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A PROCEDURE FOR THE ACID EXTRACTION AND ANALYSIS
OF STRONTIUM-90 IN SOIL

by

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With a Recommended Method for Soil Sampling

by

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TABLE OF CONTENTS

	<u>Page</u>
1. Introduction	1
2. Experimental	5
2.1 Sampling Method	5
2.2 Preparation of the Sample	5
2.3 Extraction and Separation	5
2.4 Counting	6
2.5 Reproducibility	7
2.6 Yield	9
2.7 Interferences	13
2.8 Comparison of Extraction Method and Fusion	14
2.9 Stable Strontium	15
2.10 Calcium-Strontium Separation	15
3. Conclusions	20
4. Appendix	21
4.1 Collection of Soil Samples for Strontium-90 Assay by Lyle T. Alexander	21
4.2 Analytical Procedure for the Acid Extraction and Analysis of Strontium-90 in Soil	24

Abstract

A procedure is described for the acid extraction and analysis of strontium-90 in soil. The method of collection, sample preparation, extraction, separation and counting are discussed and the reproducibility and reliability of the analytical method evaluated.

1. Introduction

There are two main purposes in the measurement of strontium-90 in soil. The first is to determine the activity per unit area as a measure of cumulative fallout at a specific location. The second is to relate the 'available' strontium-90 in the soil to its uptake by plants and eventually animals. In regard to the first point, it is generally accepted that for the majority of soils collected for fallout documentation, the strontium-90 is in a form which can be solubilized by leaching with 6 normal hydrochloric acid at room temperature. Some evidence is presented to verify this assumption and a comparison is made with the strontium-90 found by dissolving the soil sample completely after fusion with sodium carbonate. In the case of soils collected so close to a weapons testing area that the fallout particles are siliceous in nature (as would be the case at the Nevada Proving Grounds), it is doubtful whether 6 molar hydrochloric acid will have much effect.⁽¹⁾ These soils are only used for on-site fallout determination and consequently this would be considered a very special type of sample. The use of 6 normal hydrochloric acid was established as a result of experiments run on two soil samples collected in Hiroshima, Japan in 1954. Several concentrations of mineral acid up to 6 molar in concentration as well as one molar ammonium acetate were used as leaching reagents. This data is presented in Table 1.

Because of the dynamic nature of the Strontium Program, it was necessary initially to develop procedures within a relatively short period

(1) G. Welford, HASL, Private Communication.

of time. These original attempts to determine strontium-90 in soil, for fallout documentation at least, were not always successful and it is unfortunate that so many samples were analyzed using incompletely developed methods. There has been wide disagreement in results reported for a single sample among several different laboratories. Before any past soil data is used, one should be aware of the extraction method employed. It is the purpose here to present a procedure which has been severely tested and the reproducibility and reliability of which has been established. It has been shown that other extraction methods remove less strontium-90 from soil than can be leached with 6 normal hydrochloric acid. In addition, the direct milking techniques used at one time by several laboratories^(2,3) preclude the possibility of obtaining a pure strontium fraction and thereby evaluating the strontium yield for each sample. Furthermore, assay of the initial activity due to yttrium-90 milked from the impure strontium-90, requires extrapolation of a decay curve which may represent contaminating activities due to Ac^{228} , Pb^{214} , and Pb^{210} . These disadvantages could easily lead to anomalous and unreproducible results.

The procedure used at HASL involves the eventual separation of a pure strontium fraction which, when milked at equilibrium, yields an yttrium daughter activity which may be positively identified as yttrium-90 by half-life and beta absorption measurements. There is a loss of

- (2) Martell, E.A., The Chicago Sunshine Method, The University of Chicago, AECU-3262.
- (3) Kulp, J. L., Ecklemann, W. R., Schulert, A. R., Lamont Sunshine Chemical Procedures.

strontium-90 in the procedure as the separation involves a number of steps, and consequently it is necessary to correct for yield. This yield correction varies from one soil type to another, but if the sample contains negligible amounts of stable strontium, the weight of strontium carbonate recovered from the added carrier strontium, is a good measure of the recovery. However, in those cases where the stable strontium is appreciable, the yield correction must be determined using strontium-85 tracer. This isotope is a pure gamma emitter and with sufficient washing and reprecipitation, does not interfere with the measurement of yttrium-90 beta activity. It is possible to estimate the leached stable strontium by the simultaneous use of both recovery techniques. If this is to be done, complete separation of strontium from calcium must be effected. On the other hand, if a measure of the extracted stable strontium is not desired, the tracer can be used to determine the strontium yield even when calcium has not been completely separated.

It is important to realize that no strict procedure can be written for soil samples in general as soils differ markedly from one location to another. This is not only true with regard to the relative proportions of stable elements but also for the natural radioactivity which is always present. The procedure described in this report is not intended to be specific with regard to the number of fuming nitric acid separations necessary, for example, or volume conditions. These must be determined by the analyst for each separate sample.

TABLE 1

EFFICIENCY OF EXTRACTION METHODS APPLIED TO

JAPANESE SOIL SAMPLES

(Collected in January 1954 at Hiroshima)

<u>Leach Reagent</u>	<u>Sr⁹⁰ d/m/gram air-dried soil</u>	
	<u>A-1 (0-1" top)</u>	<u>I (cultivated)</u>
1.0 M NH ₄ Ac	0.67 ± 0.07	0.72 ± 0.06
0.1 M HCl	0.61 ± 0.06	0.49 ± 0.05
1.0 M HCl	0.85 ± 0.08	1.2 ± 0.08
6.0 M HCl	0.92 ± 0.08	1.8 ± 0.08

2. Experimental

2.1 Sampling Method

Most of the soils for fallout documentation and uptake studies are collected by Dr. L. T. Alexander of the United States Department of Agriculture. A description of the sampling procedure is given in section 6.1 of the Appendix.

2.2 Preparation of the Sample

The total soil sample is air-dried or placed in a 100°C oven for about 12 hours, then weighed. The entire sample is then ground and crushed, including rocks and vegetative material, to an aggregate size fine enough to be blended efficiently.

2.3 Extraction and Separation

Strontium carrier (200 milligrams) and strontium-85 tracer (about 500,000 d/m) are added to a weighed sample aliquot (500 grams). The aliquot is stirred with 6 M hydrochloric acid (1 liter) at room temperature for approximately 30 minutes and the extract is filtered and evaporated to a small volume. Nitric acid is added to decompose the leached organic material. After evaporation, most of the leached silica is dehydrated and is removed by filtration. An oxalate precipitation is carried out at pH 5.5 to precipitate the alkaline earths and leave iron in solution. Successive fuming nitric acid separations are performed until essentially all of the calcium is separated from the strontium and

the other alkaline earths.⁽⁴⁾ With proper technique, a high yield of carrier strontium can be obtained. Several acid treatments are required and the actual number depends on the amount of calcium which was leached from the soil. Following the fuming nitric acid separation, thorium, lead and any contaminating fission products remaining are scavenged with yttrium hydroxide, and radium and barium are removed by a barium chromate precipitation.

The daughter yttrium is milked after equilibrium and beta counted as a measure of the strontium-90 activity. Absorption corrections are not necessary since the weight of the precipitate can be rigidly controlled at this point. Twenty milligrams of yttrium carrier are added just prior to milking and the standards are prepared in an identical manner. The step-wise analytical procedure is given in section 6.2 of the Appendix.

2.4 Counting

Samples are mounted on plastic discs, covered with Mylar, and the assembly secured with a plastic ring. The sample is clamped into position under one of three one-inch Anton halogen-filled steel window G-M tubes (# 1007 M) which are surrounded by a guard ring (36 "pencil tubes" Anton # 315) in anticoincidence, shielded with 3 inches of mercury and beta counted for at least one hour. Backgrounds less than one count per minute are obtained using this counting system.⁽⁵⁾ More recently,

- (4) Modification of the method reported by Willard, N.H., and Goodspeed, E. W., Indus. Eng. Chem. Anal. Ed. 8, 414 (1936).
re: NYO-4700 - Manual of Standard Procedures.
- (5) Levine, H.D., Charlton, L., Graveson, H.T., Low Background Nuclear Counting Equipment, HASL-60, March 28, 1959.

beta scintillation counters with backgrounds of 0.3 to 0.2 counts per minute have also been in use. (5)

2.5 Reproducibility

In Table 2, duplicate strontium-90 analyses for some soil samples collected in the United States in 1956 are tabulated. These data attest to the satisfactory reproducibility of the method. In all cases, the analytical precision is within two standard deviations of the error due to counting.

- (5) LeVine, H. D., Charlton, L., Graveson, R. T., Low Background Nuclear Counting Equipment, HASL-60, March 23, 1959.

TABLE 2

STRONTIUM-90 IN SOIL - HCl EXTRACTION METHOD

(Duplicate Soil Aliquots Analyzed)

<u>Sample#</u>	<u>Depth</u>	<u>Sr⁹⁰ d/m/kg soil</u>	<u>Sr⁹⁰ mc/mi²</u>
6384a	0-2"	149.8 ± 5.1	5.99 ± 0.20
b		148.5 ± 6.1	5.97 ± 0.24
6381a	2-6"	29.7 ± 4.0	5.83 ± 0.78
b		25.3 ± 2.9	4.97 ± 0.57
6376a	0-2"	166.6 ± 6.6	11.63 ± 0.46
b		181.8 ± 8.3	12.69 ± 0.57
6378a	2-6"	8.9 ± 3.3	1.66 ± 0.62
b		12.4 ± 2.4	2.30 ± 0.44
6375	6-12"	2.1 ± 1.1	0.51 ± 0.27*
6385	12-18"	2.4 ± 1.1	0.67 ± 0.30*
6382a	0-6"	78.9 ± 5.7	15.29 ± 1.10
b		87.2 ± 5.2	16.89 ± 1.00
6380a	0-2"	231.6 ± 7.4	13.13 ± 0.42
b		251.8 ± 7.6	14.27 ± 0.43
6379a	2-6"	43.6 ± 6.0	7.30 ± 1.00
b		48.7 ± 4.1	8.16 ± 0.69
6383a	0-2"	275.2 ± 8.8	12.22 ± 0.39
b		301.2 ± 7.6	13.38 ± 0.34
6377a	2-6"	20.8 ± 4.1	3.64 ± 0.72
b		17.7 ± 2.7	3.10 ± 0.47

Note: Error term represents one standard deviation due to the error in counting.

* 1000 gram aliquot used for lower depth samples. Duplicates not analyzed. Data included to show lowest levels of strontium-90 which can be detected.

2.6 Yield

A comparison of the carrier and tracer yield measurements are shown in Table 3. These data were selected to show wide ranges of recovery, yet in most cases, the strontium-90 yield (determined by the tracer method) is better than 75%. In those cases where the gravimetric yield is higher than the tracer yield, it is assumed that macro amounts of stable strontium have been leached from the soil. On the basis of many other soil samples analyzed at HASL, it can be said that the strontium recovery is generally better than 80%. The majority of the loss apparently occurs in the oxalate precipitation, for in following separations, only relatively small amounts of strontium are lost by either coprecipitation or incomplete precipitation. For example, with the tracer, it was possible to determine the percentage of strontium-90 which is coprecipitated with barium as the chromate. Under the conditions of this separation, a very small and consistent amount of strontium is lost at this point. In the eight cases tabulated in Table 4, the range is 1.7 to 2.4% coprecipitation. Since the gravimetric yield of strontium is determined by weighing the carbonate precipitate, a study was made of the efficiency of this precipitation. It was shown that under the conditions used in the procedure reported here, the precipitation is quantitative.

To test the yield under the highest calcium concentration expected, 30 grams of calcium as the nitrate were spiked with strontium-87 tracer and 200 milligrams of strontium carrier added.

The radiochemical yield was 93% and was reproducible in the two separate experiments performed. This showed that the large volumes of fuming acid necessary to effect this separation, did not decrease the strontium yield in the presence of a pure calcium and strontium matrix.

TABLE 3

STRONTIUM YIELD - HCl EXTRACTION OF SOIL

(Duplicate Soil Aliquots Analyzed)

<u>Sample #</u>	<u>Yield Fraction</u>	
	<u>Sr⁸⁵</u>	<u>Grav.</u>
6384a	0.93	1.02
b	0.65	0.72
6381a	0.71	0.82
b	0.86	0.96
6376a	0.90	0.88
b	0.77	0.76
6378a	0.94	0.95
b	0.89	0.89
6375	0.85	0.84
6385	0.88	0.88
6382a	0.61	0.61
b	0.72	0.72
6380a	0.70	0.75
b	0.76	0.79
6379a	0.49	0.50
b	0.57	0.55
6383a	0.72	0.75
b	0.87	0.90
6377a	0.73	0.69
b	0.84	0.82

TABLE 4

PERCENTAGE OF STRONTIUM COPRECIPITATED

WITH BARIUM AS THE CHROMATE

<u>Sample #</u>	<u>% Sr Coprecipitated</u>
6375 A	1.9
6385 A	1.7
6376 B	1.8
6382 B	2.3
6380 B	2.0
6379 B	2.4
6383 B	2.2
6377 B	1.8

2.7 Interferences

Since the only elements which will precipitate with fuming nitric acid under the conditions used in the procedure are calcium, strontium, barium, radium, and lead, the potential radioactive interferences are radium and its daughters and barium-140 and its lanthanum daughters. Lead and La^{140} are scavenged in the first yttrium milking and radium and barium are removed in the barium chromate precipitation which immediately follows. In one soil analysis, the precipitate from the first milking was mounted and the activity followed over a period of 140 hours. There was a rapid decay initially, then a leveling off to a constant value after two weeks as shown in Figure 1. This indicated the presence of Pb^{212} , Pb^{210} and other shorter-lived radium daughter products. The level of activity after 40 hours was about the same as the activity attributed to strontium-90 at equilibrium after the second milking.

Experience has shown that soil containing milligram quantities of titanium, present analytical difficulties which are troublesome but not critical. This element invariably carries through the nitric acid separations, and until it is completely removed in the 'first milking', filtrations can be quite difficult and slow. The titanium compound (its chemical form is uncertain but there is evidence to indicate that it is a titano-silicate complex) does not appear to scavenge significant amounts of strontium.

If the procedure in the Appendix is strictly adhered to, all interferences are eliminated since a pure strontium fraction is obtained.

The decay of the milked yttrium-90 has been followed for every sample analyzed and within two standard deviations due to the error in counting, a straight line representing the established half-life (64.4 hours)⁽⁶⁾ is always found. Figure 2 shows seven examples of the decay curves obtained. In several cases where the activity has been sufficiently high, the yttrium-90 fraction has been analyzed by the beta absorption method of Harley and Hallden.⁽⁷⁾ The value for the energy found by this method agreed satisfactorily with that generally accepted (2.26 Mev).⁽⁸⁾

2.8 Comparison of Extraction Method and Fusion

By fusing an aliquot (1 lb.) of soil with sodium carbonate at temperatures around 1000° C⁽⁹⁾ and then dissolving the melt in mineral acid, one can solubilize the soil completely. If the assumption is made that the fusion analysis gives the total amount of strontium-90 in the soil, one can express the fraction or percentage of the total amount of strontium-90 removed by the hydrochloric acid extraction.

The soil samples shown in Table 5 were collected in pasture areas in the United States in 1956 and 1958. At least ten reanalyses have been carried out on each sample.⁽¹⁰⁾ The values for d/m Sr⁹⁰ per kg soil are averages and the error term is one standard deviation from the mean.

(6) Volchok, H. L., Kulp, J. L., Phys. Rev. 97, 102 (1955).

(7) Harley, J. H., and Hallden, N. A., Nucleonics, Jan. 1955, P. 32.

(8) Johnson, O. E., Johnson, R. G., Langer, L. M., Phys. Rev. 98, 1517 (1955).

(9) This work was done at the USDA Laboratories at Beltsville, Md. under the direction of Dr. L. T. Alexander.

(10) See procedure given in NYO-4700 - Manual of Standard Procedures.

For these limited number of samples, the results show that the 6 normal hydrochloric acid extraction, removes upwards of 84% of the total strontium-90. Bryant et al in England have shown good agreement also between soil fusion and HCl extraction. (11)

2.9 Stable Strontium

By using the strontium-85 tracer and the weight of the strontium found at the end of the procedure, a reasonably good estimate can be made of the stable strontium extracted by the 6N HCl. (12) It is extremely important, however, that a sufficient number of fuming nitric acid separations be employed to completely separate strontium from calcium.

Some analyses of stable strontium in soil using this method are reported in Table 6. A mean reproducibility of 11% was found for a large range of values.

2.10 Calcium-Strontium Separation

A test of calcium-strontium separation efficiency with 75% nitric acid using Ca^{45} as tracer showed calcium contamination of less than 0.2 mg in the strontium fraction. The initial Ca to Sr ratio used was 100 to 1 (2 gms. Ca against 20 mg Sr).

(11) Bryant, F. J., Chamberlain, A. C., Morgan, A., Spicer, G. S., "Radiostrontium Fallout in Biological Materials in Britain", AERE HP/R 2056.

(12) $\frac{\text{mg stable Sr in sample.}}{\text{Sr}^{85} \text{ yield}} = \frac{\text{mg Sr found}}{\text{Sr}^{85} \text{ yield}} (-) \text{ mg Sr added.}$

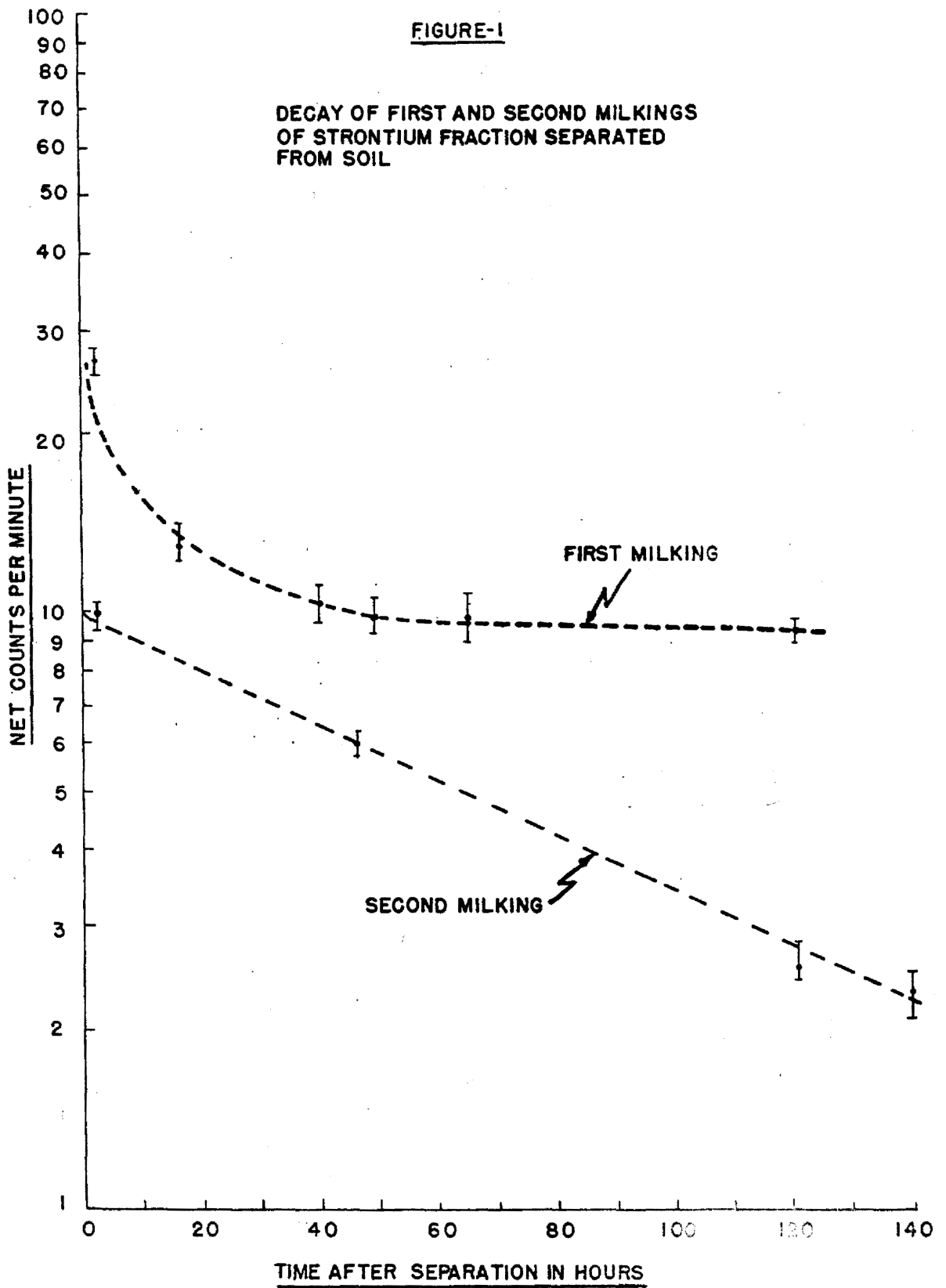


FIGURE 2

RADIOACTIVE DECAY OF YTTRIUM⁹⁰ MILKED FROM
STRONTIUM FRACTION EXTRACTED FROM SOIL
BY HCL

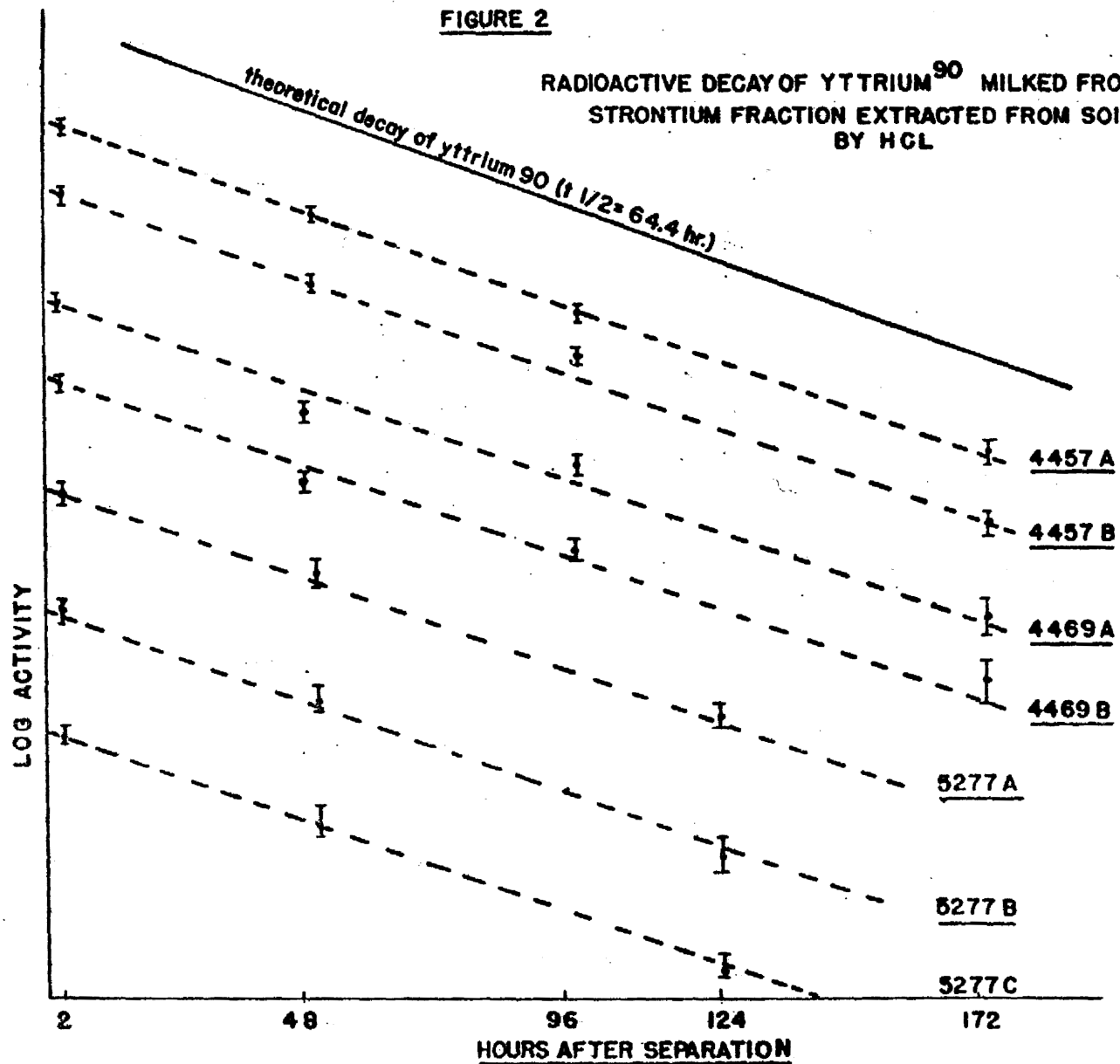


TABLE 5

Comparison of Strontium-90 in Soil by HCl Extraction and Fusion

<u>Sampling Area</u>	<u>Date Sampled</u>	<u>depth in inches</u>	<u>d/m Sr⁹⁰/kg soil</u>		<u>% Sr⁹⁰ removed by extraction</u>
			<u>Extraction</u>	<u>Fusion</u>	
Ithaca, N. Y.	summer '56	0 to ~2	224 ± 14	230 ± 19	97
McHenry Co., Ill.	10-30-58	0 to 8	164 ± 7	196 ± 3	84
Raleigh, N. C.	11-5-58	0 to 6	136 ± 8	160 ± 10	85

TABLE 6

STABLE STRONTIUM IN SOIL

(Duplicate Soil Aliquots Analyzed)

<u>Sample #</u>	<u>mg Stable Sr per kg soil</u>	<u>Sample #</u>	<u>mg Stable Sr per kg soil</u>
7015a	74	7035a	48
b	74	b	44
7017a	20	7037a	32
b	32	b	28
7019a	22	7073a	28
b	32	b	30
7021a	106	7076a	30
b	100	b	46
7023a	30	7039a	18
b	32	b	24
7025a	108	7041a	64
b	116	b	68
7027a	558	7043a	40
b	518	b	44
7029a	12	7045a	100
b	14	b	104
7031a	56	7047a	32
b	48	b	30
7033a	24	7056a	148
b	36	b	166

3. Conclusions

A procedure is presented for the extraction and analysis of total strontium-90 in soil. Available evidence shows it to be highly efficient as compared to the fusion technique for most soils and certainly more effective than other extraction methods. From an analytical standpoint, the precision is adequate and the limiting factor in the determination is the error due to sampling. The importance of site selection and sampling technique cannot be over-emphasized. The purpose of this report, however, is not to evaluate soil sampling but rather the analytical procedures involved.

4. Appendix

4.1 Collection of Soil Samples for Strontium-90 Assay⁽¹³⁾

by Lyle T. Alexander
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The sampling procedure described here is designed to get samples that will measure the total amount of strontium-90 that has fallen out in a given area. It will not evaluate the unusual case where excessive accumulations occur in low spots, at the foot of slopes, or in flooded areas.

The site should be nearly level with moderate to good permeability. There should be little or no runoff during heavy rains and no overwash at any time. Such sites are frequently found on smooth ridge crests, level farm land and in well kept lawns and grounds around institutional buildings. The site should not be near enough to buildings or trees to be sheltered during blowing rains.

Vegetation and Animal Activity

Amounts of fission products reaching the ground are undoubtedly influenced by vegetative cover. Bare ground, an alfalfa field and a bamboo grove do not intercept equal amounts of fallout. It is thought that a grass lawn or pasture makes a good vegetative cover for sampling areas. The grass also helps prevent loss by runoff of water. Well grassed areas usually have better permeability than corresponding areas

(13) See also Alexander, L.T., Hardy, E.P., and Hollister, H.L., Radioisotopes in Soil with Particular Emphasis on Strontium-90, Proc. Intern. Symp. on the Ecol. of Radioisotopes, Univ. of Minnesota, October 19-23, 1959.

of cultivated land. In wooded areas the non-uniform distribution of tree canopies will lead to unevenness in deposition of fallout materials. Soils having very high earthworm activity should be avoided because of uneven mixing of the soil to considerable depths. Rodent activity also renders areas unsuitable for sampling.

Sampling Methods and Tools

The degree of uniformity of fallout deposition has not had adequate definition. However, it is known that a sample of 1 to 2 square feet will give a good answer if the area is made up of a composite of at least 20 individual plugs or cores. These individual cores should be taken on some kind of systematic scheme or grid. An area the size of a small room is adequate for the grid. If one expects to resample a given area on a yearly basis, for example, a straight line of cores about one foot apart has been shown to be satisfactory.⁽¹³⁾ The number of cores must be known so that the analytical data can be related to a definite ground surface area.

Tools for taking the sample may be anything that will take a core or plug that is of equal area through its entire depth. On soil with reasonable base exchange capacity due either to clay or organic matter, a sample to the depth of 8 inches is adequate at the present time. As time passes, it may be necessary to go to deeper samples in order to measure all the strontium-90. A good pair of sampling tools is a 3-1/2 inch diameter "cookie cutter" that takes a 2 inch deep sample and a 3.25 inch barrel orchard auger that cuts a 3.5 inch sample.

If a single sample is to be taken at a given site, the cookie cutter is used to take out the sod to a depth of 2 inches and the auger takes the remaining 2-8 inches of soil from the hole. The soil from all 20 plugs or holes is composited to make a single sample of about ~~30~~⁶⁰ to 50 pounds. If desired, the 0-2 inch sod samples for the "cookie cutter" may be kept separate, making a sample of higher activity. Strontium-90 found in the upper 2 inches and that found in the 2 to 8 inch depth are added to give the total for the 1.34 square feet of surface represented in the samples.

Careful mixing and pulverizing of the sample is necessary to get a representative aliquot for analysis. Most of the strontium-90 may be in a small fraction of the total soil taken. Hence, care in mixing and sub-sampling can hardly be over-emphasized.

The key point to remember in sampling for strontium-90 is that all analytical values must be accurately related to surface area sampled.

At the present time we have no simple satisfactory method of sampling powder dry loose single grain soils. It is best to take samples when the soil has enough moisture to be coherent even if this requires wetting the area to be sampled by sprinkling.

4.2 Analytical Procedure for the Acid Extraction and Analysis of
Strontium-90 in Soil⁽¹⁴⁾

Carrier Solutions

- Strontium carrier - 20 mg Sr/ml
Yttrium carrier - 20 mg Y/ml⁽¹⁵⁾
Barium carrier - 20 mg Ba/ml

Apparatus

A detailed description of the apparatus employed in this procedure can be found in NYO-4700 - Manual of Standard Procedures.

CONVENTIONS

1. The commercial concentrated acids and ammonium hydroxide are indicated by the chemical symbol only.
2. Diluted acids are given as parts of acid to be added to parts of distilled water or in some cases the normalities are given.
3. All concentrations of dilutions are approximate, unless stated as exact or that preparation or dilution in a volumetric flask is required.
4. Wide range pH paper may be used for obtaining pH indicated, unless measurement with narrow range paper or a pH meter is specifically mentioned.

(14) Modification of the procedure presented in NYO-4700 - Manual of Standard Procedures.

(15) Some yttrium salts may be contaminated with thorium. A detailed procedure for the purification of the yttrium carrier solution by solvent extraction is given in NYO-4700 - Manual of Standard Procedures.

Procedure

1. Weigh out 500 gm. aliquots of the blended material into 3 liter beakers.
2. Add 200 mg of strontium carrier and carrier-free strontium tracer.⁽¹⁶⁾
3. Stir mechanically while slowly adding one liter of 6N HCl solution. (It may be necessary to add a few drops of octyl alcohol to prevent excessive frothing.)
4. Continue stirring for about 30 minutes. Allow a minimum of two hours for the insoluble material to settle.
5. Stir the mixture and filter with suction through a 24 cm No. 5 Whatman paper using a Buchner funnel.
6. Wash the soil residue with hot distilled water.
7. Wash the residue with 6N HCl and again with hot distilled water until the yellow color of iron (III) chloride is removed. Discard the residue.
8. Transfer the filtrate to a 3 liter beaker and evaporate to approximately 500 ml.
9. Cool and add one liter of HNO₃. (If there is excessive frothing, add a few drops of octyl alcohol.)
10. Evaporate to approximately 300 ml.
11. Add 500 ml of distilled water and stir. Allow to cool and filter with suction through an 11 cm glass fiber filter to remove the silica.

(16) The tracer must be checked to be certain that there is no contamination in the form of extraneous β activity.

12. Wash the silica with approximately 50 ml of hot 1:9 HNO_3 followed by several washes with distilled water. Discard the precipitate.
13. Transfer the filtrate to a 3 liter beaker and adjust the volume to approximately 1.5 liters with distilled water.
14. Add 50 gms of oxalic acid with magnetic stirring until the salt is completely dissolved.
15. Adjust the pH to 5.5 - 6.0 with NH_4OH . (If the brown color of iron (III) hydroxide persists, add more oxalic acid and readjust the pH.) Repeat if necessary. The optimum condition is an excess of oxalic acid in solution without causing crystallization of ammonium oxalate upon cooling.
16. Allow to stand for several hours, stir and filter with suction through a 15 cm No. 42 Whatman paper. Discard the filtrate.
17. Transfer the precipitate and paper to an appropriate size nickel or platinum dish and dry overnight at 110°C .
18. Ignite the oxalate precipitate in a muffle furnace at 400-500 degrees C for 2 hours. Raise the temperature to ~ 700 degrees C and continue heating for 2 hours. (Spattering is minimized by ignition in this manner.)
19. Cool the precipitate and transfer to an appropriate size beaker. Dissolve in a minimum of 1:9 HNO_3 . Gently heat to boiling.
20. Cool to room temperature. Filter through the smallest convenient size glass fiber filter using suction, to remove the insoluble material. Discard the residue.
21. Pour the solution into a suitable size beaker and evaporate to dryness. The evaporation must be done slowly to avoid spattering.

22. Dissolve the salt in distilled water and perform successive fuming nitric acid separations (the first two separations at concentrations slightly greater than 75%) until the strontium has been separated from the calcium. Samples with high calcium content will require 5 or 6 or more separations. The volumes of 75% HNO_3 solutions may be changed as required by the mass of calcium present keeping in mind that minimum volumes are always best.

Final Nitric Acid Separation

1. Allow the calcium and strontium nitrates to settle, then filter through a 2.8 cm fiber filter using a Fisher Filtrator and a fluorethene funnel. Discard the filtrate.
2. With the suction off, transfer the remaining precipitate in the beaker to the fluorethene funnel with distilled water and collect the resulting solution of nitrates in a 250 ml beaker. Apply suction and thoroughly drain the filter.
3. Evaporate slowly to dryness, then dissolve the residue in 23 ml of distilled water.
4. Add 77 ml of fuming HNO_3 (90%) with stirring. Stir for 30 minutes using a magnetic stirrer and Teflon covered bar.
5. Allow the strontium nitrate precipitate to settle and filter through a 2.8 cm glass fiber filter with a Fisher Filtrator and a fluorethene funnel. Remove as much nitric acid as possible. Discard the filtrate.
6. Dissolve the remaining precipitate in the beaker with distilled water. Transfer to the fluorethene funnel and collect the solution in a 40 ml centrifuge tube. Keep the volume at a minimum, preferably not over 20 ml.

Note 1:

If a gravimetric technique is to be used for yield determination, all of the calcium must be separated from strontium. It is important therefore, that a sufficient number of nitric acid separations be performed to insure removal of calcium. Lead and barium also precipitate under these conditions but are removed in the subsequent hydroxide and chromate scavenging steps.

First Milk

1. Add 1 ml of yttrium carrier solution.
2. Heat in a water bath regulated at approximately 90 degrees C.
3. Adjust pH to 8 with NH_4OH .
4. Cool to room temperature and allow the precipitate to settle.
5. Centrifuge for 5 minutes. Decant, pouring the supernatant liquid into another 40 ml centrifuge tube.
6. Dissolve the precipitate with a minimum amount of concentrated HCl , dilute to 5 ml and repeat steps 2 through 5. Combine the supernatant solutions. Discard the precipitate.
7. Add 1 ml barium carrier solution.
8. Add 1 ml 6M acetic acid and 2 ml of 6M ammonium acetate solution. The pH should be 5.5 (use narrow range pH paper).
9. Heat in a water bath regulated at approximately 90°C.
10. Add dropwise with stirring, 1 ml of 0.3M Na_2CrO_4 solution. The supernatant should have a chromate color. If it does not, then add more Na_2CrO_4 solution. All the barium must be removed.
11. Stir vigorously until precipitation is complete.

12. Allow to cool, then centrifuge for 5 minutes.
13. Decant, pouring the supernatant liquid into a 40 ml centrifuge tube.
14. Add 1 ml barium carrier solution and 0.5 ml of Na_2CrO_4 . Repeat steps 11 and 12.
15. Decant the supernatant liquid into a 2 oz. polyethylene bottle.
16. Add 3 drops of concentrated HCl and 1 ml yttrium carrier solution.
17. Store the solution for two weeks.

Second Milk

1. Transfer the equilibrated solution to a 40 ml centrifuge tube.
2. Heat in a water bath regulated at approximately 90°C .
3. Adjust the pH to 8 with NH_4OH , stirring continuously. Add 6 drops of H_2O_2 (30%). Continue heating to remove H_2O_2 .
4. Cool to room temperature before centrifuging. Decant, transferring the supernatant liquid to a 150 ml beaker. Record the hour and date.
5. Add 25 ml of distilled water to the precipitate in the centrifuge tube.
6. Dissolve the precipitate by adding 1:3 HCl dropwise with stirring.
7. Heat in a water bath and adjust pH to 8 with NH_4OH , stirring continuously.
8. Cool to room temperature and centrifuge for 5 minutes. Combine the supernatant liquids and save for recovery determinations.
9. Add 25 ml of distilled water to the precipitate.
10. Add 1:3 HCl dropwise until the precipitate just dissolves.
11. Add 20 mg of strontium as holdback carrier.
12. Heat in a water bath and adjust pH to 8 with NH_4OH , stirring continuously.

13. Cool to room temperature before centrifuging. Decant the supernatant liquid and discard.
14. Add 25 ml of distilled water to the precipitate and dissolve with 1:3 HCl.
15. Repeat steps 12 and 13.
16. Add 25 ml of distilled water, 2 ml of 6M ammonium acetate and 1 ml of acetic acid. The solution should be at pH 5.5.
17. Heat in a water bath regulated at $\sim 90^{\circ}\text{C}$.
18. Add 15-20 drops of saturated oxalic acid solution gradually with stirring.
19. Allow the precipitate to digest.
20. Remove from the water bath and cool to room temperature.
21. Filter through a 2.8 cm glass fiber filter using suction and a fluorethene funnel. Dry the precipitate in an oven at 110°C .
22. Mount the precipitate on a plastic disc, cover with Mylar and fasten with a plastic ring.
23. Beta count, recording the hour and date. Standardize with Y^{90} standard precipitate and mounted in a similar manner.

Strontium-85 Yield

1. Evaporate the supernatant from step 8 under Second Milk to a volume of approximately 25 ml and transfer to a 50 ml volumetric flask. Allow to cool to room temperature and dilute to volume.
2. Pipette 2 ml of this solution into a 5 ml glass vial, and dilute to approximately 5 ml.

3. Gamma count⁽¹⁷⁾, standardizing against a 25 fold dilution of the original spiking solution, prepared in the same way. Calculate the strontium recovery.

Gravimetric Yield

1. Transfer the remaining solution from step 2 under Strontium-85 Yield into a 150 ml beaker and heat to a gentle boil.
2. With continuous stirring, add approximately 5 ml of a saturated Na_2CO_3 solution. Gently heat for 10 minutes.
3. Cool and filter through a weighed 5.5 cm glass fiber filter paper. (When using the Buchner funnel to filter, care must be taken to prevent the precipitate from creeping under the filter paper. This can be done by filtering only through the center portion of the paper.)
4. Wash paper and precipitate thoroughly with distilled water.
5. Dry and weight to the nearest milligram.
6. A 10 ml aliquot of the original strontium carrier solution (20 mg per ml) is standardized as the carbonate by preparing it in the same way as described above. Calculate the strontium recovery.
7. Correct for total yield by dividing the above recovery factor by 0.96. (This is to correct for the 2 ml aliquot taken for strontium-85 yield.)

(17) This is carried out using a Baird Atomic Model 810 A bench type scintillation detector well counter with a Noralco decade scaler.