should mention the importance of outside effects on the fission process.

²H. T. Williams *et al.*, Safety Analysis of Enriched Uranium Processing, NYO-2980 (March 1960).

³Accidental Radiation Excursion at the Y-12 Plant, Y-1234 (June 1958).

Soon after the discovery of natural radioactivity, it was noted that none of the usual factors affecting chemical reactions, such as changes in temperature, had any effect upon the rate of the emission of the radioactive emissions. In fact, this was one of the reasons originally given for the fact that radioactivity was a function of the atomic nucleus and not of the extra-nuclear structure. Similarly, it should be noted that the fissionable properties of the materials concerned are entirely those of the atomic nuclei and are not greatly affected by their chemical state. Thus, U^{235} as a part of the compound UO_3 has about the same reactivity as it does as a part of the compound UO_2 . The same considerations apply to those substances which, when mixed with fissionable materials, form systems which affect the ability to sustain a nuclear chain reaction. For example, hydrogen is probably the most significant moderator. Thus, hydrogen in water has the same effect as the hydrogen of oil or acid. Critical-mass information about chemical solutions or homogeneous systems is often based on uranium-water systems. If, however, nitric acid is used as dissolving agent, one would require larger masses of uranium for the same concentration to achieve criticality. This is because nitric acid acts as a neutron poison and because the hydrogen concentration of the resulting solution, i.e. of the neutron moderator, is less than that of water. To take advantage of this possible increase in the quantity of uranium needed for criticality, one must be prepared to guarantee a minimum nitric acid acidity to assure nuclear safety. If another acid is used, such as hydrofluoric acid, the minimum critical mass is not much different than for a similar water system because of the low neutron absorption of fluorine.⁴

In the same manner, a rise of temperature of fissionable materials has no effect upon the achievement of criticality except, for example, as the system is incidentally affected by a reduction of density due to expansion, or the change in the average thermal energy of the molecules and atoms involved and, thus, of the neutrons.

Significant Control Factors

Now it is appropriate to discuss what some of the controlling factors are and how they are applicable to nuclear safety.

Shape. As mentioned earlier, by maximizing neutron leakage from a system containing fissionable material, nuclear safety can be assured. In a chemical processing plant, one should specify container and pipe sizes and shapes to achieve large surface-area-to-volume ratios. The most reactive fissionable material shape, i.e., the shape with minimal neutron leakage, is a sphere. Hence, where a reactor designer may strive

⁴N. Ketzlach, Nuclear Safety Considerations in Reprocessing Plant Design, Chemical Engineering Progress (July 1957).

for a near-spherical shape, one concerned with nuclear safety specifies thin cylindrical or slab shapes. In other words, containers of solutions can be designed to be subcritical, regardless of the quantity of fissionable material contained.

In general, the influence of shape can be further illustrated by referring to a parameter called geometric buckling, denoted by B^2 . The description of B^2 has appeared in many textbooks, such as *The Elements of Nuclear Theory* by S. Glasstone and M. Edlund. In a critical, thermal-neutron reactor, the thermal-neutron flux satisfies the wave equation

$$\nabla^2 \phi + B^2 \phi = 0 \quad ,$$

where B^2 is the lowest eigenvalue that results from solution of this equation subject to the boundary condition that ϕ becomes zero at the extrapolated boundary of the system in question. The dimension of buckling is reciprocal area.

Values for some common shapes appear in Figure 2. It is clear from this table that spherical systems have the smallest critical volume. Since neutron production occurs throughout the volume and leakage increases with surface-area-to-volume ratio, it is clear that spherical shapes are the most reactive for a given composition and should be avoided.

Fig. 2. Bucklings and minimum critical volumes for common shapes

Geometry	Buckling	Minimum Critical Volume
Sphere	$(\pi/R)^2$	$130/B^3$
Rectangular Parallelepiped	$(\pi/a)^2 + (\pi/b)^2 + (\pi/c)^2$	$161/B^3$
Cylinder	$(2.405/R)^2 + (\pi/H)$	$148/B^3$

Mass. One can see that if only a few U^{235} atoms exist in a given space, the chance is small that neutrons arising from an occasional fission will interact with these U^{235} atoms to produce additional fissions. In other words, with too few fissionable atoms present, a chain reaction is not possible. Hence, nuclear safety of a system can be ensured by limiting the mass of uranium (U^{235} atoms) in that system. It should be emphasized, however, that the critical mass value is not a single-valued function; it depends on many factors, some of which will be discussed. For a given, completely specified system or process step there is a minimum value for the critical mass for that system. Further, there is also a mass

value below which criticality can never occur in any system. In using mass as a control, the possibility of double-batching is considered. Hence, safe values rather than minimum critical masses are usually specified. In Figure 3, a listing of critical parameters, we see that 820 gm of U^{235} is the lowest mass with which one can achieve criticality in an optimum arrangement.⁵ The use of a safe value of 350 gm includes a safety factor of over 2 to ensure that double-batching is necessary before nuclear safety can be compromised.

Fig. 3. Minimum critical parameters for U^{235} assemblies*
(with infinite water reflectors)

Parameter	Minimum Critical Value	Safe Value
Mass		
Aqueous Solutions	820 gm	350 gm
Metallic Uranium	22.8 kg	10.0 kg
Volume, Aqueous Solutions	6.3 liters	4.8 liters
Diameter, Infinite Cylinder		
Aqueous Solutions	5.4 in.	5.0 in.
Metallic Uranium	3.1 in.	2.7 in.
Thickness, Infinite Slab		
Aqueous Solutions	1.7 in.	1.5 in.
Metallic Uranium	0.6 in.	0.5 in.
Concentration, Aqueous Solutions	12.1 gm/liter	10.8 gm/liter
U^{235} Enrichment of Homogeneous, Hydrogen-moderated U (w/o)	1.0	0.95

*TID-7016, Revision 1, Nuclear Safety Guide - 1961

At this point, one should mention a very basic guide, often called the "double contingency" rule. This says in effect that the simultaneous occurrence of at least two independent, unlikely events is necessary for criticality to become possible. Hence, a system would be safe if both the U^{235} content had to be double-batched and flooding by water would have to occur before criticality would be possible.

Density. A related controlling factor is the atomic density of the U^{235} . If the atomic density is lowered, i.e., if the U^{235} atoms are spaced further apart, criticality may be less likely. For unmoderated uranium metal, the critical mass of highly enriched uranium, almost pure U^{235} , is less than for a similar metal system where the uranium may be alloyed

⁵H. Paxton, et al., Nuclear Safety Guide - 1961, TID-7016.

with a nuclearly inert material like aluminum. Of course, if uranium is mixed with a neutron moderator, e.g., water or beryllium, an entirely different situation holds, and such mixtures have much smaller critical masses.

An example of this can be shown quite simply. Single batches of pure, highly enriched uranium should be limited to about 10 kg of U^{235} per batch. The BNL research reactor fuel element consists of aluminum-clad uranium-aluminum alloy. This alloy is about 8.5 w/o uranium (7.9 w/o U^{235}) in aluminum; hence, the density is about 2.89 gm/cm³. Full uranium density is about 18.7 gm/cm³. According to TID-7016, one can increase the allowable safe mass of U^{235} in a metal ingot by about a factor of 4. Hence, $10 \times 4 = 40$ kg of U^{235} as highly enriched uranium in a 8.5 w/o U-Al alloy may be considered safe as a single ingot.

Moderation. Cross sections for neutron captures which lead to fission increase greatly as the neutron energies decrease to the thermal range. This neutron thermalization takes place when fissionable atoms are mixed with certain materials called moderators. The most common moderating material found in a processing plant is the hydrogen in acids or ordinary water. The effect of neutron moderation is to decrease greatly the minimum critical mass for metallic U^{235} , about 22.8 kg, to about 0.8 kg for a homogeneously mixed U^{235} water system. Both of these values refer to the fully water-reflected situations. Figure 4 is a curve

Fig. 4. Effect of dispersing solid pieces of uranium (U^{235} enrichment 93.2%) metal in water.

obtained from Los Alamos Report LA-1958.⁶ The curve illustrates the variation of the critical masses of U^{235} as highly enriched uranium with the size of metallic pieces in water lattices. The uranium solution is the most reactive uranium system having a minimum critical mass of less than 1 kg of U^{235} . Critical mass increases with the metal size till a value of 22.8 kg of U^{235} is necessary for the reflected solid metal sphere. Each of the intermediate points represents an optimum lattice, that is, one with a minimum mass.

Concentration. The U^{235} concentration in solution also has an important effect in criticality. In the curve of Figure 4, the reduction of critical mass with decreasing size of the highly enriched uranium metal

⁶H. C. Paxton, Critical Masses of Fissionable Metals as Basic Nuclear Safety Data, LA-1958 (Jan 1955).

units was shown. Hence, homogeneous or solution data can often be used to assure the nuclear safety of heterogeneous enriched systems. However, the variation of fissionable material concentration in solutions also changes the criticality parameters significantly. There is an intermediate concentration at which the critical mass is a minimum. The variation is attributable to competing effects, principally the fast neutron-leakage probability and the neutron multiplication factor k .

A fairly simple computation can illustrate the effect of concentration on k .

$$k_{\infty} = \eta f = \frac{\eta}{1 + \left(\frac{H}{U^{235}}\right) \left(\frac{\sigma_U}{\sigma_H}\right)},$$

where k_{∞} is the multiplication factor for an infinite system, η is the average number of fission neutrons produced per thermal neutron capture, and f is the ratio of the thermal neutrons absorbed in the fuel to the number absorbed in the whole system. The σ 's are the usual microscopic cross-section values for the hydrogen of the water and U^{235} . The oxygen in the water is negligible. Obviously, as the H/U^{235} atom ratio increases, i.e., as more hydrogen is added, k_{∞} decreases slowly.

However, the systems of practical interest are finite in size, so that account of neutron leakage must be taken. This can be represented by a two neutron-energy-group notation:

$$k_{\text{eff}} = k_{\infty} U_t U_f,$$

where U_t and U_f are the thermal- and fast-neutron nonleakage probabilities, respectively, and k_{eff} is the multiplication factor of the finite system. Here, to maintain a constant value of k_{eff} , unity for criticality as H/U^{235} increases, the nonleakage probabilities must increase. In summary, at low H/U^{235} values, i.e., at high uranium concentrations, k_{eff} is large and the nonleakage probabilities relatively small. As H/U^{235} increases, k_{eff} becomes smaller and the nonleakage probabilities larger. At high H/U^{235} values, neutron absorption by the moderator, hydrogen, predominates, and the required critical mass becomes large.

There exists an $H:U^{235}$ atom ratio above which criticality is impossible. Recall that

$$k_{\infty} = 1 = \frac{\eta}{1 + \frac{H}{U^{235}} \frac{\sigma_U}{\sigma_H}}$$

for criticality in an infinite system. Since $\eta = 2.08$ and $\sigma_H/\sigma_U = 0.00048$,

$$1 + 0.00048 \frac{H}{U^{235}} = 2.08$$

Therefore,

$$H/U^{235} = 2250$$

Hence, uranium solutions having atom ratios above this value, or containing less than about 11.6 gm U^{235} per liter, cannot become critical. Note that this calculated value should be compared with the experimental value of 12.1 gm/cm³ in Figure 3.

Reflection. Surrounding fissionable material with almost any material will increase the reactivity of the system by reduction of neutron leakage. Just as the mixing of a moderator with fissionable material often increases reactivity, i.e., results in a lower mass requirement for criticality, so the addition of a neutron reflector has a similar effect. In evaluating the safety of processes, it is customary to assume more severe operating conditions than one would normally expect. Hence, most processes are designed to be safe even in the unlikely event of flooding with water. Of course, flooding of a process area is possible, because of failure of a water main or sprinkler system. A more important reason for the flooding assumption, however, is to account for the unknown neutron-reflecting properties of incidental materials, such as equipment, walls, and personnel. If a single unit or system containing fissionable material is subcritical or safe under flooding conditions, it would be safe during reasonably foreseeable abnormal conditions.

Removal of the reflector from between neighboring units, however, can increase the reactivity of an array by neutron interaction. The interaction problem is discussed later. Two examples to illustrate the effect of a reflector are noteworthy. First, Figure 5 illustrates how the addition of a thick water reflector affects the critical mass (M_C) of metal spheres of U^{235} and plutonium. An unreflected sphere of highly enriched uranium has a critical mass of about 48 kg of U^{235} , which is reduced to 22.8 kg, the value mentioned earlier. Plutonium experiences a similar reduction by a factor of two in critical mass. The second example, was inferred from some early Oak Ridge work with uranyl fluoride solutions by Beck, Callihan,

Fig. 5. Comparison of critical masses of unmoderated Pu and U^{235} spheres*

Reflector	Plutonium Critical Mass (kg)**	U^{235} Critical Mass (kg)
None	~10 (α) 15.55 (δ)	48.0
Water	~5.6 (α) 7.57 (δ)	22.8

*Critical Data for Nuclear Safety Guidance, LAMS-2415.

**Density α = 19.8 gm/cm³; Density δ = 15.65 gm/cm³.

and others, and appears as Figure 6.⁷ The reactivity increase by neutron reflection is illustrated clearly here. For a 10-in.-diameter, aluminum-contained, homogeneous reactor, water reflection reduces the required critical mass of U^{235} by about 58% of the mass needed for a bare cylinder. The reduction achieved by adding a reflector for the stainless steel case is only about 51%. The curves indicate that in both cases adding reflectors becomes somewhat less important as diameter increases. This is explained by the fact that, for a given concentration of U^{235} , a large fraction of the neutrons escape a reactor of smaller diameter and becomes available for reflection. As the reactor size increases, therefore, the critical masses with and without a reflector become more comparable.

Fig. 6. Critical aluminum reactors

Interaction. Up to now we have considered the factors affecting the criticality of units or systems within a process. It is entirely possible, however, to achieve criticality with the proper arrangement of two or more subcritical systems.

To ensure safety of a unit, the neutron leakage is increased. In doing so, however, the escaping neutrons might enter a neighboring system, resulting in inadequate leakage from the multi-unit system. Here, it should be made clear that in a two-unit interacting system the units are either both subcritical or both critical. Similarly, one cannot make a system critical simply by adding neutrons. Rather, the units must be capable of supporting a chain reaction; the neutrons leaking from one previously subcritical unit to the other can simply reestablish the neutron balance required for criticality.

⁷C. K. Beck et al., Critical Mass Studies, Part III, K-343 (April 1949).

The interaction problem in nuclear safety is a most difficult one. It must be considered when several process steps exist in one work area, when more than one batch of material is in standby storage in a process, during storage of completed fissionable material bearing components, and during transportation.

One usually endeavors to follow several basic guides in establishing the safe interaction for an array of like units. These are

1. Establish the safety of the units, assuming the most reactive, reasonable situation and assuming water reflection. In this way, one accounts for incidental, unspecified shielding in addition to possible water flooding, as by a sprinkler system.
2. Establish safe interaction by assuming an optimum array of such units, that is, an array with no water between units.
3. To provide at least 8 in. of separation between units, as one foot of water ensures virtually complete isolation of the units from each other.

There are some other factors which can be used to prevent criticality. Among these are the U^{235} assay or degree of enrichment of uranium. The degree of homogeneity in a system, and the presence of materials which parasitically absorb neutrons.

Nuclear Safety Design

In specifying the nuclear safety controls for an actual process, then, one considers how all of the factors discussed earlier effect criticality. First, one must become familiar with the process being set up. Often, the limitations placed on the process-design engineer greatly simplify the problems faced by the person concerned with nuclear safety. Some of the limitations are the total quantity of material to be processed, the capacity of the plant equipment, and the value of the finished product. However, as the processing of fissionable material becomes more competitive, time and money force the processor in the direction of handling larger batches or total quantities of fissionable material in shorter periods of time. This tendency from ultraconservative nuclear safety procedures, e.g., processing batches containing 350 gm of U^{235} or less, to less conservative methods, e.g., concentration control or moderation control, requires fairly sophisticated safety evaluations.

The usual way to resolve nuclear safety problems is, first, to compare the proposed process with safe values of mass, container size, etc., as published in the technical literature, such as the Nuclear Safety Guide mentioned earlier. Great care must be taken to determine that the safe value is applicable to the process in question. In a large number

of cases, one can use recommended nuclear safe values directly. If this approach is unsatisfactory, one should refer to criticality data. Hence, again one must be sure that any comparison of this data with the system in question is a valid one. The third possibility is that one must perform certain interpolations from existing criticality data to the system under design. Failing this, a criticality calculation must be carried out. This last possibility is generally undesirable, since large safety factors must be used and most reasonable mathematics inadequately describes the problem. To use mathematics which exactly describes the system is either not possible or not feasible from the economics viewpoint.

A further word on calculations is in order. The use of digital computers in reactor calculations has become extremely popular, being regarded today as a necessary tool for reactor design. Of course, the same calculations are applicable in establishing the nuclear safety of a process. In both applications, one must select a computational method which is not overly complex and yet yields reasonable answers. In multi-neutron-energy-group calculations, the machine cost is approximately proportional to the number of groups. Further, increase of the number of groups does not necessarily increase accuracy, the number resulting in the answer closest to the truth depending on the size and composition of the reacting system. Other difficulties in multigroup calculations are that such calculations are virtually impossible to do by hand and errors are difficult to find. One, two, or three groups are desirable for surveying reactor cores and for nuclear safety. However, with well-defined input data, multigroup methods are more accurate and are suitable for determining final reactor design. It is noteworthy that even this work must be tested by experiment, a point that those concerned with nuclear safety must appreciate.

Generally, one is concerned with two kinds of systems. First, there are homogeneous systems in which the fissionable atoms, say U^{235} , are uniformly dispersed throughout some media, such as water or air. Here, one normally encounters either all-metal, loose oxides, or water solutions of uranium. In such cases, we must be assured that no moderating material, such as water, can become mixed with the uranium atoms, except for the solutions cases, which already involve water. This is simple in the case of single metal pieces. In the case of oxides, we must ensure either that the material will be contained in water-tight vessels, or we must assume the system is (potentially) moderated. Usually, in plants, one supposes that open or unsealed containers are actually moderated and that the rugged, water-tight containers will be dry.

The second class of information refers to heterogeneous systems. When one encounters metallic pieces or oxide pellets, heterogeneous criticality data should be used. For systems of highly enriched uranium, if one always employed homogeneous data the results would be safe but often

uneconomical. In the case of low-enrichment uranium, if one employed homogeneous data an unsafe process could result if it actually involved 1-5 w/o enriched uranium pieces. The phenomenon of the greater reactivity of low-enrichment uranium, heterogeneous systems over solutions of similar enrichments of uranium is clearly illustrated in Figure 7.

Fig. 7. Estimated minimum critical masses for uranium of various low enrichments in water

w/o U ²³⁵	Homogeneous (kg U)	Heterogeneous (kg U)
1.5	1940(a)	800(b) (not mcm)
1.6	-	265(c)
3.0	114(a)	79(b)
4.9	37.8(b)	-
5.0	-	37(d)

(a)HW-54591 (1958) (c)HW-47012 (1956)

(b)HW-51983 (1957) (d)HW-57861 (1958)

Once a suitable set of criticality values has been selected, safety factors should be applied to achieve the desired safe design. There is usually a factor of about 2.1-2.3 between critical mass and safe mass to account for the possibility of "double-batching," as was described earlier. For geometric values, such as container volume or cylinder diameter, a factor of only about 1.3 is necessary. The reason here is that geometric values, e.g., pipe diameters, are less likely to be changed than mass, which is actually an administrative control.

Conclusion

It is hoped that the foregoing review gives the reader some insight into the reasons for being concerned with nuclear safety. Although the principles discussed above and the comments are generally valid, the specific problems encountered usually require detailed analysis. In many proposed process steps, one can find that the establishment of adequate safety often involves more than considering generalities.

DETERMINATION OF ENVIRONMENTAL LEVELS OF RADIUM

by

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This is a description of work in progress in the laboratories of the Radiological Sciences Group of the Division of Laboratories and Research, New York State Department of Health, Albany, under Contract No. SAPH 76262 with the U. S. Public Health Service.

To find out at first hand the problems that might arise in connection with a study to determine the impact upon a population by environmental contamination with Ra^{226} , a miniature community was set up. This consisted of five couples who turned in as samples for ten days portions of food and drink which were duplicates of the materials and amounts ingested each day. Total urine and feces samples were also submitted. The purpose was to determine "average" Ra^{226} intake in the vicinity of Albany, New York, as well as to test the feasibility of intake-output studies (1). An investigation of the latter phase was made with a group of seven individuals, one of whom was fed no Ra^{226} but who has between 1000 and 10,000 pc of Ra^{226} fixed in his skeleton. The other six were fed 500 pc of Ra^{226} via Brazil nuts at three rates of intake: two at 500 pc ingested as quickly as possible, two at 500 pc in ten equal daily portions, and two at 500 pc in twenty equal daily portions. From these seven persons, all hair from the head grown in ten months starting just before ingesting Ra^{226} was saved, samples of blood, total daily urine and feces samples, and daily portions of Brazil nuts equal in weight to those ingested were taken for analysis.

From the analytical point of view, the following logics were considered:

1. radiochemical isolation of radium isotopes with subsequent alpha counting of Ra^{226} ;
2. Rn^{222} emanation technic and subsequent alpha counting of Rn^{222} plus daughters, relating to original Ra^{226} content;
3. alpha spectrometry for quantitative and qualitative estimation of Ra^{226} in the presence of other alpha emitters; and
4. gamma spectrometry for quantitative estimation of Ra^{226} .

Early work on the radiochemical method indicated that it could be adapted to automatic counting with the Packard Tri-Carb which, in the light of the number of analyses involved (about 1000 even in a small study), appeared to be important. First trials with silver-activated ZnS were encouraging. Counting efficiencies were of the order of 30 percent at a background level of 1 cpm. Oscilloscope examination of the pulses due to background and alpha particles showed a very random distribution of energies, whereas in counting Ra^{226} plus low background, some low-level pulses would be expected with the rest at a much higher energy level. The cause was attributed to the fact that many of the Ra^{226} alpha particles were degraded to varying degrees in getting out of the solid matrices enclosing them at birth. To overcome this, the $\text{Ba-RaSO}_4 + \text{ZnS(Ag)}$ mixture was homogenized in a Wig-L-Bug dental amalgam mixer. This process was carried a step further by working out a method for spreading the alpha-emitting mixture evenly on the inside of the sample vial. The net result was to produce a spectrum of alpha pulses high at the high-energy level and with some at the low or noise level but with relatively few in between. The energy discriminator of the Tri-Carb could then be set to cut out nearly all noise pulses and still get most of the true alpha pulses. At this point the counting efficiency was about 60 percent at a background of 0.1 cpm. This allowed an analytical sensitivity of 10^{-13} c per sample without requiring an unusually long counting time. A change from glass to plastic counting vials, reduction of the volume of the sample vial from 16 ml to 3 ml, and using solid CO_2 to keep the sample chamber at -10 to -20°C without recourse to automatic cooling, permitted a background reduction to approximately 0.01 cpm. This made available an analytical sensitivity of 10^{-14} c per sample, considered the limiting sensitivity of the method. However, as long as the sample contains no Ba, the sample size may go up to 10 kg, dropping the analytical sensitivity to 10^{-18} c per gram of sample.

In the paragraphs below, the chemical aspects of this determination are described in detail. We prefer a waiting period in excess of the usual 30 days for complete equilibration with Ra daughters, to permit decay of the alpha-emitting Ra^{223} , which has about an 11.7-day half-life. This is not usually a source of concern, but might be a factor in an environment contaminated by a uranium ore-recovery plant. We have found that at this analytical sensitivity the reagent blank is important, as is the control of adsorption of Ra upon the walls of analytical vessels.

In our experience with the emanation technic, we tried first the procedure described below. It proved to be satisfactory for low-level work, that is, picocurie level work with Ra^{226} . It was used successfully to sample air at remote places, since it is readily portable; and it is adaptable to emanation analysis for Ra^{226} -containing samples as long as they can be put into solution. It permits a highly specific analytical

sensitivity of 10^{-13} c per sample. In the absence of freeze-out of Rn^{222} equipment, it is limited to samples of a size which can be put into 100 ml or so of solution. If Rn freeze-out is used, almost any sample size can be accommodated. It did not become the basic analytical method for this laboratory because we could not readily operate it continually without personnel or rerun samples to improve statistics of counting and to print out results. Also, its sensitivity of 10^{-13} c per sample is dependent upon clean Rn-collecting spheres, which seem harder to insure than clean glassware or the alpha-free plastic vials and beads used in the Tri-Carb procedure. Finally, storage of counted samples was much simpler in the Tri-Carb method, since they occupy only a few cubic centimeters each

Our experience with alpha spectrometry for radium work indicates that it could be very useful. A few samples were examined in this way and showed that often substantial fractions of "pure" Ra^{226} samples are Ra^{226} isotopes or isotopes of uranium, thorium, etc. A real problem is presentation of sample to counter. It must be in the form of a very thin, nearly weightless layer. Thus, a carrier-free radiochemical procedure is required. We are working with ion exchange resins to procure such a separation. Selective electrodeposition is another possibility we have tried and intend to study. However, the sensitivity up to now has been limited by the very small sample acceptable to an alpha spectrometer, as well as by the presence of some background, probably due mostly to the materials of construction of the Frisch grid chamber. Some very recent work by this laboratory, and at least one other group, seems to show that zero background can be achieved by the use of solid-state detectors for alpha spectrometry. In our own experience we have had an interval of 800 min without a single background pulse being registered. We find the counting efficiency of a solid-state system to be about 50 percent that of the Frisch grid or about 25-percent-absolute. We can easily produce a resolution of 35 kev, however, as opposed to about 65 kev on the Frisch grid. Thus, with zero background and long counting times one can, with specificity, achieve a sensitivity approaching that of the Tri-Carb or possibly surpassing it. We consider solid-state systems as a real improvement in radium analytical work for the near future and have designed a solid-state radon-counting chamber, but have not yet tried it.

Using gamma spectrometry, the 188-kev line for Ra^{226} was quickly found to be a "noisy" part of the spectrum. Also, the Compton contribution to the 188-kev peak from radium daughters at equilibrium was about 75 percent of the total. It was decided then to test the feasibility of using a spectral region rather than the photopeak to increase the sensitivity of the measurement, because only about 4 percent of the disintegrations of Ra^{226} emit gamma photons, and of this small number about one-half are lost by internal conversion. It was found that, when the Ra^{226} was at 30-day equilibrium with its daughters, the 188-kev peak was 3.8 times as high as

expected, while the spectral region between 240 and 380 kev yielded more than 20 times the number of photons as would be recorded at 188 kev. The work on this, recorded below, was performed in preparation for the possible use of gamma spectrometry for the analysis of large samples of water, milk, foods, soil, etc., which are put into solution and have the radium concentrated and isolated from other gamma activities by sulfate precipitation with barium added as carrier, and for testing the efficiency of gravimetric recovery.

Pretreatment of Samples

Radium analyses are made on many different types of samples, and, in most cases, we cannot be sure that the matrix remains constant from sample to sample. Therefore, it is important that the pretreatments of these samples render all the radium soluble and in a form suitable for the performance of subsequent chemistry.

Reagents

Ammonium hydroxide, 6 normal
Ammonium hydroxide, 10 percent
Ammonium hydroxide, concentrated
Hydrochloric acid, 10 percent
Citric acid, 3 normal
Nitric acid, concentrated
Lead nitrate, 100 mg Pb^{++} /ml
Barium nitrate, 25 mg Ba^{++} /ml
Detergent solution, 30 gm/l

1. Pretreatment of Water Samples

- Step 1 - Measure 1000 ml of the water sample into a 2-liter beaker.
- Step 2 - Add 50 ml of concentrated HNO_3 and 25 mg of Ba carrier.
- Step 3 - Place the beaker on the hot plate. Bring to a simmer, just under boiling, for $\frac{1}{2}$ -1 hr.
- Step 4 - Remove beaker from hot plate and let cool.

Step 5 - To beaker add conc NH_4OH , with stirring, to a pH of 7.0-7.5.

Step 6 - To the beaker add the following reagents in the following order:

- a. 5 ml of 3N citric acid;
- b. 2.5 ml of conc NH_4OH ;
- c. 200 mg Pb carrier.

2. Pretreatment of Milk Samples

Step 1 - Weigh out 100 gm of milk and pour into a large quartz dish (Note 1).

Step 2 - To the quartz dish add 25 mg Ba carrier.

Step 3 - Place the quartz dish on a hot plate, evaporate to dryness, and ignite.

Step 4 - Place the quartz dish in a preheated muffle furnace (at 650°C). Keep the door slightly open and muffle for 10 min.

Step 5 - Close the muffle door and muffle for approximately 2 hr at a temperature of 650°C .

Step 6 - Remove from the muffle furnace and cool.

Step 7 - To the quartz dish add 100 ml conc HNO_3 and evaporate to dryness on a hot plate.

Step 8 - Place quartz dish in the muffle furnace at 650°C . Keep the doors slightly open until the nitric acid fumes are gone.

Step 9 - Close the muffle furnace door and muffle for approximately $1\frac{1}{2}$ hr at 650°C .

Step 10 - Repeat steps 7 through 9 until a white ash is obtained.

Step 11 - Remove the quartz dish from the muffle furnace and cool.

Step 12 - To the quartz dish add 100 ml of 10% HCl .

Step 13 - Heat approximately for 15 min (ash should be in solution).

Step 14 - Transfer into a 2-liter beaker, rinsing the quartz dish with distilled water.

Step 15 - Repeat steps 12 through 14.

- Step 16 - Bring the final volume in the beaker to 1 liter by addition of distilled water.
- Step 17 - To the beaker add 6N NH_4OH , with stirring, to a pH of 7.0-7.5.
- Step 18 - Add the following reagents in the following order:
- 5 ml of 3N citric acid;
 - 2.5 ml of conc NH_4OH ;
 - 100 mg Pb carrier.

3. Pretreatment of Urine Samples (Note 2)

- Step 1 - Take complete daily sample of urine and place into as many 500-ml centrifuge bottles as needed (Note 3).
- Step 2 - Add 6N NH_4OH to pH of 10, centrifuge 45 min, discard supernatant (Note 4).
- Step 3 - Add 20 ml of 10% NH_4OH to each bottle. Centrifuge for 30 min. Discard supernatant.
- Step 4 - While in bottle, add 20 ml of 10% HCl to the precipitate and heat to dissolve the precipitate. Transfer solution to a 2-liter beaker. Rinse bottle with an additional 20 ml of 10% HCl and, finally, with distilled water. Add these rinsings to beaker (Note 5).
- Step 5 - Adjust final volume to 1 liter with distilled water.
- Step 6 - Add 6N NH_4OH , with stirring, to pH 7.0-7.5.
- Step 7 - Add the following reagents in the following order:
- 5 ml of 3N citric acid;
 - 2.5 ml of conc NH_4OH ;
 - 100 mg Pb carrier;
 - 25 mg Ba carrier.

4. Pretreatment of Fecal Samples

- Step 1 - Remove samples stored in freezer or cold room (Note 6).
- Step 2 - Take the complete daily sample and place in a quartz dish (Note 7).
- Step 3 - Heat on hot plate until charred or taken to dryness; then ignite.
- Step 4 - Place the quartz dish in the muffle furnace with the door slightly open at a temperature of 600-650°C until complete ignition is achieved (approximately 10 min).

- Step 5 - Close the doors, then muffle for approximately 16 to 18 hr at 650°C.
- Step 6 - Remove from muffle furnace and cool.
- Step 7 - Add 100 ml conc HNO_3 to the quartz dish by means of a pipette. (A pipette is used so that the sides of dishes can be washed down with HNO_3 .)
- Step 8 - Take to dryness on a hot plate.
- Step 9 - Place the quartz dish in a preheated (650°C) muffle furnace for approximately 10 min with the door slightly open.
- Step 10 - Close the door and muffle for $1\frac{1}{2}$ -2 hr at 650°C.
- Step 11 - Repeat steps 7 through 10 until a white ash is achieved.
- Step 12 - Remove from the muffle furnace and cool.
- Step 13 - Add 50 ml of 10% HCl to the dish and heat on a hot plate until ash is in solution.
- Step 14 - Transfer the solution to a 2-liter beaker, rinsing with distilled water.
- Step 15 - Repeat steps 13 and 14.
- Step 16 - Adjust the final volume to 1 liter with distilled water.
- Step 17 - Add 6N NH_4OH , with stirring, to a pH of 7.0-7.5.
- Step 18 - Add the following reagents in the following order:
 - a. 5 ml of 3N citric acid;
 - b. 2.5 ml of conc NH_4OH ;
 - c. 100 mg Pb carrier;
 - d. 25 mg Ba carrier.

5. Pretreatment of Blood Samples

- Step 1 - Remove blood sample from cold room storage and leave overnight to come to room temperature.
- Step 2 - Weigh the test tube containing the blood sample.
- Step 3 - Rinse the blood from the tube, with distilled water, into a platinum-clad crucible. Make sure all the blood is removed.
- Step 4 - Dry the tube, weigh it, and subtract this from the weight of the tube and the blood. This will give the weight of the blood sample.

- Step 5 - To the platinum-clad crucible add 25 mg Ba carrier.
- Step 6 - Take to dryness on the hot plate. Exercise care, as blood will tend to spatter when almost dry. Use low heat.
- Step 7 - Place the crucible on the edge of preheated (300-350°C) muffle furnace with the door wide open for approximately 15 min.
- Step 8 - Raise the heat of the muffle furnace to 600-650°C, keeping the door open slightly for approximately 15 min.
- Step 9 - Close the door and muffle for approximately $1\frac{1}{2}$ - 2 hr.
- Step 10 - Remove the crucible from the muffle furnace and cool.
- Step 11 - Add 20 ml of conc HNO_3 to the crucible. Place on the hot plate and take to dryness, using low heat.
- Step 12 - Place in a preheated (600-650°C) muffle furnace for approximately 10 min with the door slightly open.
- Step 13 - Close the door and muffle for $1-1\frac{1}{2}$ hr at 650°C.
- Step 14 - Remove from the muffle furnace and cool.
- Step 15 - Repeat steps 11 through 14.
- Step 16 - Add 50 ml of 10% HCl to the crucible. Heat on hot plate and transfer to a 2-liter beaker. The ash should go into solution at this point.
- Step 17 - Repeat step 16.
- Step 18 - Add 6N NH_4OH , with stirring, to a pH of 7.0-7.5.
- Step 19 - Add the following reagents in the following order:
- 5 ml of 3N citric acid;
 - 2.5 ml of conc NH_4OH ;
 - 100 mg Pb carrier.

6. Pretreatment of Human Hair Samples

- Step 1 - Place the sample in a Petri dish, and place the dish and sample in a drying oven at a temperature of 100-105°C; dry overnight.
- Step 2 - Weigh the sample after drying.

- Step 3 - Place the sample in a large funnel. Place the hair sample in a rapid-flow filter paper set in a large funnel. Wash with two 100-ml portions of detergent.
- Step 4 - Rinse with two 100-ml portions of distilled water.
- Step 5 - Place the filter paper containing the washed hair in a small quartz dish.
- Step 6 - Heat on a hot plate until the sample is dry.
- Step 7 - Add 50 ml conc HNO_3 to the quartz dish and take to dryness on the hot plate.
- Step 8 - Place the dish in a preheated (650°C) muffle furnace with the door slightly open for 10 min.
- Step 9 - Close the door and muffle for $1-1\frac{1}{2}$ hr at 650°C .
- Step 10 - Remove from the muffle furnace and cool.
- Step 11 - Repeat steps 7 through 10.
- Step 12 - Add 50 ml of 10% HCl and heat on the hot plate until ash is in solution.
- Step 13 - Transfer the contents to a 2-liter beaker, washing with distilled water.
- Step 14 - Repeat steps 12 and 13.
- Step 15 - Adjust final volume to 1 liter with distilled water.
- Step 16 - Add 6N NH_4OH , with stirring, to a pH of 7.0-7.5.
- Step 17 - Add the following reagents in the following order:
 - a. 5 ml of 3N citric acid;
 - b. 2.5 ml of conc NH_4OH ;
 - c. 100 mg Pb carrier;
 - d. 25 mg Ba carrier.

7. Pretreatment of Brazil Nut Samples

- Step 1 - Weigh the Brazil nuts and place the weighed portion in a Waring Blendor and grind.
- Step 2 - Transfer the ground sample into a quartz dish, using distilled water.
- Step 3 - Place the quartz dish on a hot plate and evaporate to dryness; ignite.

- Step 4 - Place the quartz dish in a muffle furnace for approximately 10 min with the door slightly open. Then close the door and muffle at 650°C for $2-2\frac{1}{2}$ hr.
- Step 5 - Remove the quartz dish from the muffle furnace and cool.
- Step 6 - Add 50 ml conc HNO_3 to a quartz dish, using a pipette. Take the sample to dryness on the hot plate.
- Step 7 - Place the quartz dish in a preheated (650°C) muffle furnace for approximately 10 min with the door slightly open.
- Step 8 - Close the door and muffle for $1\frac{1}{2}$ -2 hr at 650°C . A white ash should result.
- Step 9 - Repeat steps 6 through 8.
- Step 10 - Remove the quartz dish from the muffle furnace and cool.
- Step 11 - Add 50 ml of 10% HCl to the quartz dish. Heat on a hot plate until ash is in solution.
- Step 12 - Transfer the contents to a 2-liter beaker, using distilled water as a wash.
- Step 13 - Repeat steps 11 and 12.
- Step 14 - Adjust the final volume in the beaker to 1 liter with distilled water.
- Step 15 - Add 6N NH_4OH , with stirring, to pH of 7.0-7.5.
- Step 16 - Add the following reagents in the following order:
 - a. 5 ml of 3N citric acid;
 - b. 2.5 ml of conc NH_4OH ;
 - c. 100 mg Pb carrier;
 - d. 25 mg Ba carrier.

8. Pretreatment of Food Samples (coffee beans, cocoa beans, and banana flakes)

- Step 1 - Weigh the sample and place in a quartz dish.
- Step 2 - Place the quartz dish on a hot plate and heat until the sample is charred. (Ignition on a hot plate is not feasible with these samples.)
- Step 3 - Place the quartz dish in a preheated muffle furnace. Exercise care with banana flakes and ground coffee, as these samples tend to splatter. Heat for approximately 15 min with the door open.

- Step 4 - Close the door and muffle for 3-4 hr at 650°C. It may sometimes be necessary to muffle overnight, depending on the original weight of the sample.
- Step 5 - Remove the quartz dish from the muffle and cool.
- Step 6 - Add 50 ml concentrated HNO_3 to the quartz dish and take to dryness on the hot plate.
- Step 7 - Place the quartz dish in the muffle furnace with the door slightly open for approximately 10 min.
- Step 8 - Close the door and muffle at 650°C for $1-1\frac{1}{2}$ hr.
- Step 9 - Repeat steps 6 through 8.
- Step 10 - Remove the quartz dish from the muffle furnace and cool.
- Step 11 - Add 50 ml of 10% HCl to the quartz dish and heat on a hot plate, until the ash is in solution.
- Step 12 - Transfer the contents of the quartz dish into a 2-liter beaker, using distilled water as a wash.
- Step 13 - Repeat steps 11 and 12.
- Step 14 - Adjust the final volume in the beaker to 1 liter, using distilled water.
- Step 15 - Add 6N NH_4OH , with stirring, to pH of 7.0-7.5.
- Step 16 - Add the following reagents in the following order:
- 5 ml of 3N citric acid;
 - 2.5 ml of conc NH_4OH ;
 - 100 mg Pb carrier;
 - 25 mg Ba carrier.

Notes - Pretreatment of Samples

- The quartz dishes were purchased from Scientific Glass Apparatus Co., Bloomfield, N. J. Fused quartz dishes, 4 in. deep x 6 in. x $10\frac{1}{4}$ in., with a smooth interior finish, cost \$18.00 each.
- The pretreatment of urine samples was adapted from the method of Harley and Foti.⁽²⁾
- Daily sample per person ranges from 1-1.5 liters. The pH of urine is approximately 6.

4. Use pH paper to check pH. A considerable amount of precipitate will form, and the use of a refrigerated centrifuge is recommended.
5. If further processing is to be postponed, the solutions may be stored in flasks at this point.
6. The collection and storage of fecal samples is discussed in a previous report.⁽¹⁾
7. These are fused quartz dishes, $2\frac{1}{2}$ in. deep x 6 in. x 3 in. with a smooth interior finish. They, too, were purchased from Scientific Glass Apparatus Co.

Radium Chemistry

Radium is separated from its matrix by coprecipitation with barium sulfate, purified by solution, and reprecipitated by an EDTA cycle. This is a modification of the method previously reported by this laboratory for radium analysis in food samples⁽¹⁾ and has been adapted from the method used by the Robert A. Taft Sanitary Engineering Center.⁽³⁾

Reagents

Sulfuric acid, 18 normal

0.1% Methyl orange

Nitric acid, conc

Ethylenediaminetetraacetic acid (EDTA, M/4), disodium salt

Ammonium hydroxide, 6 normal

Acetic acid, glacial

Procedure

- Step 1 - Heat the solutions obtained from the pretreatment of samples to boiling. To the hot solutions, add 5 to 10 drops of methyl orange indicator. Then add 18N H_2SO_4 slowly and with stirring to a pH of 1.5. A pink color should obtain. Rinse and remove stirring rods.
- Step 2 - Digest for one hour on a hot plate.
- Step 3 - Remove from hot plate and allow to cool overnight.
- Step 4 - Filter through prepared Gooch crucibles, using suction (Note 1).

- Step 5 - Wash precipitate in crucible with three 10-ml portions of conc HNO_3 .
- Step 6 - Wash precipitate in crucible with one 20-ml portion of distilled water.
- Step 7 - Transfer the crucible and contents to a 400-ml beaker and add:
- a. 20 ml distilled water;
 - b. 20 ml M/4 EDTA;
 - c. 10 ml 6N NH_4OH (Note 2).
- Step 8 - Heat solution to boiling and keep just under boiling until all the precipitate dissolves. Keep pH greater than 10 by adding 6N NH_4OH as required (Note 3).
- Step 9 - Rinse crucible with distilled water and remove from beaker (Note 4).
- Step 10 - Check beaker to be sure all precipitate is in solution.
- Step 11 - While hot, filter through large-size (18.5-cm) Whatman No. 40 paper. Catch the filtrate in another 400-ml beaker.
- Step 12 - To the original 400-ml beaker add the following:
- a. Gooch crucible;
 - b. 10 ml distilled water;
 - c. 10 ml M/4 EDTA;
 - d. 5 ml 6N NH_4OH .
- Step 13 - Heat to boiling and repeat step 9. Maintain a pH of 10.
- Step 14 - Filter while hot onto filter paper containing asbestos and collect filtrate into beaker used for previous filtrate (Step 11). (See Note 5.)
- Step 15 - Heat combined filtrates to just under boiling and simmer for 10-15 min (Note 6).
- Step 16 - To hot solution add glacial acetic acid dropwise and with stirring to pH 4.5-4.0. Rinse and remove stirring rods. Note and record date and time (Note 7). If precipitate does not form, a few drops of 18N H_2SO_4 may be added. Care must be taken to keep pH above 3.5.
- Step 17 - Allow the precipitate to settle overnight.

Step 18 - Filter through Whatman No. 42 ashless filter paper (15 cm). Rinse and scrub beaker with distilled water and rubber policeman (Note 8).

Step 19 - Transfer filter paper and precipitate to platinum crucible and char off paper under an infrared lamp (Note 9).

Step 20 - Transfer platinum crucible to muffle and heat at 650-700°C for 1-1½ hr.

Step 21 - Cool in desiccator and weigh.

Notes - Radium Chemistry

1. It is essential that Gooch crucibles be prepared in the following manner:
 - a. Add enough asbestos suspension to crucibles so that an even mat is obtained upon applying suction.
 - b. Dry crucibles in oven at 100°C for approximately 30 min to 1 hr, and muffle at 650°C for half an hour. This step insures a better mat and allows a better distinction to be made between the asbestos and the precipitate.
 - c. All the precipitate must be removed from beakers by means of distilled water and rubber policeman.
2. Use large amount of EDTA (50 ml more than usual) if large amount of precipitate is anticipated.
3.
 - a. Asbestos and precipitate will tend to loosen after solution becomes hot. No attempt should be made to "dig" precipitate and asbestos from crucible.
 - b. Precipitate will tend to settle to the bottom while asbestos tends to suspend in solution.
 - c. Stirring vigorously will tend to speed solution of precipitate.
 - d. Approximately one-half hour will suffice for complete solution.
4. Forceps may be used to remove crucible from solutions. At this point, a wash with sufficient force will remove any remaining asbestos and precipitate from the crucible. Be sure that washings go into beaker and rinse inside and outside of crucible wall before removing from the beaker.

5. This step will tend to dissolve any remaining precipitate that might remain with the asbestos.
6. Simmering at this point will drive off radon and allow radon daughters to decay to radium D.
7. This is the zero time. From this time ingrowth of radium daughters will occur.
8.
 - a. The residual ash weight of the filter paper should be recorded so that it can be subtracted from the final weight.
 - b. When filtering, the solution should not be allowed to go over half the volume of the funnel due to the creeping nature of BaSO_4 .
 - c. Check filtrate for any signs of precipitation.
9.
 - a. Charring while the paper is wet is quicker.
 - b. Be sure paper does not burst into flame.

Counting Procedures

Preparation of Sample-Scintillator Mixture

The precipitate is counted for alpha activity in a beta scintillation spectrometer using $\text{ZnS}(\text{Ag})$ as the scintillator.

- Step 1 - Transfer weighed precipitate to a plastic Wig-L-Bug vial (Note 1).
- Step 2 - Add 100 mg $\text{ZnS}(\text{Ag})$ (Note 2).
- Step 3 - Using a cardboard shield with a hole in the center so that only the opening of the vial shows through the shield, spray the inside of the vial with Krylon crystal clear No. 1303 spray coating. The spray can should be held approximately 10 in. from the vial opening (see Figure 1).
- Step 4 - Add one small plastic bead to the vial (Note 3).
- Step 5 - Quickly snap on cover and place the vial on a Wig-L-Bug amalgamator. Set for 2 min or longer, depending on the amount of precipitate (Note 4).
- Step 6 - The mixture of scintillator and precipitate should be completely adhered to the walls of the vial.

Fig. 1
Method of spraying interior of vial.

Figure 2 shows the Wig-L-Bug amalgamator and vials containing the final precipitate and the scintillator. These vials are ready to be sprayed and then placed on the amalgamator. The vials in the upper right of the picture have been so processed and can now be assembled.

Fig. 2

Wig-L-Bug amalgamator and vials containing final precipitate and scintillator.

Assembly of Vials for Counting

The automatic sample changer cannot accommodate the small Wig-L-Bug vial. Therefore, it is necessary to place this vial inside a larger 3-dram plastic vial. Since the slots of the sample changer are much larger than even the 3-dram vial, an oversize cap must be glued to the mouth of the 3-dram vial. Figure 3 shows a sketch of the assembled vials. The foil-covered plug is used to raise the Wig-L-Bug vial above the level of the plastic cap. The aluminum foil disc and aluminum plug covering are used as reflectors.

Fig. 3. Assembly of vials for counting.

Step 1 - Cut a No. 1 cork stopper in half. Cover this with foil and glue to the plastic cap (Note 5).

Step 2 - Glue the Wig-L-Bug vial to the foil-covered plug.

Step 3 - Then glue the aluminum disc to the top of the Wig-L-Bug vial (Note 6).

Step 4 - Insert the 3-dram plastic vial into a Wheaton vial plastic cap. The rim of the vial should be coated with glue to hold it in place (Note 7).

Counting of Samples

A Packard Tri-Carb automatic liquid scintillation spectrometer, model 314X, (see Figure 4) is used. Figure 5 shows the freezer unit and the automatic sample changer. The freezer compressor is disconnected, and dry ice is used for cooling. This eliminates the possibility of random counts being thrown into the system when the compressor goes on or off. Furthermore, the use of dry ice floods the freezer compartment with carbon dioxide gas and reduces the possibility of ambient radon levels in

Fig. 4. Model 314X Packard Tri-Carb liquid scintillation spectrometer.

Fig. 5. Freezer unit and automatic sample changer.

air contributing to background. The instrument settings are as follows:

High voltage: 780 volts

Tap: No. 2

Attenuator: 16

Mode: 4

Discriminators: $5 \rightarrow \infty$
 $7 \rightarrow \infty$

The two discriminator settings are used simultaneously. In this manner, each sample receives two counts simultaneously, and this serves as a check on the instrument. Backgrounds of less than 0.02 cpm are obtained, and a counting efficiency of about 50 percent is achieved. Table 1 shows the data obtained from a typical reagent blank and background. Each sample was counted twenty times and each count was of 100-min duration.

Table 1

A TYPICAL REAGENT BLANK AND BACKGROUND

	Average cpm	Standard Deviation, cpm	E_{95}	Discriminator Setting
Urine blank	0.14	0.04	0.017	$5 \rightarrow \infty$
Urine blank	0.13	0.03	0.016	$7 \rightarrow \infty$
Background	0.002	0.002		$5 \rightarrow \infty$
Background	0.001	0.001		$7 \rightarrow \infty$

Notes - Counting Procedures

1. Plastic Wig-L-Bug vials can be obtained from Spex Industries, Inc., Hollis 23, New York.
2. ZnS(Ag), type No. 130, can be obtained from Sylvania Electric Products, Inc., Chemical and Metallurgical Division, Towanda, Pennsylvania.
3. Plastic beads can be obtained from Spex Industries, Inc.
4. The Wig-L-Bug amalgamator is manufactured by the Crescent Dental Manufacturing Company, Chicago, Illinois, and can be obtained from Spex Industries, Inc.
5. The glue is made by taking three parts benzene and one part ethylene dichloride and adding enough poly-isobutyl methacrylate to the desired viscosity. The Wheaton vial plastic caps can be obtained from the Packard Instrument Company, LaGrange, Illinois. The aluminum foil is the heavy-duty household type obtainable in any grocery store or supermarket.
6. Aluminum discs are made from the heavy-duty aluminum foil by cutting the proper circles.
7. The 3-dram plastic vials can be obtained locally.

Determination of Radium-226 by Gamma Counting

Ra^{226} emits gamma photons of 188-kev energy. The isotope emits four gamma photons for every 100 disintegrations, approximately 50 percent of which are lost due to internal conversion.⁽⁴⁾ Thus, only about two gamma photons per hundred disintegrations are available for detection. The counting efficiency of the well-type gamma scintillation spectrometer approaches 30 percent. Therefore, the overall efficiency for gamma counting Ra^{226} directly would be about 0.6 percent. Although this low efficiency makes difficult the detection of picocurie-level quantities of Ra^{226} by direct gamma counting, a mitigating factor, the ingrowth of radium B, makes available nearly four times as many 188-kev photons due to Compton scattering and makes available more than twelve times as many photons between 220 kev and 360 kev as at 188 kev which can be related to Ra^{226} content.

A spectrum of a standard solution of Ra^{226} in equilibrium with its daughters was taken by means of a well-type gamma scintillation spectrometer. Radium-B energy peaks at 240, 295, and 352 kev were discernible.

These peaks represent 98 percent of the decay energy of radium B. Therefore, a study of the relationship of the counting rates of the radium-B region, 220 kev to 360 kev, with that of the Ra^{226} peak, 188 kev, was in order. The counting rate of the radium-B region was found to be twelve times greater than that recorded for the Ra^{226} peak. If, as was suspected, Compton scattering from the radium-B region was probably contributing to the counting rate at the Ra^{226} peak, the counting rate at the Ra^{226} peak would not be representative of the actual activity of the Ra^{226} present. Therefore, to determine the true counting rate due to Ra^{226} only, at the Ra^{226} peak, and to study the relationship between the counting rates of radium B and Ra^{226} throughout the buildup period and at equilibrium, it was necessary to effect a physical separation of Ra^{226} from its gamma-emitting daughters.

A 10-ml aliquot of a standard solution of radium was pipetted into a Wheaton vial. The vial was placed in a specially prepared steam bath for 6.5 hr. The original volume of the radium solution was maintained throughout this period by occasionally adding distilled water. The first 30 min of this simmering period is sufficient to expel the radon in equilibrium with radium. The ensuing 300 min were allowed for the decay of the radon daughters, while the newly formed radon was being expelled. At the end of 6.5 hr, the vial was capped, sealed with tape, and counted at the Ra^{226} peak. The counting rate recorded at this time was considered to be truly representative of Ra^{226} . Immediately following this, the sample was counted at the radium-B region; at this point the counting rate for the radium-B region was only slightly above background, indicating a reasonably good separation. A study of the buildup in this sample was made by measuring counting rates of Ra^{226} and radium B at intervals throughout the 30-day buildup period. At equilibrium it was found that the counting rate of radium B had increased to about 35 times the initial counting rate. The counting rate of the Ra^{226} increased by a factor of 3.8. Therefore, the counting rate at the Ra^{226} peak at any time after zero time is not indicative of the actual activity of Ra^{226} , and the increase is most probably due to Compton scattering from the higher-energy gamma emissions from the ingrowing radium B. For purposes of identification, the counting rate at the Ra^{226} peak after zero time is referred to as "apparent" Ra^{226} .

A series of standard solutions of 500, 1000, 5000, and 10,000 pc Ra^{226} was taken through the physical separation from its gamma-emitting daughters. A buildup study was conducted with these standards for 30 days, following the procedure described above. For each standard, a graph was drawn showing the counting rate of actual Ra^{226} , apparent Ra^{226} , radium B throughout the buildup period. These graphs indicate that at any given time during the buildup or at equilibrium a determinable ratio of the counting rates exists between radium B and actual Ra^{226} , and between radium B and apparent Ra^{226} . The ratios of counting rates between radium B

and actual Ra^{226} were calculated for various times throughout the buildup period for each standard. A

Fig. 6. Comparison of ratios of cpm radium B to actual Ra^{226} for varying activities from zero time to equilibrium.

plot was made of these ratios vs the buildup time (see Figure 6). A straight line resulted which levelled off at equilibrium. For the two standards of higher activity this line coincided, but the lines representing the two standards of lower activity deviated somewhat. The counting statistics for the two standards of lower activity were quite poor. The limitations of this graph will be discussed later. It can be used to determine the actual amount of Ra^{226} present in a sample by counting the radium B at a known time during buildup or at equilibrium. This specific buildup time will correspond to a definite ratio of counting rates of radium B and actual Ra^{226} . This ratio,

J, can be immediately obtained from the graph, and the value of actual Ra^{226} can be calculated according to the following equation:

$$\frac{\text{Ra B (cpm)}}{\text{Actual } \text{Ra}^{226} \text{ (cpm)}} = J$$

The ratio of counting rates between radium B and apparent Ra^{226} were calculated and plotted vs buildup time (see Figure 7). This ratio is constant

Fig. 7. Comparison of ratios of cpm radium B to apparent Ra^{226} for varying activities during buildup time.

for samples in equilibrium, and the graph should be used in conjunction with Figure 6 to determine actual Ra^{226} when the buildup time for the sample is unknown. This is accomplished by simultaneously counting the Ra^{226} peak and the radium-B region. The calculation of the ratio of their counting rates gives a value K which corresponds to a specific buildup time which can be obtained from the graph. Since buildup time can be determined and the counting rate of radium B is known, Figure 6 can be used to determine the activity of Ra^{226} .

Analysis of Errors

Probably the greatest single source of error lies in the mode of counting. The equipment used was a NaI(Tl) well-type crystal and a Baird Atomic single-channel gamma system with a model 540 automatic scanner (see Figure 8). The system was set to count successively 10 kev of the spectrum for a pre-set time of 8 min. From the standpoint of energy spread, or window width, this was satisfactory for Ra^{226} peak counting, but the pre-set counting time was inadequate statistically for counting the two lower-level standards. This probably accounts for their deviations in Figure 6. The radium-B region is represented by a 240-kev spread, and each 10 kev was counted for 8 min successively. The counts from the 24 portions of the region, each representing 10 kev, were totaled and divided by eight to determine the counting rate, so that at no one instant

Fig. 8. Baird Atomic single-channel gamma system and model 540 automatic scanner.

was the entire region being counted. The specific time of count was taken as midpoint in the scan. The 8-min maximum pre-set counting time did not affect the counting statistics for the radium-B region nearly as much as it did that for the Ra^{226} peak, but it did contribute to limitations.

Discussion

In using this procedure for radium-containing samples, a spectrum analysis should be made to determine the presence of impurities that might interfere in the pertinent portion of the radium spectrum (160-400 kev). If impurities are present, they must be removed to ensure the effectiveness of this method. Ideally, the Ra^{226} peak and the radium-B region should be counted simultaneously. Therefore, if a multichannel analyzer is available, this should be the instrument of choice. If, however, a single-channel analyzer is to be used, then the simultaneous counting of the Ra^{226} peak and the radium-B region can be accomplished by connecting an additional pulse-height analyzer and scaler into the system.

Determination of Radium-226 by Emanation Methods

The determination of Ra^{226} by the radon emanation method has certain compelling advantages over other methods of radium analysis. Probably the two most important are (1) its specificity, and (2) the fact that chemical losses are kept to a minimum.

Several methods of counting radon make use of either an ionization chamber or some type of scintillation system. At this laboratory we have developed a portable transfer and counting system which is simple, versatile, and compact enough so that radon analyses can be made in the field.

Fig. 1. Counting system.

The counting system is designed around an ionization chamber and a Cary model 31 electrometer, incorporating a Leeds and Northrup 0-10 millivolt recorder as a readout (see Figure 9). The circuit in the electrometer is arranged in a manner to produce a slow pulse counter. This is accomplished by using a 10^{11} -ohm resistor in the electrometer circuit, which has a total capacitance of 10^{-11} farad. This produces a large enough pulse from each alpha disintegration so that it is

easily distinguished from noise and yet the decay time of the pulse is in the order of one second. This, of necessity, puts a limitation on the counter.

It can be used only for activities of the order of 1 pc and under. At the same time, the use of the slow pulse enables us to count radon gas without removing oxygen from the system. Oxygen is an electronegative gas and is collected slowly. However, with our system, the rise time of the pulse is greater than the collection time of the O_2^- ion. Neither is it necessary to remove other types of contaminants, such as water vapor and carbon dioxide. The ion chambers are of sufficiently large volume (500-1000 ml) so that it is not necessary to freeze the radon out, and the total carrier gas can be transferred to the counting chamber. The use of a slow pulse counter permits a simple design for our transfer system and, in turn, makes the emanation procedure a simple one (see Figure 10).

Fig. 10. Slow pulse counter.

Procedure

1. The radium sample is put into solution.
2. Allow the carrier gas (aged nitrogen) to bubble through the sample and flow into a previously evacuated ion chamber.
3. The radon in the ion chamber is allowed to come to equilibrium with its alpha-emitting daughters and is then counted.

Backgrounds for the system are of the order of 0.1 cpm. Counting efficiencies are 40 percent, considering a possible count rate of 6.66 cpm/pc for the three alpha emitters. The two radon daughters will have a 2π geometry. The sensitivity is of the order of 10^{-13} c. By subjecting our data to a rigorous statistical treatment, a more exact number of 0.28 cpm is obtained.⁽⁵⁾

Radium Determination by Alpha Spectrometry

Another method of radium analysis which has definite potential is alpha spectrometry with a Frisch grid. The Frisch grid is a gridded ionization chamber which has a fine mesh wire placed midway between cathode and anode. The voltage applied to this grid is one-half that applied to the cathode; the anode is kept at ground potential. The signal produced from each alpha disintegration is taken off the grid and the anode. The slow-moving positive ions are collected on the cathode and do not affect the pulse height. Thus, a true alpha-energy relationship is obtained for the isotopes under consideration. The instrument can be calibrated by use of a source such as Pu^{239} . Since Pu^{239} is usually accompanied by contamination due to Am^{241} , two distinct alpha-energy peaks are obtained; the distance, in volts or channels, that separate these two energy peaks is determined. Once this calibration is completed, an analysis of any alpha-emitting material can be performed by presenting this material to the instrument in a nearly weightless form. Sometimes a weightless sample is obtained by electrodeposition of the element involved. However, in the case of radium, which is a member of the alkaline earth series, electrodeposition is not feasible, and there is a two-fold problem: (1) purification of radium from other contaminants, and (2) final deposition of radium in a carrier-free form.

Fig. 11. Frisch grid.

We are currently investigating the feasibility of purification of radium by ion exchange⁽⁶⁾ and final deposition by evaporation technics. The radium-containing solution is passed through a resin column, and the radium is purified by selective elutions of impurities. The radium is finally eluted onto a platinum disc and evaporated to dryness. Preliminary data indicate that counting efficiencies are nearly 50 percent for 4π geometry. Backgrounds in the Ra^{226} region are of the order of 0.06 cpm for a window of 150 kev, and the sensitivity is estimated to be around 0.5 pc. Figure 11 shows the Frisch grid used at this laboratory.

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RADIUM-226 IN THE DIET IN THREE U.S. CITIES

by

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In conjunction with the strontium-90-monitoring program at the Health and Safety Laboratory (HASL), a diet study of the strontium-90 level in food has been conducted at three cities in the United States. This study began in March 1960 and is continuing. To date, there have been four food samplings at each of the cities (New York, Chicago, and San Francisco) taken at approximately three-month intervals. The Sr^{90} data have been reported in the HASL Quarterly Summary Reports (2,3)

In the determination of Sr^{89} and Sr^{90} , a barium chromate separation was introduced to remove barium-140, radium, and lead. This step is still performed, and, since August 1960 each chromate precipitate has been dissolved in perchloric acid and stored for Ra^{226} analysis. It is expected that the radium program will parallel the strontium program and will include bone analyses.

Radium-226 in these samples has been determined by the emanation of the gaseous daughter radon-222 from the radium-bearing solution by bubbling an inert counting gas through the solution. The radon is collected in a 2-liter ion chamber, and pulses from radon and its two alpha-emitting daughters are counted.

Experimental

The emanation technique for determining radium-226 has been described by many previous authors. This report merely indicates the adaptation of the general principles to the samples and equipment available at the Health and Safety Laboratory. In addition, the results of the measurements on foods are believed to be of general interest in evaluating the probable source of radium-226 in the human body.

This particular experimental program required more careful attention to instrument calibration than had been required for normal use of the equipment in measuring breath samples. In addition, a study was made of the recovery of radium as a byproduct of the HASL procedure for determining strontium-90, and measurements were made of the precision obtainable with the method.

Counting Apparatus

The chambers available for gas counting at HASL are two-liter, stainless steel ionization chambers. The chambers and the associated electronic circuitry were designed and built at HASL. The preamplifier, amplifier, and power supply are transistorized, and the counting data are recorded automatically on a punched paper tape.

The chambers are operated as fast pulse counters and require that oxygen be absent. Air samples are mixed with an excess of hydrogen and the mixture passed over a platinum catalyst. The counting gas used to bring the system up to pressure is forming gas. External to the chambers there is a closed plumbing system which includes a pressure gauge, the catalyst for removal of oxygen, a drierite tube, and a vacuum connection. A block diagram of the apparatus is shown in Figure 1.

Fig. 1. Radon-generating and counting apparatus

The chamber backgrounds range from 5-10 counts per hour, and the radon from 1 pc of radium-226 yields 225 counts per hour at 5 hr after introduction of the sample.

Counter Standardization

To standardize our two-liter radon gas-counting chambers, we initially prepared a solution containing 0.1 μ gm radium-226 obtained from NBS, in one liter of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ carrier (0.2% $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 5% HCl). The original vial was sealed after transfer of the radium and any residual activity was allowed to build up. After 30 days the vial showed no activity over background in the gross gamma spectrum. Aliquots of this standard solution were then placed in radon emanating towers and radon was allowed to build up. The radon from these three aliquots of standard NBS radium solution (each containing about 100 pc) was then generated several times into 7 chambers. A factorial was run, and from the analysis of the factorial it was determined that there was no difference between any of the chambers or between any of our aliquots. The calibration factor as determined from these standards for each of the chambers was found to be 225 cph/pc radium-226 at 5 hr after introduction of the sample into the chamber.

Emanation Technique

The emanation efficiency of radon was then checked to insure that radon was being effectively removed from the radium-bearing solution. This was done by emanating radon into a chamber and immediately running a repeat emanation into an adjacent chamber. Allowing for the buildup of radon during the emanation, we found the generation efficiency to be 99.5%. It was found that, if the samples are stored in a refrigerator before the radon is emanated into the counting chamber, the sweeping efficiency for removal of radon from solution is increased because of formation of smaller bubbles.

Since the radon emanation towers must be used repeatedly, a check was run to insure that no cross contamination between samples could occur. After cleaning the towers by soaking overnight in 14 N HCl and BaCl₂, distilled water was placed in the flasks, and radon was allowed to build up. Several of these towers, all of which had contained high-level samples or standards, were then de-emanated into the counting chambers. No observable activity over background was found.

Procedure

As part of the HASL strontium-90 determination (see Appendix I), a purification step is included just before the yttrium precipitation to remove barium, lead, and radium isotopes. The purification involves the precipitation of radium and barium as the chromate. This precipitate (containing 20 mg of barium carrier) is then dissolved with a few drops of H₂O₂ and 5 ml of perchloric acid. The solution is then transferred with distilled water to an emanation tower which has been coated with a thin layer of silicone grease.

Radon is then removed from solution to establish time zero in the buildup of radon by passing about 200 cc/min of forming gas (80% N₂ + 20% H₂) through the solution for 10 min. The flask is then stored under refrigeration for about a week (71% buildup in 7 days). The sample is then flushed with forming gas, this time collecting the radon exit gas in a two-liter ionization chamber. The forming gas is bubbled through the sample at a rate of 200 cc/min for 10 min. The hydrogen in the forming gas combines with any residual oxygen in the sample in the presence of the platinum black, and is removed as water in the drierite. Radon daughters are then allowed to build up in the chamber for 5 hr, and the sample is counted overnight or for at least 12 hr. The data are printed out at 0.5-hr intervals on a punched paper tape.

The reagents used in the procedure were analyzed, and it was determined that in each sample there is a reagent blank due to radium-226 of 2 cph or ~0.01 pc. This is subtracted from the counting rate of each sample.

Calculations

Radon decays appreciably during the 12-hr counting interval, and a decay correction must therefore be made. To allow the equilibration of radon-222 daughters, the first 5 hr of counting data are discarded; then the counting data for the next 12 hr is summed, background subtracted, and this net count is multiplied by a factor to yield cph at 5 hr. The factor is computed from the expression

$$F = \frac{\lambda}{1 - e^{-\lambda t}} \text{ hr}^{-1} ,$$

where

$$\lambda = \text{radon decay constant} = 7.55 \times 10^{-3} \text{ hr}^{-1}$$

t = counting interval in hours.

For a 12-hr count,

$$F = 0.0872 \text{ hr}^{-1} .$$

The complete expression to convert counting data to pc of radium-226 is

$$\text{pc Ra}^{226} = \left[\frac{\lambda}{1 - e^{-\lambda t}} \right] \frac{[C - B]}{[F_B][225][Y]} - 0.01 ,$$

where

F_B = the buildup factor of radon-222 from radium-226

225 = cph at 5 hr for 1 pc radium-226

0.01 = reagent blank correction

Y = fractional radiometric recovery

C = total counts in counting interval

B = chamber background in counting interval.

Method Standardization

The initial work undertaken with the NBS radium solution established our calibration factor for the counters. Aliquots of this standard are run periodically to assure us that the counting system is under control.

In order to check the chemical recovery of radium, foods which had been run to determine their natural radium content were rerun, this

time spiking the ash with a known amount of radium-226. The chromate fraction was then dissolved and the radon generated in the usual way. Also, our standard strontium-90 vegetation sample was processed with a radium-226 spike added. This sample is composed of ashed oats, contains quite a bit of silica, and should be considered as one of the most difficult samples encountered. The results of the spiked samples are shown in Table I.

Table I

RADIOCHEMICAL YIELD OF SPIKED VEGETATION SAMPLES

Sample	HASL #	Ra ²²⁶ Found (pc)	Ra ²²⁶ Added (pc)	Percent Ra Recovery
Milk	7604A	1.9	2.1	94.3
Milk	7604B	1.8	2.1	91.6
Standard Vegetable	13973A	1.9	2.1	92.9
Standard Vegetable	13973B	1.9	2.1	91.5
Eggs	F0056	3.6	4.1	88.4
White Bread	13664A	3.6	4.1	88.0
White Bread	13664B	3.5	4.1	85.5
Fresh Vegetable	13962A	3.5	4.1	86.2
Fresh Vegetable	13962B	3.5	4.1	84.5
Fresh Fruit	13830A	3.4	4.0	85.5
Fresh Fruit	13830B	3.3	3.9	86.5
Avg.				88.6%

In order to determine the overall precision of the analysis, our sample of lowest activity was chosen, and several chemical analyses and repeat generations were run. Five different samples of Perry, New York, milk ash (10-gm aliquots) were analyzed, and each sample was emanated five times and counted in a different chamber each time. The results of this study are shown in Table II.

Table II

REPEAT ANALYSES (cph) OF FIVE PERRY MILK SAMPLES

Sample	Generation 1	2	3	4	5
Milk-#13447	70	70	72	80	61
M0002	74	76	79	82	80
M0028	59	56	54	69	65
M0052	71	83	83	79	75
M0065	68	73	73	76	76
Average 72.2 ± 8.1					

Although this study indicates a general precision of about 11%, it must be noted that milk ash is one of the least difficult samples to analyze chemically. We believe that a more appropriate estimate is a subjective error estimate of about $\pm 20\%$.

Procedure for BaSO₄ Measurement

After de-emanation, the sample is transferred to a beaker, heated, and a few drops of H₂SO₄ added to precipitate RaBaSO₄. The sample is allowed to digest overnight, the precipitate is filtered on glass fiber filter paper, dried, and weighed. Any sample which has a barium content equal to or greater than 20 mg is considered acceptable. The data from samples with a lower barium content are rejected, and the samples rerun. Because our minimum sample size is equivalent to about 500 gm of wet sample weight, there are usually a few milligrams of barium recovered from the sample exclusive of the 20 mg of barium carrier added. The natural barium present in the samples appears to be a rather variable quantity, and this did not allow us to use the barium gravimetric recovery to correct the sample data; instead it is used as a coarse yield indicator in our radium analysis. Although it is impossible to use the barium gravimetric recovery to correct for chemical loss of radium in the procedure, each sample is spiked with strontium-85 tracer and the radiometric recovery of strontium is determined directly after the RaBaCrO₄ precipitation. Since the strontium recovery should be quite similar to the radium recovery, this figure has been used to correct all of the radium results. The average strontium recovery of all the samples in this study was found to be 90%, and this compares well with our observed radium-226 recovery from spiked samples.

Direct Radium Measurement

As an afterthought, it was decided to count the radium-bearing BaSO₄ precipitates. The BaSO₄ which had been filtered on 1-in. glass fiber filter paper for weighing was covered with a 1-in. ZnS-coated MYLAR circle⁽⁴⁾ and mounted on the HASL ring and disc. These samples were then counted with a bare phototube. Each sample was counted for at least 5 hr. Standards and blanks were prepared by precipitating several weights of barium with and without a radium-226 spike. The counting data could then be corrected for self absorption, background, and counter efficiency.

Results

The comparison of the results by alpha counting and radon emanation are shown in Table III. The results are in good agreement, considering the large factors which must be used to correct for alpha absorption in about 20 mg of barium carrier.

Table III
COMPARISON OF α COUNTING AND RADON EMANATION TECHNIQUE

Sample	New York				Chicago				San Francisco			
	Survey 2		Survey 3		Survey 1		Survey 2		Survey 2		Survey 3	
	pc Ra ²²⁶ , sample				pc Ra ²²⁶ , sample				pc Ra ²²⁶ , sample			
	α ct	Rn Eman.	α ct	Rn Eman.	α ct	Rn Eman.	α ct	Rn Eman.	α ct	Rn Eman.	α ct	Rn Eman.
Whole Wheat Bread	0.61	0.60	0.70	0.66	0.77	0.72	1.09	1.09	-	-	1.15	0.94
White Bread	0.76	0.83	1.08	1.00	0.88	0.76	0.91	0.84	1.24	1.21	0.99	0.89
Flour	-	-	3.10	2.81	4.93	2.83	2.61	3.95	-	-	1.85	1.54
Milk	0.44	0.30	0.37	0.30	0.55	0.22	0.34	0.31	0.58	0.29	0.31	0.25
Potatoes	0.88	0.85	2.50	2.28	1.01	0.63	0.85	0.68	0.72	0.60	2.30	1.54
Macaroni	1.51	1.57	2.24	2.38	1.55	1.06	2.16	2.54	1.33	1.59	-	-
Dried Beans	0.86	0.68	-	-	0.61	0.50	0.65	0.59	0.92	0.80	1.00	0.91
Canned Vegetables	1.12	0.80	0.68	0.60	1.00	0.71	1.00	1.00	0.86	0.71	0.85	0.85
Fresh Vegetables	2.15	1.85	1.68	1.54	1.13	1.13	0.92	0.85	0.92	0.83	1.23	1.14
Root Vegetables	1.19	1.17	2.88	2.50	0.49	0.56	2.08	2.08	1.48	1.26	1.94	2.35
Canned Fruit	0.98	0.67	1.24	1.16	1.34	0.98	1.00	0.84	1.17	1.27	1.06	0.77
Fruit Juice	1.38	1.40	1.15	1.12	1.18	1.20	1.41	1.42	1.56	1.01	1.00	1.08
Fresh Fruit	1.05	0.89	6.06	5.69	0.98	0.69	1.54	0.95	1.68	1.76	1.54	1.16
Rice	1.25	1.12	1.30	1.41	1.29	0.82	0.41	0.49	1.20	1.14	1.87	1.33
Eggs	7.12	10.10	15.26	17.30	10.72	11.40	-	-	8.42	8.92	6.56	8.99
Fresh Fish	4.12	3.43	1.91	1.98	4.18	2.45	2.98	2.83	2.83	2.67	4.78	4.24
Shellfish	3.66	2.93	2.07	1.88	0.95	1.02	6.51	6.12	5.17	4.09	4.91	4.49
Meat	1.15	1.98	2.86	2.69	3.08	2.38	3.39	3.20	3.55	3.41	3.76	3.45
Poultry	4.03	3.06	3.50	3.34	5.88	3.50	10.67	5.72	12.03	10.67	3.28	2.51

Results

The data obtained from three surveys in each of the three U.S. cities are shown in Table IV, in terms of pc/kilo of original sample. Table V gives the results in terms of pc/year/person. The consumption figures

Table IV
Ra²²⁶ IN FOODSTUFFS (pc Ra²²⁶ PER KILO ORIGINAL MATERIAL)

Food Type	New York			Chicago			San Francisco		
	Survey 2 June 1960	Survey 3 Oct 1960	Survey 4 Feb 1961	Survey 1 May 1960	Survey 2 Sept 1960	Survey 3 Jan 1961	Survey 2 Aug 1960	Survey 3 Jan 1961	Survey 4 Mar 1961
Whole Wheat Bread	3.3	1.2	4.0	3.5	3.0	2.3	3.0**	2.8	3.3
White Bread	3.2	1.5	2.9	3.3	2.0	2.9	2.9	2.5	2.8
Flour, white	2.7	1.7	0.8	2.4	2.0	5.2	1.35	0.84	1.2
Milk, liquid	0.25	0.24	0.22	0.24	0.22	0.16	0.22	0.20	2.0
Potatoes	2.0	2.5	2.3	1.4	0.77	0.93	1.0*	2.0	1.0
Macaroni	2.1	1.8	2.0	1.6	1.9	2.3	1.2	1.7	1.6
Dried Beans	6.1	3.2	4.3	7.0*	2.5	5.3	2.3	4.1	4.0
Canned Vegetables	2.2	0.54	1.6	1.8	1.1	1.8	0.91	1.0	1.3
Fresh Vegetables	2.4	1.2	1.8	2.2	0.57	1.3	0.66	0.84	0.86
Root Vegetables	3.4	2.3	1.4	2.0*	1.8	1.9**	2.6*	2.4	1.2
Canned Fruit	0.37	0.37	0.35	1.2	0.26	1.1	0.50	0.73	2.0
Fruit Juices	1.6	0.49	0.73	0.68	0.86	0.63	0.71	0.62	0.53
Fresh Fruit	1.5	2.8	2.3	1.4	0.57	0.98**	0.91	0.65	1.5
Rice	1.5	1.0	1.1	0.70	0.37	0.70	0.63	0.80	0.53
Eggs	4.1	7.9	3.2	2.7	3.7**	4.8	2.6	1.9	2.0
Fresh Fish	1.2	0.68	1.5	0.71	1.0	1.2	0.80	1.2	0.76
Shellfish	1.2	1.1	2.4	2.5	1.7	1.5	2.0	1.0	1.8
Meat	0.44	0.47	0.63	0.45	0.64	0.86	0.81	0.55	0.37
Poultry	0.73	0.86	0.42	0.79	1.4	0.94	1.9	0.49	0.35
Water	0.011	-	-	0.020	-	-	0.008	-	-

* Data corrected by barium recovery as well as by strontium recovery.

** Missing sample; average value used for computing sums.

Table V
 Ra^{226} IN FOODSTUFFS (pc Ra^{226} CONSUMED PER YEAR)

Food Type	New York			Chicago			San Francisco		
	Survey 2 June 1960	Survey 3 Oct 1960	Survey 4 Feb 1961	Survey 1 May 1960	Survey 2 Sept 1960	Survey 3 Jan 1961	Survey 2 Aug 1960	Survey 3 Jan 1961	Survey 4 Mar 1961
Whole Wheat Bread	36	13	44	38	33	25	34**	31	36
White Bread	118	54	109	123	76	109	106	94	105
Flour	117	74	35	106	84	225	58	36	51
Milk, liquid	56	54	49	53	49	36	49	44	44
Potatoes	90	113	105	64	35	42	46*	91	45
Macaroni	6.2	5.3	5.9	4.8	5.8	6.8	3.5	5.1	4.9
Dried Beans	18	9.7	13	21*	7.5	16	6.8	12	12
Canned Vegetables	44	11	32	37	22	36	18	20	26
Fresh Vegetables	105	53	76	97	25	57	28	36	37
Root Vegetables	57	39	24	34*	31	32**	44*	40	21
Canned Fruit	9.7	9.5	9.1	31	6.7	29	13	19	51
Fruit Juices	31	9.3	14	13	16	12	14	12	10
Fresh Fruit	99	192	154	92	39	66**	62	44	99
Rice	4.6	3.1	3.3	2.1	1.1	2.1	1.9	2.4	1.6
Eggs	66	127	52	44	61**	77	41	31	32
Fresh Fish	9.6	5.4	12	5.7	8.3	9.6	6.4	9.2	6.1
Shellfish	1.2	1.1	2.4	2.5	1.7	1.5	2.0	1.0	1.8
Meat	32	34	46	32	47	63	59	40	27
Poultry	12	15	7.1	13	23	16	32	8.4	5.9
Water	4.6	-	-	8.9	-	-	3.7	-	-

* Data corrected by barium recovery as well as by strontium recovery.

** Missing sample; average value used for computing sums.

used to convert the per kilo data to yearly Ra^{226} uptake per person were obtained from Department of Agriculture⁽⁵⁾ data tabulated in Food Consumption of Households in the United States. An explanation of the consumption figures used in this laboratory is given in detail in HASL-90.⁽⁶⁾ From these data, the average daily consumption for persons in these three cities may be computed:

New York	Chicago	San Francisco
2.3 pc Ra^{226} /day	2.1 pc Ra^{226} /day	1.7 pc Ra^{226} /day

With our best estimate of the yearly calcium intake per person (383 gm), the radium-to-calcium ratio may also be computed:

New York	Chicago	San Francisco
2.2 pc Ra^{226} /gm Ca	2.0 pc Ra^{226} /gm Ca	1.6 pc Ra^{226} /gm Ca

The work of Walton *et al.*⁽⁷⁾ indicates a radium/calcium ratio for human bone in New York of 0.024 pc radium-226/gm calcium. Radium is thus more highly discriminated against than strontium where the observed ratio is four. HASL will have more directly applicable bone data from its current program.

Rapid Radium Determination

After the data in Tables IV and V had been collected, we decided to spot check the results by rerunning a few samples of ash which had been analyzed in the strontium determination, this time using a more direct method. We did this because known spiked samples run through a laboratory process may bear little relation to samples run on a routine basis.

A sample was randomly selected, and radium in this ash was determined by a rapid, direct method (see Appendix II) in which there is relatively little chance of radium being lost

A comparison of the results from this method and the longer strontium method are shown in Table VI.

Table VI

COMPARISON OF RADIUM RESULTS FROM TWO METHODS

	Direct Method, pc Ra ²²⁶	Barium Chromate Method, pc Ra ²²⁶
S.F. 3 - Root Vegetable	2.84	2.71

Other check samples are being run by this method and are now in process in the Laboratory

Appendix I

Procedure for Determination of Ra²²⁶ in Foods(8)

Place the weighed food in a tray and dry it in an oven at 50-60°C for 12 hr. Then, completely ash the sample at 500°C. Grind and weigh the residue

Transfer a weighed aliquot of the ash to a platinum crucible and add four times the amount of Na₂CO₃, mixing thoroughly. Add 1 ml of strontium carrier (20 mg/Sr/ml), 1 ml of strontium-85 spike solution, and 1 ml of barium carrier (20 mg barium/ml). Fuse at 900°C to a clear melt.

Transfer the melt to a beaker and add 25 ml of H₂O and sufficient 60% HClO₄ to dissolve the carbonates.

Add a 25-ml excess of 60% HClO_4 and evaporate until HClO_4 fumes are visible. Dissolve the perchlorates in distilled water. Heat the solution to 80°C and filter hot through #40 Whatman paper.

Transfer any remaining silica to the filter paper with hot 1:9 HNO_3 . Wash the silica several times with hot 1:9 HNO_3 and discard.

Add 1 ml of calcium carrier (200 mg calcium/ml). Precipitate alkaline earth nitrates with fuming HNO_3 (90%). Filter, discard the filtrate, and transfer the barium, radium, calcium and strontium nitrates into a beaker with distilled water. Evaporate to dryness and dissolve the residue in 23 ml of distilled water. Add 77 ml of fuming HNO_3 . Stir and cool to room temperature.

Filter the nitrate precipitate and discard the filtrate. Dissolve the precipitate with distilled water and collect the solution in a 40-ml centrifuge tube.

Add 1 ml of yttrium carrier (20 mg yttrium/ml). Heat in a water bath at 90°C and adjust the pH to 8 with NH_4OH . Cool, centrifuge, and decant the supernatant liquid into a 40-ml centrifuge tube. Dissolve the precipitate in a minimum of HCl ; dilute to 10 ml. Repeat the precipitation, combine the supernates, and discard the precipitate. Add 1 ml acetic acid (360 gm/liter) and 2 ml ammonium acetate (463 gm/liter). The pH should be 5.5. Heat in a water bath at 90°C . Add dropwise, with stirring, 1 ml of Na_2CrO_4 solution (48.6 gm anhydrous Na_2CrO_4 /liter). Stir vigorously until precipitation is complete. Cool, centrifuge, decant, and retain the supernate for strontium analysis. Dissolve the radium-barium chromate precipitate with 5 ml of 60% HClO_4 and 6 drops of cold 30% H_2O_2 .

Appendix II

Rapid Method for Radium Determination

To 5 gm of vegetation ash add 1 ml of barium carrier (20 mg barium/ml) and dilute to about 100 ml with water. Heat and add HCl dropwise until the foaming stops. Add NH_4OH dropwise until a permanent white hydroxide forms, then add HCl dropwise until the pH is 1. Precipitate BaSO_4 from the hot solution by adding 5 ml of ammonium sulphate (6 mg NH_4SO_4 /ml). Cool the solution in a water bath to room temperature. Filter through #42 Whatman filter paper, and wash the precipitate thoroughly with distilled water. Ash the precipitate in a platinum crucible at 900°C for 30 min. Add about 20 ml of HF and a few drops of H_2SO_4 to the ash, and completely evaporate the HF . Transfer the residue to a beaker with distilled water and filter through a #42 Whatman filter paper. Wash the precipitate thoroughly with distilled water. Ash the precipitate in a platinum crucible

(at 900°C). Add by eye an amount of Na_2CO_3 equal to the BaSO_4 . Fuse the BaSO_4 and Na_2CO_3 over a Fisher blast burner for 30 min. Dissolve the melt in 60% HClO_4 . Transfer this solution to a radon bubbler.

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COMPARISON OF TWO METHODS FOR DETERMINING RADIUM-226 IN SOIL SAMPLES

by

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Introduction

The subject of this paper deals with a comparison of two methods of determining radium-226 in soils: the familiar sodium carbonate-fusion method, and a nitric acid-leaching method. The use of leaching as a technique for obtaining radium, not to mention other elements, is certainly not new. As far back as 1931, Piggot conducted one of the first experiments on the leachability of radium. However, Piggot met with little success due to poor technique. In 1938, L. V. Komlev of the Radium Institute of the Soviet Union succeeded, by prolonged heating with distilled water, in extracting 18% of the radium retained in powdered granite. Moving closer to our present era, work carried on by I. E. Starik and N. I. Polevaya, at the All Union Geological Institute of the Soviet Union, centered around the leachability of radium from minerals. Some of the conclusions that were obtained from their experiments involved the dependence of leachability on time, in other words, leachability as a function of time. More recent studies made with hydrochloric and nitric acids as leaching solutions indicated that there are two routes by which radium passes into the solutions: leaching and dissolution. Work done by K. B. Zaborenka showed the relationship between particle size and leachability with Monazite samples.

Although the conclusions drawn by the above-mentioned authors were based upon experiments with minerals and mineral-type matrices, the work done with some soils at the Health and Safety Laboratory shows similar results. This work, as stated earlier, consisted in comparing the sodium carbonate-fusion method with a nitric acid leach. The work was done with seven soils whose types included granitic sediments, lake sediments, river sediments, and sea sands. It should be noted at this point that these soil samples were primarily taken for strontium analysis and were taken at a depth of 6 to 8 in. Thus, these samples were not taken by the regular radium-sampling technique which consists of deeper sampling of the soil. (Unfortunately, they were the only samples available at the time of starting the project.)

Methods

The sodium carbonate method consisted in taking a sample of approximately 5.0 gm and adding 25 gm of sodium carbonate (anhydrous). These are first ground in a mortar with pestle, then mixed thoroughly and put into a platinum crucible. They are fused at 900°C in a muffle furnace until a clear liquid is observed, which is removed and allowed to cool. The result is a light bluish-colored fusion having a homogeneous appearance. The fusion is removed from the crucible and transferred to a beaker. Perchloric acid is slowly added at first until the initial effervescence subsides; then the remainder of the perchloric is added, 150 ml in all. The platinum crucible is washed several times with perchloric acid and finally with water to remove any particles of the fusion that may adhere. The sample is slightly warmed to accelerate the disintegration of the fusion. When all the soluble fraction of the fusion has been dissolved, it is filtered through #41H Whatman paper. The remaining insoluble or silica portion which was first washed from the paper is dehydrated and vaporized with hydrofluoric acid. The remaining residue, if any, is again mixed with sodium carbonate, refused at 900°C, cooled, and dissolved in perchloric acid. Both fractions are then transferred to a radon flask and run by the radon emanation method. The method is based on the principle that micro-micro-gram amounts of radium-226 are measured by counting the gaseous daughter product, radon-222. The first step is to de-emanate the sample by flushing for 20 min with a forming gas consisting of 20 parts of hydrogen and 80 parts of nitrogen. The reason for the de-emanation is to remove any radon that may be present in the solution. The samples are then stored in the refrigerator for a period of 7 days to allow for buildup. (The 7-day period allows for the growth of 71% of the total radon.) The sample is then emanated into an ionization chamber by flushing with the forming gas for 20 min and counted over night for a period of 17 hr. (The reason for the longer period is that the first 5 hr are disregarded so as not to include the short-lived daughter. Thus, the samples are actually counted for 12 hr.)

The leaching technique consists of using approximately 5-gm samples. After placing in a platinum dish, the sample is treated with 20 ml of hydrofluoric acid (48%), which is added very slowly and cautiously at first. The samples are put on a sand bath and allowed to come to dryness. They are then cooled and transferred to a 250-ml beaker. A total volume of 100 ml of dilute nitric acid is added to each, and the samples are allowed to boil gently for a period of from 15 to 20 min. They are then removed from the hot plate and allowed to stand overnight. The following morning the samples are filtered through #41H Whatman paper, and the residue is washed with 1.1 nitric acid three times, followed by distilled water washings. The filtrate is then brought down to dryness and cooled. It is picked up with perchloric acid and transferred to a radon flask. The beaker is washed three times with perchloric acid. The samples are then run by radon emanation to determine radium-226 content.

The results as noted in Table I show that the recoveries from both methods have a variation per sample ranging from 2.2% to 15.2%.

Table I

Sample Number	Difference in Percentage of Recoveries between Na_2CO_3 and HNO_3 Methods
1	4.8%
2	2.2%
3	15.2%
4	5.2%
5	11.7%
6	4.8%
7	6.2%
Average difference is 7.2%	

Samples run by the leaching method but with varying time periods of leaching, namely, from a fast leach (about 5 min) to a more prolonged treatment as mentioned in the above procedure, showed that the longer the treatment the better and more uniform the recoveries. The fast or short treatment gave recoveries under 50%, while the prolonged treatment gave recoveries of 85% and higher.

Experiments run with one soil sample in which the size of the aliquots (5, 10, 25, and 50 gm) varied, showed no marked variation in the amount of radium-226 per gram recovered.

Conclusions

The conclusions reached, which are based on the use of a sediment-type soil which had been sifted and thoroughly mixed into a uniform blend are:

- (1) Variation of the size of the sample shows no marked effect on the recovery obtained per gram.
- (2) The longer the leaching period, the better and more uniform are the results obtained.
- (3) The leaching method is a simplified and direct method for determining radium-226 in the above type of soil with fairly good reliability.

This report is based on a preliminary study, and work is continually going on at present to improve the procedure.