# Determination of Strontium-90 in Water

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By J. O. JOHNSON *and* K. W. EDWARDS

RADIOCHEMICAL ANALYSIS OF WATER

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*A description of a method for the determination of strontium-90 in waters free of strontium-89, or for determination of gross radiostrontium activity as strontium-90*

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# DETERMINATION OF STRONTIUM-90 IN WATER

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**ABSTRACT**

A method is described for the determination of strontium-90 in waters free of strontium-89, or for determination of gross radiostrontium activity as strontium-90. The method is suitable for use on natural water samples and other aqueous systems in the absence of high concentrations of organic substances which form stable complexes with strontium. The minimum detection limit at the 95-percent confidence level is 0.55 picocuries per liter for the recommended 500-milliliter sample.

## INTRODUCTION

Nuclear fission produces two important isotopes of strontium: strontium-90, with a half life of 27.7 years, and strontium-89, with a half life of 50.5 days. Although strontium-89 is formed in greater quantities, strontium-90 is much more important in terms of world-wide distribution because of its longer half life. Except for short periods following atmospheric nuclear testing, strontium-90 is the predominant radioisotope of this element on the earth's surface. This nuclide is now widely distributed in man's environment from stratospheric and tropospheric fallout and from disposal of industrial waste. It is often present in detectable concentrations in soils, foods, water, and biological materials.

The method described in this paper is based on the work of Hahn and Straub (1955). Dissolved radiostrontium is first concentrated by precipitation as the carbonate, a small amount of stable strontium being used as an isotopic carrier. The carbonate precipitate is dissolved in a small amount of acid, and strontium nitrate is precipitated by the addition of fuming nitric acid. The nitrate precipitate is washed with anhydrous acetone to remove calcium. The remaining residue is dissolved in distilled water, the solution is boiled to remove acetone, and strontium nitrate is again precipitated with fuming nitric acid and washed with acetone.

Iron and barium carriers are added and a hydroxide precipitation is made. The ferric hydroxide is a suitable carrier for several fission-product activities including those of the rare earths, zirconium, niobium, and yttrium. The supernatant solution contains strontium-90, free of daughter activity; the growth of yttrium-90 is measured from the time of this precipitation. Addition of sodium chromate to the supernate precipitates the barium, which carries with it any barium-140 and isotopes of radium and lead.

Strontium is finally precipitated as the oxalate, and the amount of radiostrontium is determined by measuring the beta activity after a 21-day aging period. The chemical recovery is determined gravimetrically.

The method described is applicable to the determination of strontium-90 in aqueous solutions free of strontium-89 and organics such as ethylenediamine tetraacetic acid (EDTA) which form strong complexes with strontium. The method may also be used for total strontium radioactivity ($Sr^{89}+Sr^{90}$) reported as strontium-90. In the latter case, approximately 45 percent of the strontium-89 activity is reported as strontium-90.

## REAGENTS

Reagent grade chemicals should be used throughout, unless otherwise specified.

Ammonium hydroxide: Concentrated and 6 *M* (molar solution).

Sodium carbonate: 1 *M* and 0.1 *M*.

Nitric acid: Fuming, concentrated, 6 *M*, and 1 *M*.

Acetic acid: 6 *M*.

Ethanol: 95 percent.

Diethyl ether.

Acetone: Anhydrous.

Sodium chromate: 1.5 *M*.

Ammonium acetate: 6 *M*.

Ammonium oxalate: Saturated solution.

Phenolphthalein: Indicator solution.

Thymolphthalein: Indicator solution.

Aluminum foil: 3.5 milligrams per square centimeter or less.

Iron carrier solution (5 mg $Fe^{+3}$ per milliliter): Dissolve 500 mg of standard iron wire in a slight excess of nitric acid and dilute to 100 ml.

Barium carrier solution (3.00 mg $Ba^{+2}$ per ml): Dissolve 1.33 grams of $BaCl_2 \cdot 2H_2O$ in distilled water. Add a few drops of concentrated nitric acid and dilute to 250 ml.

Strontium carrier solution (4.00 mg $Sr^{+2}$ per ml): Dry "anhydrous" strontium nitrate overnight at 105° C and cool in a desiccator. Weigh out 9.66 g of the dried salt and dissolve in distilled water. Add 2 ml of

concentrated nitric acid and dilute to 1 liter. A more exacting procedure is described by Glendenin (1951, p. 1461), but the added work is generally not warranted unless the strontium nitrate contains radioactive impurities which contribute significantly to the reagent blank.

Strontium-90 standard solutions: Strontium-90 standard solutions calibrated to $\pm 1.5$ percent are commercially available (Sommerville, 1963, p. 195). In purchasing standards, it is essential that the concentration of stable isotopic carrier be known. Dilute the standard to approximately 50 pc per ml (picocuries per ml) using appropriate safety precautions (see Barker and Robinson, 1963, p. A28). It will generally be necessary to add both acid and inactive strontium carrier at the time of dilution. The final solution should be approximately 0.1 $N$ (normal solution) in hydrogen ion (HCL or $HNO_3$) and should have a chemical strontium carrier concentration of 0.1 to 10 mg per l. Allowance must be made for the decay of strontium-90 with time. The strontium-90 activity, $A$, at any time, $t$, expressed in years, is $A=A_o e^{-0.002502t}$ where $A_o$ is the known activity when time equals zero. The decay amounts to approximately 2.5 percent per year.

## SPECIAL APPARATUS

Hot plate.

Filtration apparatus for 25-millimeter filters (available from Millipore Filter Corp., Bedford, Mass.).

Ring and disk mounting assemblies, 1-inch diameter (available from Atomic Accessories Inc., Valley Stream, N.Y.).

Rigid copper backing disks for filters, 0.875-inch diameter by 0.016-inch thickness.

Analytical balance sensitive to $\pm 0.1$ mg.

Low-background beta counter having instrumental beta background of less than 2.0 cpm (counts per minute).

## PREPARATION OF STRONTIUM-90 REFERENCE STANDARDS

Three or more permanent strontium-90–yttrium-90 standards should be prepared by direct precipitation of strontium oxalate. To 30 ml distilled water in a 100-ml beaker add 1 ml of 6 $M$ acetic acid and 2 ml of 6 $M$ ammonium acetate. Mix thoroughly and add 5 ml of strontium carrier (4 mg Sr per ml) and 5 ml of strontium-90 standard solution (approx 50 pc per ml). Stir the solution thoroughly and follow steps 13–15 of the procedure. Store the standards in a clean, dry place and count periodically on the low-background beta counter to determine the counting efficiency. The standards should be aged for 21 days before use.

New reference standards should be prepared whenever a new batch

of aluminum foil is used, and the foil itself should be checked for radioactive contamination. The standards must also be corrected for radioactive decay; strontium-90 has a half life of 27.7 years, and its activity decreases by roughly 2.5 percent per year. It is generally advisable to prepare new standards at least once a year.

## PROCEDURE

Two blanks should be run with each set of samples to check for contamination of reagents and to permit an accurate blank correction to be made. Occasional standards and "spiked" samples (samples containing a known amount of added standard) should also be run through the entire procedure as checks, but need not be run routinely unless an estimate of strontium-90 is desired in less than 21 days.

1. To 500 ml of clear water sample in an 800 ml beaker, add 20 mg of strontium carrier (5 ml of 4 mg $Sr^{+2}$ per ml). Place on a hot plate and heat to boiling. Add a few drops of thymolphthalein indicator. Make the solution basic to the indicator (blue color) by dropwise additions of concentrated ammonium hydroxide; add an additional 6 ml of ammonium hydroxide.
2. Add 15 ml of 1.0 *M* sodium carbonate. Stir thoroughly, cover the beaker with a watchglass, and digest on a steam bath for 1 hour. Add more ammonium hydroxide, if required, to maintain the blue color of thymolphthalein. (Add more indicator if the color fades.)
3. Remove the beaker from the steam bath and allow the precipitate to settle while the solution cools to room temperature.
4. Carefully decant or draw off as much as possible of the supernatant solution without disturbing the precipitate. Transfer the insoluble material to a 50-ml graduated centrifuge tube and police the beaker with 0.1 *M* sodium carbonate. Centrifuge and discard the supernatant liquid.
5. Cautiously add 1 *N* nitric acid dropwise to the centrifuge tube until the carbonate precipitate is completely dissolved. Bring the volume up to 5 ml with distilled water. (Note: The solids in the centrifuge tube may not completely dissolve because of the presence of silica or other insoluble matter.) Add 25 ml of fuming nitric acid. (Caution! Use rubber gloves and face shield, and work in a hood. Do not inhale vapors.) Cool, stir, and centrifuge.
6. Using the above safety precautions, pour off the nitric acid as completely as possible, cool the tube below room temperature in a cold water or ice bath, and cautiously add 25 ml of anhydrous acetone to the residue. Stir thoroughly and centrifuge, again discarding the supernate.

7. Repeat step 6.
8. Dissolve the nitrates in 5 ml of distilled water and place the tube in a boiling water bath until the odor of acetone is gone. (Caution! Be sure acetone is completely removed.)
9. Cool the tube below room temperature and again precipitate strontium nitrate by adding 25 ml of fuming nitric acid. Swirl, cool, and centrifuge. Discard the supernate.
10. Dissolve the precipitate in 10 ml of distilled water and add 5 mg of ferric carrier (1 ml of 5 mg $Fe^{+3}$ per ml) and 15 mg of barium carrier (5 ml of 3 mg $Ba^{+2}$ per ml). While stirring, add concentrated ammonium hydroxide dropwise until ferric hydroxide begins to precipitate, then add several drops excess. Centrifuge and decant the supernatant liquid into a clean centrifuge tube. Discard the ferric hydroxide precipitate (which contains the yttrium daughter of $Sr^{90}$). Note the time and date.
11. Add a drop or two of phenolphthalein indicator solution, followed by dropwise addition of 6 *N* nitric acid until the pink color disappears; then add 1 ml of 6 *M* acetic acid and 2 ml of 6 *M* ammonium acetate. Place the sample tubes in a boiling water bath and add, while agitating the sample, 1 ml of 1.5 *M* sodium chromate. Agitate for 1 minute and continue heating for 5–10 minutes.
12. Cool the samples to room temperature, centrifuge, and decant the supernate into a 100-ml beaker. Discard the precipitate.
13. Add 2 ml of concentrated ammonium hydroxide and heat to boiling. Then add 5 ml of saturated ammonium oxalate solution and stir. Allow the precipitate to settle and the solution to cool to room temperature.
14. Filter through a tared 25-mm filter paper (Whatman No. 42) supported on the sintered glass disk of a microanalytical filtration assembly. Wash the precipitate with three 5-ml portions of distilled water and then with small volumes of 95 percent ethanol and diethyl ether. Dry at room temperature in a desiccator. Weigh as strontium oxalate monohydrate ($SrC_2O_4 \cdot H_2O$) and determine the gravimetric yield.
15. Put the filter on a copper disk, 0.875-inch diameter, in the base of a ring and disk assembly, 1-inch diameter. Cover with a small piece of aluminum foil (3.5 mg per sq cm or less) and secure the ring in place. Store the sample for at least 21 days to allow yttrium-90 to reach more than 99.5 percent of its equilibrium activity.
16. Count the sample for 100 minutes on a low-background beta counter and compute the strontium-90 concentration of the sample.

## CALCULATION OF RESULTS

A suggested data sheet for tabulation and calculation of results is shown in figure 1. Although this form is intended for use when strontium–89 is absent from the sample, it may be easily modified to report results of gross radiostrontium ($Sr^{90}+Sr^{89}$) as strontium–90.

Strontium-90
Analytical Data Form

Sample No._____

Pretreatment_____

Sample vol., V_____ml (Sr) in sample_____ppm  Sr in sample, $W_s$_____mg

Sr carrier added, $W_c$_____mg

Total Sr, $W_c + W_s$ _____mg

Sr-Y separation: Date_____ Time_____

Counting: Date_____Time_____

Net growth time of $Y^{90}$ _____days

Recovery:

| Weight of filter paper: | Weight of filter paper + $SrC_2O_4 \cdot H_2O$ |
|---|---|
| Gross _____ | Gross_____ |
| Tare _____ | Tare _____ |
| Net _____$W_1$ | Net _____$W_2$ |

Theoretical weight of $SrC_2O_4 \cdot H_2O$ _____ = $W_t$ = 2.210 ($W_c$ + $W_s$)

Recovery (g) $= \frac{W_2 - W_1}{W_t}$  g= _____

Counting efficiency (e) of $Sr^{90}$ - $Y^{90}$ standards  e = _____cpm per pc $Sr^{90}$

Overall efficiency (E) = e · g  E = _____cpm per pc $Sr^{90}$

Counting data:

Observed count rate, R, for counting time of _____min.  R = _____cpm

Blank  B = _____cpm

Net count rate, A, of sample = R-B  A = _____cpm

Concentration of $Sr^{90}$ in sample = $\frac{1000}{V} \cdot \frac{A}{E}$ =_____ ± _____pc/l

Analyst_____ Date_____ Checked by_____Date_____

FIGURE 1.—Strontium-90 analytical data form.

The concentration, in picocuries per liter, of strontium–90 in the sample is given by the equation:

$$Sr^{90}=\frac{1000}{V}\times\frac{A}{eg}$$

where

$V$=volume of sample in milliliters,
$A$=net counting rate,
$e$=effective counting efficiency from strontium–90, and
$g$=chemical recovery.

The counting efficiency, $e$, is the number of counts per minute (of the aged precipitate) per picocurie of strontium–90 in the sample. Since both strontium–90 and its daughter, yttrium–90 are counted, this is not a true counting efficiency for strontium–90 only, but rather an effective counting efficiency which must be used in the calculations. It is determined by counting an aged strontium–90 standard for 100 minutes or longer and dividing the count rate by the calculated amount (picocuries) of strontium–90 present in the standard after any necessary corrections for decay are made.

The chemical recovery, $g$, is obtained by dividing the experimental weight of strontium oxalate monohydrate by the theoretical weight calculated for complete recovery. The latter must take into account both the amount of strontium carrier added and the weight of strontium initially present in the water sample aliquot. Since stable strontium is frequently found in natural water, a preliminary analysis for this element should be made. $W_s$, the weight in milligrams of strontium in the sample, may be calculated from the equation:

$$W_s=\mathrm{Sr}\times\frac{V}{10^3}$$

where

Sr=concentration, in parts per million, of strontium in the sample, and
$V$=sample volume in milliliters.

The recovery is then calculated from the equation:

$$g=\frac{W_2-W_1}{2.210(W_c+W_s)}$$

where

$(W_2-W_1)$=experimental weight of strontium oxalate found, and
$W_c$=weight of strontium carrier added.

## ACCURACY

The accuracy of this method for low levels of strontium-90 in water free of strontium-89 is normally limited by counting statistics. Another major source of error is in the determination of the gravimetric yield of strontium oxalate. Error in the standards is normally small (<3 percent) but should not be neglected. A small error may also be caused by uncertainty in the chemical concentration of dissolved strontium in the sample.

The minimum detection limit (MDL) obtainable by using the equipment available at the Denver radiochemical laboratory (U.S. Geological Survey's Water Resources Division) is 0.55 pc per l. This limit is based on a counting efficiency of 1.8 cpm per pc of strontium-90 and a statistical blank (background plus reagent blank) of 2.0 cpm. Variations is these quantities will increase or decrease the MDL. Experimental results, whether less than or greater than the MDL, should be reported as obtained.

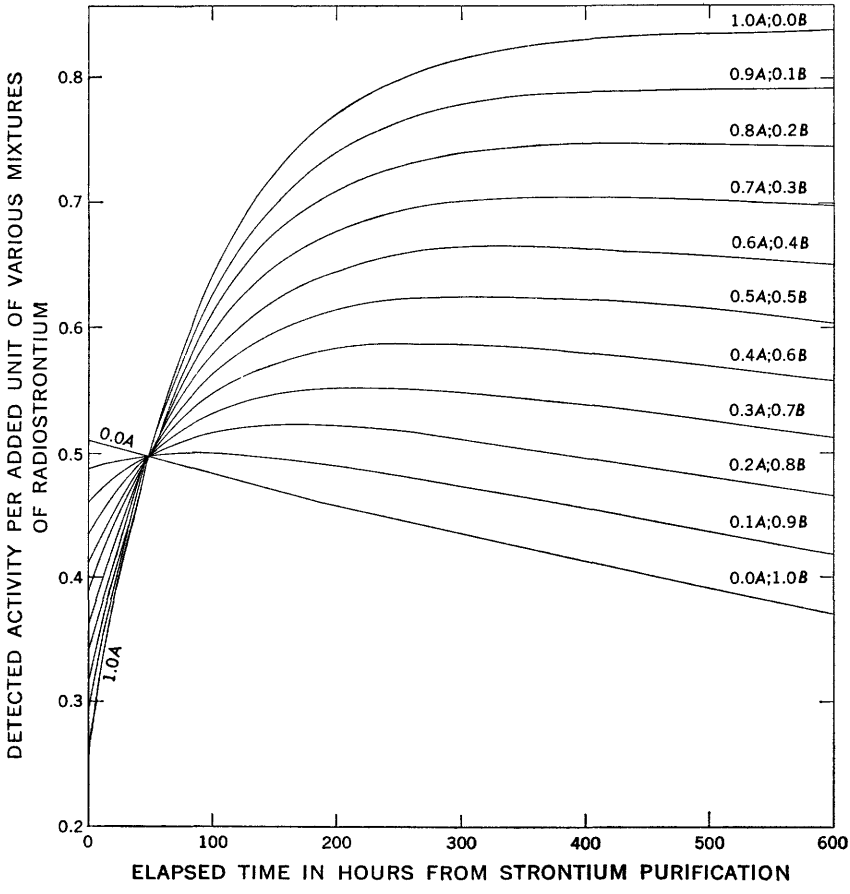
The accuracy of the method for concentrations of strontium-90 greater than about 1 pc per l is limited by the accuracy of standards and chemical recovery, as well as by counting statistics. On the basis of the work of Hahn and Straub (1955) and experience in the Denver radiochemical laboratory, the accuracy of the method is taken to be $\pm 10$ percent for concentrations greater than 5 pc per l. For weaker concentrations, counting statistics exceed 10-percent error, and results should be reported as $\pm 0.55$ pc per l. It is desirable for each laboratory to run random samples with and without added strontium-90 "spikes," so that an experimental evaluation of the error at concentrations in excess of the MDL can be obtained.

Interference due to other fission products (with the exception of $Sr^{89}$) is negligible within the accuracy of the method (Glendenin, 1951). Natural sources of radioactivity should also cause negligible error. Because of the significant fission yield of strontium-89, interference due to this nuclide can be expected at times of recent atmospheric nuclear testing and in areas of underground nuclear testing. The presence of this nuclide will cause results to be high by approximately 45 percent of the strontium-89 concentration when the recommended 21-day aging period is used. If the method is used under conditions where such interference may occur, results should be reported as the strontium-90 equivalent of the gross radiostrontium activity.

## DISCUSSION

This method is recommended for use on clear water samples free of suspended material. Other samples should be clarified by suitable means before the analysis is performed.

A rough estimate of the amount of strontium-89, when present, may be obtained by plotting a growth-decay curve of the activity in the final precipitate. The curve is then compared with figure 2. Sample counts made in the first 250 hours are most useful because the beta activity of yttrium-90 changes most rapidly in that interval. A similar graph must be prepared for a counter that has efficiencies differing from those shown in figure 2.




*Explanation*

$A$=fraction of strontium-90 activity
$B$=fraction of strontium-89 activity

The following counting efficiencies were assumed:
Strontium-90=0.26
Yttrium-90= .58
Strontium-89= .51

Counting efficiencies were obtained on a low-background beta counter. The radiostrontium was carried with 36 mg of strontium oxalate.

FIGURE 2.—Counting efficiencies of various radiostrontium mixtures at 100-hour intervals.

If time is of no consequence, strontium-89 may be estimated by counting the sample at the end of the 21-day aging period and again after a total aging time of 51 days. After 21 days, any change in activity will be due almost entirely to strontium-89 decay; the activity of this nuclide is reduced by one-third for each 30 days of decay. (The activity of $Sr^{89}$ after 51 days is therefore two-thirds of the $Sr^{89}$ activity at the end of 21 days.)

It should be recognized that the statistical uncertainties in strontium-89 and strontium-90 activities may be considerable when these quantities are determined from decay data on low-activity samples. A preferable method for strontium-90 in the presence of strontium-89 involves the separation of yttrium-90 and measurement of its activity. This procedure has been used by many investigators and will be described in a separate report.

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