

APPENDIX A

SAVANNAH RIVER SITE ANALYTICAL AND COUNTING PROCEDURES FOR RADIONUCLIDES

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This appendix presents the sample preparation and analysis methods used to measure [radionuclides](#) in environmental samples collected at or in the vicinity of the SRS by the contractor. We focused on those procedures used to measure radionuclides that were determined in this report to be potentially quite useful to the [dose reconstruction](#). The researchers who are involved in the next phase of the dose reconstruction will most likely concentrate their efforts on these radionuclides in their calculations.

The following discussion addresses methods used to measure key radionuclides in ambient air, vegetation and agricultural products, milk, wild game, fish, sediments and soil, and water.

AIR SAMPLE PREPARATION AND ANALYSIS

Based on the evaluation of [environmental monitoring](#) in [Chapter 8](#), the key contaminants in air that appear to be most useful to a dose reconstruction are radioiodine and [tritium](#). The following discussion thus focuses on the analyses of air samples for these two radionuclides. Except for details concerning specific [analytical procedures](#), information on sample preparation and analyses were obtained primarily from routine monitoring reports. See [Chapter 7, Table 7-1](#) for a complete description of the various monitoring report series.

Analysis of Air Filters for Iodine

The Health Physics Control Laboratory was responsible for sample preparation and analysis of environmental and regional survey samples beginning with the preoperational survey. Preoperational monitoring of the Savannah River Site (SRS) was conducted in 1951 and 1952 and results are reported in [Reinig \(1952\)](#) and [Reining et al. \(1953\)](#). [Du Pont \(1953a\)](#) contains details of the sampling procedures followed during this period. All samples collected in the field were taken to the Sample Receiving Room in Building 735A and placed in the proper samples storage shelf section. Procedures for laboratory analyses are described below as they are found in [Du Pont \(1953b\)](#).

Air sampling equipment was protected from the elements in housing called 614 buildings. Initially, airborne [radioactivity](#) analysis consisted of continuous [beta](#) counting of filter paper to determine radon and thoron [concentrations](#). The period from January 1953 to July 1953 was a time of transition to a routine site monitoring program, coinciding with the startup of operations. Airborne particulates were collected by continuous sampling of air, at 2.5 cubic feet per minute (cfm), through a CWS #6 filter. The filters were collected weekly. Two sizes of [air filters](#) were used: 2 × 2-in. and 8 × 10-in. filters. (The smaller filters were changed to 2-in. diameter filters and the flow rate was decreased to 2 cfm in mid-1955.) After collection, 3 days were allowed for decay of radon and thoron daughters. The smaller filters were counted for [gross alpha activity](#), using a scintillation counter, and for [gross beta](#) activity, using an end-window Geiger-Mueller (GM) tube. The larger filters were analyzed for the number of particles from global particulate

[fallout](#) using radioautograph techniques. These filters were assessed for the number of particles per area.

Monitoring for radioiodine in air began in mid-1955. Silver nitrate impregnated HV70 filters were used to collect radioiodine. The flow of air through these filters was 2 cfm, and the filters were changed weekly. The filters were analyzed in the laboratory using a technique that involved dissolution of the filter and extraction with chloroform. Details of this procedure can be found in [Du Pont \(1959a\)](#) and are summarized here. The filters were first cut into pieces and dissolved in nitric and hydrochloric acids. Later in the procedure CHCl_3 was added to the solution. The iodine was later recovered by silver iodide precipitation. The precipitate produced was collected on a millipore filter. The dried filter, with precipitate, was then counted on a Geiger-Mueller counter calibrated with ^{131}I .

In early 1962, the silver nitrate-impregnated HV70 filters were replaced with charcoal filters. These filters were counted directly using [gamma](#) pulse height analysis. Gamma-emitting radionuclides (including ^7Be , $^{141,144}\text{Ce}$, $^{134,137}\text{Cs}$, ^{40}K , ^{54}Mn , $^{103,106}\text{Ru}$, $^{95}\text{Zr/Nb}$, and ^{131}I) were determined by counting each particulate or charcoal air filter in a 9×9 -in. sodium iodide [NaI(Tl)] well detector with a 400-channel gamma spectrometer through 1985.

Beginning in 1986, all samples were analyzed for gamma-emitting radionuclides using a hyper-pure germanium (HPGe) detector. A detailed description can be found in [Du Pont \(1989\)](#).

Detection Limits

Detection limits were reported in semiannual and annual reports for radioiodine from 1957 onward and are presented in [Table A-1](#). In addition, the original data sets typically reported a detection limit when an individual measurement was below detection. The exception was during 1961, 1963, and 1964, when values of “0” were used to represent measurements below the detection limit.

The sensitivity or limit of detection for radioiodine in air reported after 1960 (0.018 pCi m^{-3}) is consistent with detection limits reported elsewhere. [Sill and Flygare \(1960\)](#) reported a detection limit of 13 pCi m^{-3} at a flow rate of $1 \text{ ft}^3 \text{ min}^{-1}$ for a collection time of 1 hour. This correlates to a detection limit of approximately 0.015 pCi m^{-3} for a 2-week collection time and a flow rate of $2.5 \text{ ft}^3 \text{ min}^{-1}$. A detection limit of 0.1 pCi m^{-3} at a flow rate of $0.35 \text{ ft}^3 \text{ min}^{-1}$ and a collection time of 7 days was reported in [APHA \(1972\)](#). This correlates to a detection limit of approximately 0.007 pCi m^{-3} for a 2-week collection time and a flow rate of $2.5 \text{ ft}^3 \text{ min}^{-1}$.

In principle, the upper limit of detection is dependent on the state of the iodine and the adsorption capacity of the charcoal. In practice, however, it is limited by the dead time of the detector. This would become appreciable for samples containing more than 1 mCi ($1 \times 10^{12} \text{ pCi}$) of activity, which exceeds the amount likely to be collected in any environmental sample ([APHA 1989](#)). For comparison, sampling of the maximum measured air concentration at F-Area in 1964 (0.37 pCi m^{-3}) at a flow rate of $2.5 \text{ ft}^3 \text{ min}^{-1}$ for 2 weeks would result in the collection of about 500 pCi total activity.

Table A-1. Detection Limits Reported in Semiannual and Annual Reports for Radioiodine in Air Samples

Time Period	Reported detection limit ($10^{-14}\mu\text{Ci mL}^{-1}$)
Jan – June 1957	3.7 ± 0.15
July-Dec 1957	2.3 ± 0.09
Jan – June 1958	2.3 ± 0.09
July-Dec 1958	2.3 ± 0.1
Jan – June 1959	3.3 ± 0.2
July-Dec 1959	3.6 ± 0.1
Jan – June 1960	3.7 ± 0.1
July – Dec 1960	1.8 ± 1.1
Jan – June 1961	1.8 ± 1.2
July – Dec 1961	1.8 ± 1.2
June 1962	1.8 ± 1.2
July 1963	1.8 ± 1.2
1964 through 1965	1.8 ± 0.2
1966 through 1970	1.8 ± 0.2
1971 through 1982	1.8 ± 0.2
1983 through 1985	1.8 ± 1.2
1983 through 1990	1.8 ± 1.2

Analysis of Water Vapor and Rainwater for Tritium

Tritium monitoring in air was initiated in 1956. Tritiated water was captured using silica gel samplers. The water was recovered from the gel in the laboratory via distillation [Du Pont \(1959a\)](#). The distillate was then analyzed using scintillation counting methods described later in this appendix on [water sample preparation and analysis](#).

Rainwater was also analyzed for tritium and other radionuclides. Tritium data were determined to be the most useful for a dose reconstruction, as discussed in [Chapter 8](#). Rainwater samples were analyzed using scintillation counting methods described later in this appendix on [water sample preparation and analysis](#).

Detection Limits

Detection limits were reported in semiannual and annual reports for airborne tritium samples from 1956 onward and are presented in [Table A-2](#) for semiannual and annual averages. In addition, the original data sets typically reported a detection limit when an individual measurement was below the detection limit.

Table A-2. Detection Limits Reported in Semiannual and Annual Reports for Tritium in Air Samples (1956–1980)

Time period	Reported detection limit (pCi L ⁻¹ water vapor)	Reported detection limit (pCi m ⁻³ air) ^a
Jan 1956–June 1958	1000	Not reported per volume of air
July–Dec 1958	6300 ± 900	Not reported per volume of air
Jan–June 1959	4500 ± 600	Not reported per volume of air
July–Dec 1959	3900 ± 200	Not reported per volume of air
Jan–June 1960	3800 ± 300	Not reported per volume of air
July–Dec 1960	4000 ± 400	Not reported per volume of air
Jan–June 1961	4000	40
July–Dec 1961	4000 ± 300	60
Jan–June 1962	3000 ± 200	60
1963–1968	3000 ± 200	60
1969–1970	1000 ± 100	60
1971 – 1973	300 ± 20	10
1974–1980	300 ± 10	Not reported per volume of air

^a Approximate, varied with absolute humidity.

[Table A-3](#) summarizes the reported lower limits of detection (LLDs) for tritium in rainwater since 1962. The reported LLDs have been relatively stable since 1971.

Table A-3. Lower Limits of Detection for Rainwater Tritium Reported in Semiannual and Annual Reports from 1962 through 1991

Year	LLD (pCi mL ⁻¹) ^a	Standard deviation ^b
1962–1968	3 ± 2	.003
1969–1970	1 ± 1	.003
1971–1973	0.3 ± 0.02	.003
1974–1982	0.3 ± 0.01	NR ^c
1983	0.35 ± 0.05	NR
1984–1986	0.3 ± 0.05	NR
1987	0.54	NR
1988–1991	0.4	NR

^a Based on statistical counting error (90 or 95% confidence levels).
^b Calculated from spike recovery values.
^c NR = not reported.

Uncertainties Associated with Air Sampling Procedures

Iodine

The apparatus for sampling iodine in [ambient](#) air consists of a cylinder of flexible acetate plastic filled with activated charcoal held in place by a screen. A high-efficiency filter is also used for removal of particulate matter. Air is drawn through the apparatus, and iodine is adsorbed by the charcoal, which can be directly counted for activity determination. Before May 1962, a silver nitrate filter was used to collect radioiodine.

The apparatus used at the SRS initially consisted of silver nitrate-impregnated filters located downline from a 2-in. diameter high-efficiency asbestos paper filter. Silver nitrate filters were replaced by charcoal cartridges in March and April 1962. A continuous flow rate of $2.5 \text{ ft}^3 \text{ min}^{-1}$ was reported. The filters were collected weekly or biweekly.

Asbestos paper filters were reported to be used in 1971. Mixed fiber papers, including the cellulose-asbestos type, are highly efficient, exhibit low pressure drop, and have relatively low flow reduction because of loading [APHA \(1977\)](#). It is extremely difficult to remove dust and other particulate matter from these types of filters, but they are commonly used to collect [radioactive](#) contaminants whose activity can be determined by direct counting of the filters. The filters effectively collect any iodine adsorbed to particulates and a small amount of vaporous iodine. The remainder of vaporous iodine is adsorbed by the charcoal cartridge.

Activated coconut charcoal was reported to be used after April 1962. Silver nitrate was used before that time, until in-plant testing showed that collection efficiencies were far less than the 99% initially reported. Ordinary charcoal is activated by heating it with steam to 800–900°C. This results in the formation of a porous submicroscopic internal structure, which has a very high surface area that can approach $10,000 \text{ ft}^2 \text{ g}^{-1}$ of charcoal ([ACGIH 1989](#)).

Coconut charcoal has a naturally high K^+ content and high pH, both of which enhance adsorption of iodine. This material has been preferred as the natural base material for nuclear air cleaning applications ([Holladay 1979](#)).

Iodine is a fairly reactive element and can be found in the air in several chemical and physical forms including gaseous vapor, vapor adsorbed on particulates, or as a gaseous or solid iodine compound. Activated charcoal may not be as effective for removal of iodine compounds. For example, methyl iodide (CH_3I) is quite poorly adsorbed under humid conditions ([APHA 1972](#); [ACGIH 1978](#)). However, the capacity of activated charcoal to adsorb organic iodides can be enhanced by impregnation with chemicals such as I_2 , KI, triethylenediamine (TEDA), and hexamethylenetetramine (HMTA).

Although activated charcoal is an excellent adsorbent material, there are a few problems associated with its use: precisely, its high adsorbent capability. The process of adsorption is nonspecific and can result in collection of other gases, such as radon, xenon, and krypton. In addition, the majority of adsorbed iodine is usually concentrated on the initial portion of the charcoal bed, which can result in counter geometry problems. The use of silver zeolite cartridges drastically reduces the retention of noble gases. [Cline \(1981\)](#) reported ^{133}Xe retention on silver zeolite to be 15,000 times less than on charcoal. We found no evidence of silver zeolite filters being used within the time period of interest.

For elemental iodine vapor, collection efficiencies for activated charcoal can approach 100%. This is apparently true for all iodine [isotopes](#) produced in major quantities in fission processes, but only ^{131}I has a [half-life](#) long enough to be of major importance. Collection efficiencies for other forms of iodine, as previously discussed, may be much less. However, with the employment of charcoal impregnated with KI or TEDA, the collection of all forms of nonparticulate iodine will approach 100% ([APHA 1989](#)).

[Holladay \(1979\)](#) reported that any good grade of activated carbon, with or without impregnant, will deliver a decontamination factor of 100 (i.e., 99% efficient) for elemental iodine with any combination of temperature and humidity encountered in a nuclear air-cleaning system.

The second and subsequent editions (the first edition was unavailable) of [ACGIH \(1962, 1967, 1972, 1978\)](#) have reported collection efficiencies of elemental iodine greater than 99% for activated charcoal.

[Sill and Flygare \(1960\)](#) conducted a series of experiments that demonstrated the [efficiency](#) of charcoal as an adsorbent for iodine. In a laboratory run, which used a series of five 0.25-in. segments (5/8-in. diameter) of activated charcoal and a flow rate of 1–1.5 ft³ min⁻¹, the activity found in the segments was 58 900, 4 600, 490, 80, and 0 c/m, respectively. The efficiency was excellent (all of the activity was collected in the first four segments and none was collected in the fifth segment) considering the small amount of carbon and the relatively high flow rate. For field samples, most of the activity (about 80%) was also collected in the first 0.25 in. of the cartridge. When two cartridges were placed in series, the first cartridge retained more than 99% of the total activity collected by both cartridges.

Flow measurement [accuracy](#) of about 3% is obtainable with most commonly employed properly calibrated devices. A calibration accuracy of 5–10% is achievable depending on how well the distribution of iodine in the calibration standard conforms to the actual distribution of iodine in the sample cartridge ([ACGIH 1962](#)).

Various factors can potentially affect the collection efficiency of activated charcoal. In general, the collection efficiencies for elemental iodine are stable with regard to several operating parameters. Efficiency increases with pH and bed depth; decreases with high temperature, highly intense [radiation](#) fields, aging, and weathering; and is not affected by charcoal mesh size or relative humidity under 100% ([Holladay 1979](#)). Holladay (1979) suggests that ignition caused by radioiodine decay heat can be avoided by maintaining air flow in excess of 5 ft min⁻¹. The SRS flow rate of 2.5 ft³ min⁻¹ through a 2-in. diameter filter correlates to a flow rate of approximately 115 ft min⁻¹. The factors that result in decreased efficiency for collection of elemental iodine are not likely to have been encountered during routine environmental sampling by the SRS.

Particulate Sampling

[Biases](#) associated with particulate sampling, using an air filter, would affect gross beta, ⁹⁰Sr and ¹³⁷Cs results. The two most important contributors to particulate sampling uncertainty are (1) the volume of air sampled and (2) the total efficiency factor, which incorporates collection efficiency of samplers and filters. The collection efficiency of the ambient samplers is one significant source of negative bias (measurement will be lower than true value).

The volume of air sampled at each SRS monitoring location was calculated by multiplying the flow rate by the time period of collection. This assumes that the flow rate is constant, which is not always the case. Electrical surges and filter loading can affect the flow rate. These variables are situation-specific and would require a study of the monitors used at the Site. Unfortunately, no studies of flow rates could be found at the SRS.

The total collection efficiency of an air sampler can be viewed as having two components:

1. The *inlet collection efficiency* of the sampling device (how accurately the device draws the ambient [aerosol](#) into the filter)
2. The *filter collection efficiency* (the amount of the material drawn into the filter that is retained by the filter, i.e., does not pass through it).

For monitoring of SRS releases and global fallout, inlet collection efficiency is not likely to be an important factor. The particle sizes that are subject to large-scale transport are small enough that inlet collection efficiency is expected to be high.

From a review of the technical literature, filter collection efficiency is a much less important source of bias than the inlet collection efficiency, which was discussed in the previous section. A similar conclusion is reached by [Eisenbud \(1973\)](#), which states:

The uncertainties in estimating the human hazard from inhaling radioactive dust are so great that small differences of the order of 10 to 20% owing to imperfection in filter performance are relatively unimportant and would not affect one's evaluation of a given set of data. All the commercial filter media, when used properly, have efficiencies that are more than adequate to serve the purpose.

Tritium Sampling

Tritium in Air. Tritium in air was sampled by pumping air through a silica gel column, which collected the water vapor. Columns were changed every 2 weeks. The water vapor was separated from the silica gel by distillation. The radioactivity of tritium in the vapor was then determined by liquid scintillation counting. The air concentration was calculated by taking into account the volume of the air sampled and the absolute humidity during the sampling period. Because recovery of water is very near 100% ([Murphy et al. 1991](#)), the sources of uncertainty in the sampling procedure would be inaccuracies in the volume and absolute humidity. We could find no uncertainty values associated with these data reported in SRS documents.

Tritium in Rainwater. Rainwater was collected in pans and analyzed in the laboratory for tritium. The major source of uncertainty in the sampling procedure would be inaccuracy in the volume collected. We could find no uncertainty values associated with these data reported in SRS documents.

Uncertainties Associated with Laboratory Analyses

Beginning in 1958, uncertainties associated with laboratory analyses, based on the analyses of spiked samples, were reported in semiannual and annual reports. Unfortunately, standard deviations were not reported for iodine in air. [Table A-4](#) presents standard deviations for tritium in low-level samples for the years 1958 through 1980.

Table A-4. Standard Deviations Reported in Semiannual and Annual Reports for Tritium in Water Vapor Samples

Time period	Reported standard deviation (%) ^a
Jan–June 1958	5
July–Dec 1958	6
Jan–June 1959	3
July–Dec 1959	6
Jan–June 1960	6
July–Dec 1960	6
Jan–June 1961	5
1962–1973	3
1974–1980	Not reported

^a Calculated using spike recovery values.

VEGETATION AND AGRICULTURAL PRODUCT SAMPLE PREPARATION AND ANALYSIS

Based on the evaluation of environmental monitoring in [Chapter 9](#), the key contaminants in air that appear to be most useful to a dose reconstruction are ¹³¹I and tritium. The following discussion thus focuses on the analyses of vegetation and agricultural product samples for these two radionuclides. Except for details concerning specific analytical procedures, information on sample preparation and analyses were obtained primarily from routine monitoring reports. See [Chapter 7, Table 7-1](#) for a complete description of the various monitoring report series.

Vegetation and Agricultural Product Sample Preparation

Following collection, plant samples were oven dried at 80–90°C for 24 hours. A portion of each sample was retained before drying for tritium analysis of free water obtained through freeze-drying. Concentrations were reported as activity per gram (dry weight), except tritium, which was reported as activity per milliliter, and radioiodine, which was reported on a wet weight basis through June 1961.

Analysis of Vegetation and Agricultural Products Samples for Iodine and Gamma-Emitting Radionuclides

Concentrations of ¹³¹I were reported from 1955 through 1991. Before 1961, radioiodine concentrations were determined by counting on a GM counter calibrated with ¹³¹I ([Du Pont 1959b](#)). Undried vegetation and agricultural product samples were first digested with chromic and sulfuric acids, and the radioiodine was reduced with a 30% solution of phosphoric acid and removed by distillation. A chemical separation technique involving chloroform extraction followed by iodine recovery using silver iodide precipitation was then used to isolate the

radioiodine. In 1961, the chloroform extraction procedure was replaced by gamma spectrometry (described below).

Gamma-emitting radionuclides (including ^7Be , $^{141,144}\text{Ce}$, $^{134,137}\text{Cs}$, ^{40}K , ^{54}Mn , $^{103,106}\text{Ru}$, $^{95}\text{Zr/Nb}$, and ^{131}I) in vegetation were determined by counting dried, briquetted samples in a 9 × 9-in. NaI(Tl) well detector with a 400-channel gamma spectrometer from July 1961 through 1985. The plant material was dried at temperatures less than 110°C, briquetted in a hydraulic press, and canned with a commercially available canner. Beginning in 1986, all samples were analyzed using a HPGe detector.

Gamma-emitting radionuclide concentrations in agricultural products were measured by counting a bottled sample in hydrochloric acid solution. The methods of detection were not always explicitly stated, but it is assumed that samples were counted similarly to vegetation using a 9 × 9-in. NaI(Tl) well detector through 1985 and a HPGe detector thereafter.

Analysis of Vegetation and Agricultural Product Samples for Tritium

Tritium concentrations in vegetation and agricultural products were reported from 1974 through 1991. Free water was obtained by freeze-drying and counted using a liquid scintillation detector. The LLD for tritium from 1974 through 1985 was 1 pCi mL⁻¹ and for 1986 through 1991 ranged from 1.09 to 1.85 pCi mL⁻¹ for a short count (20 minutes) and from 0.28 to 0.38 pCi mL⁻¹ for a long count (300 minutes).

Agricultural products were prepared in a manner similar to that used for eating. Peelings, seeds, and other nonedible portions were removed. Wheat, containing the whole grains only, and oats, containing both grains and husks, were processed unwashed. In general, the majority of samples have been collected during the harvest season.

Analysis procedures for tritium and strontium were the same as those described for vegetation. Concentrations have been reported as picocuries per gram wet weight, except for tritium, which was reported as picocuries per milliliter free water. The analysis procedures for meat samples were not explicitly stated, but it is assumed that analysis procedures were similar to those described for [wild game](#).

MILK SAMPLE PREPARATION AND ANALYSIS

Based on the evaluation of environmental monitoring in [Chapter 10](#), the key contaminants in air which appear to be most useful to a dose reconstruction are ^{131}I , ^{137}Cs and $^{89,90}\text{Sr}$. The following discussion thus focuses on the analyses of milk samples for these radionuclides. Except for details concerning specific analytical procedures, information on sample preparation and analyses were obtained primarily from routine monitoring reports. See [Chapter 7, Table 7-1](#) for a complete description of the various monitoring report series.

As of 1961, it is stated that controls were established in the laboratory groups when the “rerun” system was started. Spiked samples were analyzed with sets of routine samples and at intervals established by the laboratory supervision. In addition to this program, routine samples were selected randomly and analyzed again a week or more later. Although it was reported ([Marter and Boulogne 1961](#)) that the results of the spike samples and the laboratory “reruns” were published monthly, such results have not been found when reviewing the documents. Results of the SRS’s participation in the interlaboratory cross-check program are provided in

annual reports starting in 1977. An appendix detailing the SRS's quality control program can be found in the annual reports starting in 1980.

The minimum detection limit with 90% confidence interval was reported for milk analyses based on statistical counting error. No self-absorption corrections were applied, but probably contribute minimally to the total [uncertainty](#). Percentage standard deviations were also reported based on the spike recovery values. It was stated that these values were applicable to the reported 6-month average data. These data are summarized for ^{131}I and ^{90}Sr in Tables [A-5](#) and [A-6](#), respectively.

Analysis of Milk Samples for Iodine

The earliest analyses (1956–1960) used a radiochemical separation technique and the sample was counted with a calibrated GM counter. An [ion exchange](#) - gamma spectrometric technique was introduced in 1960 that greatly improved the [sensitivity](#) of the analysis. This general technique has remained essentially the same ever since. Subsequent improvements resulted from using deep well detectors, larger crystals, and more sophisticated multichannel analyzers. The sample size and counting time, which also affect the sensitivity of the analyses, have also changed over time. [Table A-5](#) summarizes the [detection limit](#) that was achieved for milk sample analysis. A description of the techniques used is provided in the following paragraphs.

Before the third quarter of 1960, milk samples were analyzed for radioiodine using a chemical separation technique that involved a chloroform extraction procedure to extract the iodine from other elements, followed by iodine recovery using silver iodide precipitation. To prepare the milk for chloroform extraction, most of the water was removed by alkaline distillation. The organic fraction of the milk was digested with chromic and sulfuric acids. The iodine was reduced with phosphoric acid and removed by distillation ([Du Pont 1959a](#)). The final sample (filter paper on a planchet) was counted on a GM counter calibrated with ^{131}I . For procedure control, a [spike](#) and a blank were included with each group of samples. According to [Du Pont \(1959a\)](#), the manual for standard operating procedures at the time, the results were corrected if the recovery efficiency of the procedure was less than 95%. All results were corrected for decay. It would appear that a 100 mL sample of milk was used for the analysis. Sample counting time is not reported.

An ion exchange - gamma spectrometric technique was introduced in 1960 that greatly improved the sensitivity of the analysis. The new technique was first described in the March 21–25, 1960, Control and Methods Weekly Report ([Du Pont 1960b](#)). It was introduced in the second half of 1960 for routine analysis of ^{131}I in milk ([Boni 1960, 1962; Du Pont 1960b](#)). The technique involved the direct absorption of ^{131}I on anion exchange resin, transfer of the resin to a 500-mL polyethylene bottle, and the subsequent analysis on top of a 3 × 3-in. sodium iodide, thallium activated crystal (NaI(Tl)), gamma detector. A 1-gal sample of milk was used during a 10-minute counting time with a 200 RIDL multichannel analyzer. Although the third quarterly report for 1960 ([Du Pont 1960c](#)) gives a detection limit of 9 pCi L⁻¹, the minimum detection limit was reported as 11.0 pCi L⁻¹ in subsequent tabulations of the results and a subsequent memo ([Boni 1960](#)). This suggests that for routine analyses, it was not possible to achieve the sensitivity initially anticipated. The reports state that a correction for [background](#) was made in the analysis ([Boni 1960](#)). The procedure was also reported at the annual Health Physics Society Meeting in

1962 ([Boni 1962](#)) with a minimum detection limit of 3.5×10^{-15} Ci mL⁻¹. Again, this suggests that for routine analysis this sensitivity was not achieved.

Table A-5. Changes in Detection Limit for Radioiodine in Milk Samples

Time period	Reported detection limit (pCi L ⁻¹)	Standard deviation (%)
January–June 1957	120 ± 5	22
July–December 1957	Not reported	Not reported
January–June 1958	92 ± 5.3	18
July–December 1958	100 ± 6	23
January–June 1959	150 ± 10	26
July-Dec, 1959	160 ± 10	15
January–June 1960	140 ± 7	10
July–December 1960	10 ± 1.5	2.5
January–June 1961	9.8 ± 1.5	11
July–December 1961	5.4 ± 1.0	15
June 1962	2.2 ± 0.2	10
July 1963	11.3	Not reported
1964 through 1965	2.2 ± 0.5	10
1966 through 1970	5 ^a	Not reported
1971 through 1982	1 ± 0.5	Not reported
1983 through 1985	1.2 ± 0.5	Not reported
1983 through 1990	3 ^b	Not reported

^a Detection limit reported as 2.2 ± 0.5 pCi L⁻¹ (10% Std. Dev.) in the annual reports, but 5 pCi L⁻¹ appears to be the norm based on the aperture cards. It is not clear what (sample size, counting time) accounts for the difference.

^b Detection limit is reported as 1.2 ± 0.5 pCi L⁻¹ in the minimum detectable concentration table but as 3 pCi L⁻¹ in text of the annual reports. It is possible that the detection limit for ¹³¹I in milk was erroneously reported in the text and that the error was propagated in subsequent reports.

The detection limit was reduced from 11.0 to 6 pCi L⁻¹ starting in July 1961. This improvement appears to have resulted from counting the sample directly in a well NaI detector and no longer transferring the resin to a 500-mL polyethylene bottle; however, no explicit documentation for this has been found to date.

A further improvement on the ion exchange technique was introduced for the routine analysis of milk during the last week of June 1962 ([Du Pont 1960b](#)). The milk sample was counted directly with a large (9 × 9-in.) NaI(Tl) crystal with a deep (3.25 × 6-in.) well ([Boni 1962](#)). The sample size and sample counting time remained unchanged. The minimum detection limit was reported as 2.2 ± 0.2 pCi L⁻¹. The [uncertainty](#) was based on statistical counting error (90% confidence interval) ([Du Pont 1963](#)). The sample size was reduced to one-half gallon in July 1963 and the minimum detection limit was reported as increasing to 11.3 pCi L⁻¹.

In 1980, the milk sample size was 3.8 L (1 gal). The sample was counted for 200 minutes on a (9 × 9-in.) NaI(Tl) well detector. The detection limit was reported as 1 ± 0.5 pCi L⁻¹. Based on the reported detection limit it would appear that this procedure was used from 1971 through 1982.

In 1983, a 2-L (slightly in excess of one-half gallon) sample of whole milk was passed through an anion exchange resin (“Dowex L-X8”) column. The column was counted in a (9 × 9-in.) NaI(Tl) well detector.

The 1989 and 1990 annual monitoring reports ([Cummins et al. 1990](#), [1991](#)) state that one-half gallon of fresh raw milk was obtained from each sample location, but just 1-L [aliquots](#) (0.2642 gal) were determined by direct count on a high purity germanium (HPGe) detector. The count time is not specified.

Problems associated with the analytical procedures are occasionally noted in the reports. However, it is difficult to relate this information to the reported measurements. For example, in the September 26–30, 1960, weekly report ([Du Pont 1960d](#)) it is stated that the ¹³¹I recoveries in spiked milk were suddenly low and variable. Close control of the pH of the spike solution was found to be very important. The presence of sodium hydroxide in the milk inhibited the concentration of ionic iodine by the anion resin. It was speculated that high basicity probably caused saponification of the butterfat that absorbs iodine and inhibits complex formation with the resin.

Analysis of Milk Samples for Cesium

In 1963, milk samples were counted directly in 500-mL volumes in 16-oz narrow-mouth polyethylene bottles for ¹³⁷Cs ([Boni 1963](#)). If no other [isotopes](#) were present, a sensitivity of 23 pCi L⁻¹ was reported for a 10-minute count time. By 1965, one-half gallon milk samples were passed through an ion column. The ¹³⁷Cs in the column effluent was concentrated on an ion exchange column for gamma spectrometric analysis. A minimum sensitivity of 11 pCi L⁻¹ was reported ([Du Pont 1965](#)). A two-part ion exchange column was used to sequentially separate and concentrate radioiodine and cesium from the same sample of milk (1 gal). The second part of the column contained granular potassium cobalt ferrocyanide (KCFC), a highly selective absorbent for cesium. A minimum sensitivity of 3 pCi L⁻¹ with a 10-minute count time and a 9 × 9-in. well crystal was reported ([Marter 1965](#)).

By 1972, ¹³⁷Cs was removed from the sample by passing approximately 2 L of milk through a KCFC resin column. The column was counted directly using a 9 × 9-in. NaI(Tl) well detector with a 400-channel gamma spectrometer ([Du Pont 1973](#)). This procedure continued through 1986. From 1987 through 1990, a HPGe detector was used to count a 1-L aliquot of milk directly.

Analysis of Milk Samples for Strontium

The method used to analyze ⁹⁰Sr in milk samples appears to have changed very little over the entire time period of the monitoring program. The milk was first passed through an ion exchange resin to chemically extract the strontium, followed by acid leaching of the resin. The short-lived ⁹⁰Y daughter was removed from the eluate before ingrowth was allowed to begin. After equilibrium of ⁹⁰Y with ⁹⁰Sr was established, the ⁹⁰Y was again stripped from the solution and counted with a low background beta counter. The minimum detection limit for the analysis has remained very similar throughout the entire time period as a consequence. [Table A-6](#) summarizes the detection limit achieved for milk sample analysis. In April 1961, ⁹⁰Sr determinations in milk were made using a di-2-ethylhexyl phosphoric acid (HDEHP) extraction

procedure that used NH_4OH instead of NaOH in the neutralization step. Total radiostrontium ($^{89,90}\text{Sr}$) was determined using a rhodizonic acid procedure.

In 1962, milk samples were prepared using a chemical extraction process that involved ion exchange, acid leaching, dissolving in a dilute solution of HCl , and extraction ^{90}Y into HDEHP in toluene solvent. The ^{90}Y was finally counted on a planchet in a low background beta counter. A 500-mL sample of milk and a counting time of 60 minutes were (Butler 1962). The minimum detection limit was stated as 1.0 ± 0.1 pCi L^{-1} based on statistical counting error (90% confidence interval). In March 1964 (Du Pont 1964), the analytical procedures for determination of ^{90}Sr and $^{89,90}\text{Sr}$ were combined to reduce analysis time and to improve precision. Recovery of ^{90}Sr was $82\% \pm 5\%$, and total radiostrontium was $68\% \pm 5\%$. In 1965 a rhodizonic acid separations procedure was used. It had a minimum detection limit of 1.0 ± 0.1 pCi L^{-1} .

The same procedure appears to have been used from 1972 through 1990 for the analysis of ^{90}Sr in milk. One-half-gallon samples were collected and 0.5-L aliquots were analyzed. The strontium and yttrium were removed as chlorides by a slurry of the whole milk with a cation resin. The resin was leached with 8N nitric acid. The acid was evaporated to dryness and dissolved in 0.08N hydrochloric acid. To begin the ^{90}Y ingrowth, ^{90}Y is removed from the ^{90}Sr by liquid ion-exchange using HDEHP in toluene. Equilibration of ^{90}Y with ^{90}Sr is approached over a 15-day period, after which the short-lived ^{90}Y daughter is stripped and counted in a low-level gas flow beta proportional counter (Du Pont 1973). The amount of ^{90}Sr is calculated by relating the ^{90}Y buildup to the original ^{90}Sr concentration. The sample count times are known to have changed—a 50-minute count was used from 1974 through 1982 and a 20-minute count time was used from 1983 through 1985. These differences probably account for the small changes in the minimum detection limit for the analysis (Table A-6).

Table A-6. Changes in Detection Limit for ^{90}Sr in Milk Samples

Time period	Reported detection limit (pCi L^{-1})	Standard deviation (%)
1959	Not reported	Not reported
1960	1	Not reported
January–June 1961	1.6 ± 0.3	11
July–December 1961	1.0 ± 0.1	7
1962 through 1973	1.0 ± 0.1	7
1974 through 1982	1.1 ± 0.12	Not reported
1983 through 1985	2.4 ± 0.75	Not reported
1986 through 1988	1.62	Not reported
1988 through 1991	1.9	Not reported

WILD GAME SAMPLE PREPARATION AND ANALYSIS

Based on the evaluation of environmental monitoring in Chapter 11, the key contaminants in wild game that appear to be most useful to a dose reconstruction are ^{137}Cs and $^{89,90}\text{Sr}$. The following discussion thus focuses on the analyses of wild game samples for these two radionuclides. Except for details concerning specific analytical procedures, information on sample preparation and analyses were obtained primarily from routine monitoring reports. See

[Chapter 7, Table 7-1](#) for a complete description of the various monitoring report series. Methods of analysis and lower limits of detection have not always been explicitly stated in the environmental monitoring reports. The following paragraphs summarize the information given in these reports regarding sample preparation and analysis (primarily for deer). It is assumed that similar methods were used for other wild game samples. All concentrations have been reported as picocuries per gram wet weight.

Analysis of Wild Game for Cesium

Between 1965 and 1969, approximately 20% of the total number of deer harvested were monitored for ^{137}Cs and [nonvolatile beta](#) activity by random sampling of foreleg flesh and bone for laboratory analysis. Additionally, deer were monitored for external [contamination](#) with a Thyac GM survey meter. Beginning in 1970, all individual deer were monitored in the field by 2-minute duplicate counts using two different portable NaI 2 × 2-in. detectors before their release to the hunter. Details regarding the operation of this instrument can be found in [Rabon and Johnson \(1973\)](#) and [McMahan and Wright \(1973\)](#). Nonvolatile beta concentrations were reported for deer muscle and bone tissue before 1969, but the methods of sample preparation and analysis were not clearly specified. However, a gas-flow proportional detector was likely used, following wet-ashing of collected tissue with nitric acid and hydrogen peroxide.

Gamma spectrometry was first used in 1956 to identify gamma-emitting radionuclides in environmental samples ([Harvey and Rabon 1965](#)). While this process identified specific radionuclides, average nonvolatile beta concentrations were predominantly reported through the early 1960s. In 1962, concentrations of specific radionuclides in wild game samples began to be routinely reported.

Cesium-137 concentrations have been consistently reported for deer muscle tissue samples since 1965. Tissue samples were collected for laboratory analysis from approximately 20% of the total number of deer harvested before 1970. Since 1970, a fraction (ranging from 2 to 20%) of the total number of deer harvested have been analyzed in the laboratory to verify the field measurements. The SRS environmental monitoring reports did not specify methods of sample preparation or analysis before 1987. However, [Rabon \(1968\)](#) and [McMahan and Wright \(1973\)](#) detailed a laboratory method of analysis for deer collected from the SRS. A 500-g (wet weight) sample of muscle was wet-ashed in nitric acid and hydrogen peroxide and subsequently placed in a 3 × 6-in. well of a 9 × 9-in. NaI(Tl) crystal connected to a 400-channel pulse height analyzer for counting.

[Table A-7](#) compares data comparing field and laboratory measurements of ^{137}Cs in deer from aperture card printouts for several years between 1972 and 1981 and the Savannah River Plant Site Environmental Reports for 1985 through 1991. In general, the field and laboratory measurements have been in good agreement, and neither method appears to have provided consistently higher values. [Figure A-1](#) shows concentrations measured in the field as a function of concentrations measured in the laboratory for the same years described in [Table A-7](#). The relationship appears very linear with a slope of 1 through about 35 pCi g⁻¹. Beyond this concentration, the field measurements appear to slightly underestimate the concentrations measured in the laboratory. However, this should not have presented a problem because all animals with field estimates of 25 pCi g⁻¹ or greater were sampled for laboratory analysis. [McMahan and Wright \(1973\)](#) also reported a plot of field estimates versus laboratory estimates,

and the data appeared linear with a slope of 1 to about 30 pCi g⁻¹. Beyond 30 pCi g⁻¹, the field estimates again appeared to slightly underestimate the laboratory estimates although there were few data points.

Table A-7. Comparison of ¹³⁷Cs Concentrations Measured in the Field and Laboratory

Year	Ratio of field to laboratory	
	measurements	Number of samples
1972 ^a	0.93	20
1974 ^a	1.01	8
1975 ^a	1.21	56
1977 ^a	0.96	82
1978 ^a	0.98	79
1979 ^a	1.01	52
1980 ^a	0.71	58
1981 ^a	1.13	53
1985	1.21	42
1986	1.37	41
1987	0.90	35
1988	1.20	67
1989	0.96	96
1990	0.69	93
1991	0.69	124 ^b
<u>Overall average</u>	0.96	Total number = 906

^a Data are from aperture card printouts.
^b Includes measurements for both deer and hogs.

Methods of sample preparation and analysis for feral hogs and other fur-bearing animals have generally not been explicitly described in the environmental monitoring reports, but it is assumed that analysis techniques similar to those described for deer were used.

Methods of sample preparation and analysis for waterfowl have also not been explicitly described in the environmental monitoring reports. However, [Straney et al. \(1975\)](#), [Fendley et al. \(1977\)](#), and [Dombay et al. \(1977\)](#) described a method that was used for counting 500-g samples as well as individual whole birds collected from the SRS. A Packard Model 446 Armac liquid scintillation detector equipped with a Packard tri-carb scintillation gamma spectrometer was used for radiocesium counting in these studies.

Thyroid samples were monitored for ¹³¹I by the SRS using the same detection methods as described for ¹³⁷Cs. The LLD reported for ¹³¹I in 1965 was 6 pCi g⁻¹ and has been 1 pCi g⁻¹ since 1976. Beginning in 1984, thyroid samples were analyzed for ¹²⁹I by the University of Tennessee, Memphis. Samples were analyzed by the Center for Health Sciences (1984–1986) and the Department of Physiology and Biophysics (1987–1991). The detection method or LLD for these samples were not specified in the SRS environmental reports.

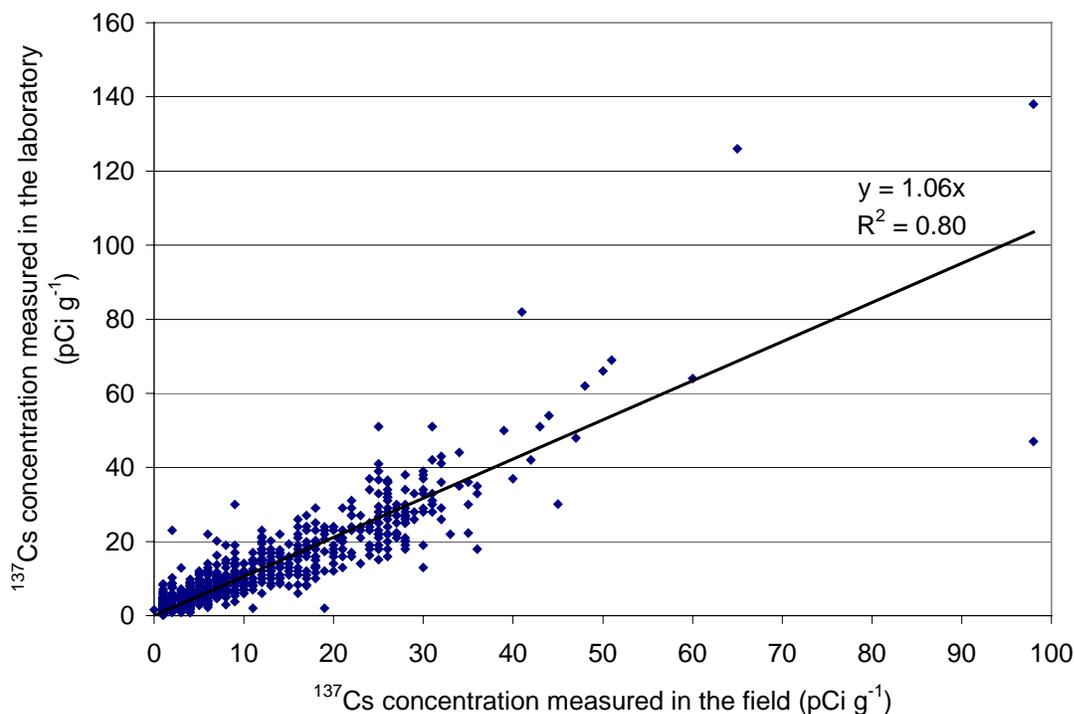


Figure A-1. Relationship between ^{137}Cs concentrations measured in the field and laboratory.

Analysis of Wild Game for Strontium

Bone samples were analyzed for radiostrontium by the SRS using a low-background gas-flow proportional counter ([Du Pont 1977](#)). Samples were ashed in a furnace at 700–900°C, leached with 6N hydrochloric acid, evaporated to dryness, and dissolved in 0.08N hydrochloric acid. Yttrium-90 was then stripped from the strontium by liquid ion exchange using di-2-ethylhexyl phosphoric acid. Equilibrium was then established with the short-lived ^{90}Y daughter over a 15-day period, which was then once again stripped. The remaining radiostrontium was then transferred to a stainless steel planchet for counting. [Rabon \(1968\)](#) described a method for separating radiostrontium from large amounts of calcium by using potassium rhodizonate as a selective precipitating agent.

FISH SAMPLE PREPARATION AND ANALYSIS

Based on the evaluation of environmental monitoring in [Chapter 14](#), the key contaminants in fish, which appear to be most useful to a dose reconstruction, are ^{65}Zn , ^{137}Cs and $^{89,90}\text{Sr}$. The following discussion thus focuses on the analyses of fish samples for these radionuclides. Except for details concerning specific analytical procedures, information on sample preparation and analyses were obtained primarily from routine monitoring reports. See [Chapter 7, Table 7-1](#) for a complete description of the various monitoring report series.

Analysis of Fish Samples for Cesium and Zinc

[Composite](#) flesh samples were analyzed for ^{137}Cs from 1961 through 1970; beginning in 1971, homogenized whole individual fish were analyzed. In 1990 and 1991, samples were blended and decanted and placed in sample bottles for analysis. Sample preparation methods were not clearly specified between 1971 and 1990, but samples were most likely prepared in a similar fashion. Through at least 1965, samples of muscle or homogenized fish were wet-ashed in nitric acid and hydrogen peroxide and subsequently placed in a bottle for analysis ([Harvey and Rabon 1965](#)). Methods of sample preparation for counting were not clearly specified until 1990, when blended samples were analyzed with no further preparation.

Before July 1961, only nonvolatile beta concentrations in fish muscle and bone tissue were routinely reported. Nonvolatile beta concentrations were also reported for fish through June 1969, but the methods of sample preparation and analysis were not clearly specified. However, following wet-ashing of collected tissue with nitric acid and hydrogen peroxide, a gas-flow proportional detector was likely used.

Gamma spectrometry was first used in 1956 to identify gamma-emitting radionuclides, such as ^{65}Zn and ^{137}Cs , in environmental samples ([Harvey and Rabon 1965](#)). While this process served to identify specific radionuclides, average nonvolatile beta concentrations were predominantly reported through the early 1960s. In July 1961, concentrations of specific radionuclides in fish samples began to be routinely reported.

Since July 1961, samples have been analyzed in a 3 × 6-in. well of a 9 × 9-in. NaI(Tl) crystal connected to a 400-channel pulse height analyzer. Beginning in 1986, both NaI and HPGe detectors were used, and HPGe detectors have been used exclusively since 1989.

Analysis of Fish Bone Samples for Strontium

Strontium-89,90 concentrations were reported for fish bone samples from 1961 through 1980. Bone samples for all species were composited for monthly analysis. Samples were analyzed using a low-background gas-flow proportional counter. Further details regarding the counting procedures for radiostrontium are discussed in the wild game sample preparation and analysis section.

SEDIMENT/SOIL SAMPLE PREPARATION AND ANALYSIS

Based on the evaluation of environmental monitoring in Chapters [12.1](#) and [12.2](#), the key contaminants in sediments and soil which appear to be most useful to a dose reconstruction are the [long-lived alpha](#)-emitting radionuclides, [uranium](#) and [plutonium](#). The following discussion thus focuses on the analyses of sediment or soil samples for these two radionuclides. Except for details concerning specific analytical procedures, information on sample preparation and analyses were obtained primarily from routine monitoring reports. See [Chapter 7, Table 7-1](#) for a complete description of the various monitoring report series.

According to in [Du Pont \(1953b\)](#), sample preparation in the early years of the program consisted first of drying and sifting the sample, using a No. 8 sieve. Approximately 5 grams of this sample was ground, using an electric mortar and pestle, until the entire sample could pass through a 200-mesh sieve. One gram of this material was placed in a crucible and ashed in a muffle furnace. The ash was dissolved using nitric and hydrofluoric acids. Dried residue was then analyzed for gross alpha concentrations using a ZnS scintillation detector through 1982 and was

analyzed using a gas flow proportional counter from 1983 through 1991. For specific determination of uranium and plutonium, the uranium and plutonium were extracted using tri-n-butyl phosphate (TPB) and then back-extracted into distilled water. The sample is dried on planchet. Alpha pulse height analysis was then used to determine the ratio of uranium activity to plutonium activity. [Du Pont \(1989\)](#) does not contain the procedures used to extract of uranium and plutonium from soil samples. However, a procedure for triisooctylamine (TIOA) extraction for vegetation samples. Since the TBP extraction was used for both types of [media](#) earlier, it could be assumed that the TIOA extraction was also used for sediment and soil samples, beginning in the early 1980s.

WATER SAMPLE PREPARATION AND ANALYSIS

The Health Physics Control Laboratory was responsible for sample preparation and analysis of environmental and regional survey samples beginning with the preoperational survey, and are quite well documented. Preoperational monitoring of the SRS was conducted in 1951 and 1952 and is reported in [Reinig et al. \(1953\)](#). Water samples from about 15 locations along the river were analyzed for gross alpha, gross beta, uranium/plutonium alpha, radon, radium, and ⁴⁰K content. The earliest sampling and procedures guide for SRS environmental samples was dated May 1953 and provided concise steps in obtaining and handling weekly water samples ([Du Pont 1953a](#)).

A jug sinker was used to obtain water samples when there was sufficient water depth to do so. A jug sinker was a device designed to hold either a 1-gal or a 1-L water jug. It was constructed of iron with the bottom and side runners of wood. The bottles were held in place by an iron hasp and a strap with a center hole that enclosed the jug neck. A rope was attached to a pail-type handle for lowering into the water. Random samples were obtained by lowering the jug sinker to the bottom of the river, stream, pond, or well to be sampled and raising the bottle slowly to allow filling. When water depth was not sufficient, bottles were held on their sides with the mouth pointing upstream, about 1 ft below the surface of the water. All samples collected in the field were returned to the Sample Receiving Room in Building 735A ([Du Pont 1953a](#)).

At the time of plant startup, analysis of water samples was limited primarily to gross alpha and nonvolatile beta measurements. The original procedures, outlined in 1953, gave “an approximate value for the level of alpha and beta contamination in water samples. Self-absorption of [radiation](#) in the sample and loss of volatile emitters lead to variation in results. Consequently, the method serves only as a rough check and must be supplemented and supported by specific analyses.” Uranium nitrate-spiked samples were used as a control, with a reported average alpha recovery of 35% and a standard deviation of 19%. Self-absorption was determined by an analysis of 11 spiked samples of tap water with a recovery of 55% (standard deviation of 12%). Samples were evaporated to a small volume (100 mL) and transferred by pipette to a stainless steel planchet. After evaporation, the planchet was flamed, mounted on a card, and sent to the counting room for gross activity counting.

Special analyses for uranium by fluorophotometry, potassium by spectrophotometry, thorium by spectrophotometry, and plutonium by tributyl phosphate (TBP) extraction were described in the initial procedures ([Du Pont 1953a](#)). For tritium analysis in the 1950s, the tricarb scintillation method was described and the calculations for their spike method and method for converting

counts per 30 minutes of an unspiked sample to microcuries per liter of tritium were laid out ([Du Pont 1959a](#)).

As 1960 approached, there were continuing efforts to review and modify procedures, especially for sampling and analysis of onsite samples ([Johnson 1960](#)). To inventory radioactive waste released to [effluent](#) streams, technical standards were requested to separately address methods for the release for short-lived versus long-lived [radioactive materials](#) (isotopes with [half-lives](#) less than or greater than 15 days, respectively). For beta activity analysis, a 100-mL sample was obtained from each flowing weir from the disassembly basin effluent once per shift. The samples were mixed in proportion to the flow from each weir. For alpha activity measurements, one additional sample was submitted to the laboratory “on each Wednesday 12–4 shift” ([Johnson 1960](#)). A method and step-by-step worksheet guided the analyst to estimate the ^{90}Sr content of the total release.

Routine tritium monitoring of the river began as early as 1958, and as early as 1960, samples from key locations were routinely analyzed for radioiodine, radiostrontium, and radiocesium. By late 1960, ion exchange media were used to concentrate radiostrontium and radiocesium in water samples, resulting in a roughly four-fold decrease in the detection limits from approximately 4 to 0.8 pCi L⁻¹ ([Du Pont 1960a](#)). Analysis for ^{90}Sr in the river samples began in September 1959 ([Van Wyck 1960](#)). Routine analysis of river samples for specific radionuclides by gamma spectroscopy did not begin until 1963. Some of the monthly and semiannual reports for the early years of operation do provide data from decay studies that were periodically performed on river water samples. Radioactivity release limits in 1960 specified “no limit” for tritium released to plant effluent streams, [seepage basins](#), or the disposal pits ([Johnson 1960](#)). By 1964, the annual operating release guide was 100,000 Ci of tritium to the streams ([Ashley 1965](#)).

As 1960 approached, there was a general expansion of the quantitative analytical techniques for a variety of environmental samples. With the automation of gamma spectrometry, isotopic analysis was possible for routine sampling of effluent streams, river water, [reactor](#) area effluent, biological specimens, and other samples not previously analyzed quantitatively ([Johnson 1960](#)). The Site made progress on increasing the sensitivity of the tritium analysis, especially for large volume samples. Working with personnel at the University of California and at the University of Chicago, the analytical laboratory made a number of recommendations to improve the sensitivity for tritium analysis ([Butler 1960](#)). A solvent was developed and modified for use in the liquid scintillation process that permitted use of relatively large samples without serious loss of efficiency ([Albenesius and Meyer 1962](#)).

By September 1962, the analytical procedure used for tritium analysis was fairly well established at SRS. Low energy of the tritium beta, an average of 6 keV, required internal counting systems. At this time, the liquid scintillation provided a rapid and sensitive technique to determine tritium concentration in streams and river water samples. (In liquid scintillation counting, the tritiated water is dissolved in a solvent that contains an organic scintillator. Particles of [radioactive decay](#) [beta] excite the organic molecules, which then emit light pulses. Light pulses detected by a photomultiplier tube, amplified and electronically counted.)

For the basic tritium analytical procedure, the tri-carb liquid scintillation counter was placed in operation by June 1958 ([Du Pont 1958](#)). The optimum conditions for counting with the organic scintillator solution were described. The efficiency was reported as 5.3% for a 3-mL water sample dissolved in the scintillator solution. The background was approximately 50 cpm using “Wheaton Co., low K-40 content, vials.” The tritium analytical procedure, described in 1953 and 1959 ([Du](#)

[Pont 1953a, 1959a](#)) was modified for more sensitive analysis of water samples ([Butler 1960](#)). Two methods were compared for the accurate determination of tritium in urine and water: liquid scintillation counting and vibrating reed electrometer rate-of-drift determination ([Butler 1961](#)).

A new type of water sampler was used beginning in the spring of 1964. This sampler used an ion column to collect radioactive materials from a large volume of water and was designed to operate continuously without electrical power. A water wheel drove two piston pumps. One of these pumps passed water through a prefilter and the ion column. The other pump, which was geared much slower, delivered water directly into a 2-gal container. Because each pump had a fixed gear ratio, the volume of water in the container could be used to determine the volume of water that had passed through the ion column. For the first few months of operation (April through October 1964), the volumes of water sampled ranged from 40 to 96 L depending on the river flow rate. A comparison of the results obtained at the downstream Savannah River sampling location during this period, using both the ion exchange sampler and the standard paddle wheel sampler, found that the average concentrations for all radionuclides, except ^{131}I , were consistently higher for the ion exchange sampler. This difference was attributed to possible settling of radionuclides associated with suspended solids within the container of the paddle wheel sampler over the sampling period. Because the volume of water sampled with the ion exchange sampler was two to four times greater than the volume collected by the paddle wheel sampler, the number of positive analyses was also consistently higher for this new sampling technique ([Du Pont 1964](#)).

It is not clear from the available information how long SRS used the ion-column equipped samplers that were originally tested in 1964. For the first few months of 1965, aperture card data are reported as prefilter, ion column, and total, indicating that these samplers were put into routine use. However, by the early 1970s when sampling methods were first described in the annual, offsite monitoring reports, ion-exchange results were no longer used as part of the sampling collection process. The 1972 annual monitoring report describes continuous sampling of Savannah River water as follows:

. . . a sampler consisting of a 'Plexiglass' water wheel suspended on two pontoons. As the water wheel is turned by flowing water, a small cup (or cups) on one paddle picks up a sample of water and deposits it into a trough. The sampled water flows by gravity from the trough through connecting tubing into a large polyethylene jug which trails the sampler. The sampled water (up to six gallons) is collected weekly at river locations above and below SRP. Increased analytical sensitivity for water samples (containing insufficient radioactivity for direct processing) is achieved through concentration of radionuclides by ion exchange. The ion exchange column is counted directly for gamma emitting radionuclides ([Du Pont 1973](#)).

The sampling equipment used by the SRS does not appear to have been modified from that time up through the early 1990s when the ISCO samplers were installed.

By the early 1970s, the procedures for water collection and counting were standard for the time. Tritium was measured in distilled water samples with a liquid scintillation spectrometer. Alpha and beta-emitting radionuclides were measured by passing 25 L of water through a cation-anion resin column and direct counting the column using a NaI(Tl) well detector with a 400-channel gamma spectrometer. The resin column was then eluted with nitric acid for subsequent strontium analysis. Strontium-90 was recovered from a portion of the sample by liquid

ion exchange. Equilibrium of ^{90}Y was allowed over a 15-day period and then the short-lived ^{90}Y daughter was counted in a low-level gas flow proportional counter ([Du Pont 1975](#)).

The analytical procedure for the determination of ^{35}S was adapted for use with stream and river water and used routinely, as reported in biweekly Environmental Monitoring and Allied Studies ([Du Pont 1959c](#)). The procedure was extended in early 1962 to determine ^{32}P levels in reactor [moderator](#) and disassembly basin weir water. The wastewater sample was passed through a cation column to remove ^{239}Np , then a step removed iodine. Following a second cation column treatment, an ammonia phosphate precipitation was done. This precipitate contained the ^{32}P , which was then plancheted and counted.

By 1966, a technique based on liquid ion exchange was developed to determine ^{35}S in water because the previous method was lengthy and produced low, variable recoveries. Overall, the recovery of ^{35}S in this procedure was 85%, and the method was routinely used during this time ([Du Pont 1966](#)).

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