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Options for ^{89}Sr and ^{90}Sr Determination

Summary There are many methods (Table 1) available for the measurement of radiostrontium (Table 2) from environmental, building materials, or biological samples. Typically, analysts are interested in the measurement of the fission products ^{89}Sr (decays to stable ^{89}Y) and ^{90}Sr (decays to β^- emitting ^{90}Y). Stable strontium or ^{85}Sr may also be used as a chemical yield tracer. Methods typically begin with a concentration or matrix removal step, followed by the separation of strontium from interfering nuclides using Sr Resin (Figure 1A). Methods may also incorporate steps to discriminate between ^{89}Sr and ^{90}Sr, including multiple counts, nuclide selective counting techniques and ingrowth and secondary separations of ^{90}Y (daughter of ^{90}Sr). Measurement instrumentation includes low background gas flow proportional counting (GFPC), liquid scintillation (LSC), Cerenkov counting, and inductively coupled plasma-mass spectrometry (ICP-MS).

This application note will offer guidance in choosing an appropriate method for the determination of radiostrontium, taking into account process knowledge, available measurement equipment and data quality objectives (required detection limits, urgency of measurement, age of sample, and need for $^{89/90}$Sr discrimination). The measurement methods are meant be to used in concert with the appropriate sample preparation method for the matrix being analyzed. For a more comprehensive treatment of sample preparation methods, see the application notes available at http://www.eichrom.com/eichrom/appnotes/applications/index.aspx. A detailed discussion of interferences for the various measurement techniques can also be found in references [2] and [5].

Table 1. Summary of $^{89/90}$Sr Method Options

Method	Primary Separation	Primary Measurement	Secondary Separation	Secondary Measurement	Sr Yield Monitor	Ref.
ICP-MS	1A	^{90}Sr by ICP-MS	None	None	Stable Sr	1
Total $^{89/90}$Sr	1A	$^{89/90}$Sr by GFPC/LSC	None	None	Stable Sr	4,5
^{90}Y Direct	1C	^{90}Y by GFPC/LSC/Cerenkov	None	None	Stable Sr	6
Two Count ^{89}Sr and ^{90}Sr	1A	$^{89/90}$Sr by GFPC/LSC	None	$^{89/90}$Sr by GFPC/LSC*	Stable Sr	2
Rapid ^{89}Sr and ^{90}Sr	1A	^{89}Sr by Cerenkov	None	$^{89/90}$Sr by LSC	Stable Sr	5
Cerenkov ^{89}Sr and ^{90}Sr(^{90}Y)	1A	^{89}Sr by Cerenkov	1B or 1C	^{90}Y by Cerenkov	Stable Sr/^{85}Sr	3
Gas Flow Porportional	1A	$^{89/90}$Sr by GFPC	1B or 1C	^{90}Y by GFPC	Stable Sr/^{85}Sr	4

*^{89}Sr/^{90}Sr descrimination by solving equations for ^{89}Sr decay and ^{90}Y ingrowth during time between 2 measurements

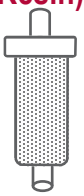
Table 2. Properties of Selected Nuclides

Nuclide	Half-Life	Decay Mode	Energy	Detector Suitable for Measurement: GFPC	LSC	Cerenkov	MS/AES	Gamma
Stabel Sr	^{84}Sr (0.56%), ^{86}Sr(9.86%), ^{87}Sr (7.0%), ^{88}Sr (82.58%)			No	No	No	Yes	No
^{85}Sr	64.849 days	ε/γ	γ = 514 keV (96%)	No	Yes	No	No	Yes
^{89}Sr	50.563 days	β^-	β_{max} = 1500 keV β_{mean} = 587 keV	Yes	Yes	Yes	No	No
^{90}Sr	28.79 years	β^-	β_{max} = 546 keV β_{mean} = 196 keV	Yes	Yes	No	Yes	No
^{90}Y	64 hours	β^-	β_{max} = 2280 keV β_{mean} = 934 keV	Yes	Yes	Yes	No	No

Figure 1. Strontium Separation Options

A. Sr separation (Sr Resin)

Sr Resin
2-4 mL in cartridges



(1) Precondition Sr Resin with 3 bed volumes 8M HNO_3.

(2) Load sample at 1-2 mL/min.

(3) Rinse sample tube with 5 mL 8M HNO_3.

(4) Add tube rinse to Sr Resin. Elute at 1-2 mL/min.

(5) Rinse Sr Resin sequentially with*
- 3 bed volumes 8M HNO_3.
- 3 bed volumes 3M HNO_3 - 0.05M oxalic acid.
- 3 bed volumes 8M HNO_3.

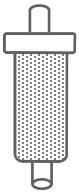
(6) Dispose of (1) to (5) as waste.

(7) Strip Sr with 5 bed volumes 0.05M HNO_3 at 1 mL/min.

*Rinse solutions and volumes listed are general guidelines. See detailed app. notes for recommended rinsing for each matrix.

B. Sr/^{90}Y Separation (Sr Resin)

Sr Resin
2 mL cartridge



(1) Dissolve Sr Residue from planchet used for total $^{89/90}$Sr measurement with 5 mL 8M HNO_3. (Or acidify Cerenkov sample to 8M HNO_3.)

(2) Using transfer pipet, transfer dissolved residue to 15mL c-tube.

(3) Rinse planchet with 5 mL 8M HNO_3. Add to 15 mL c-tube.

(4) Precondition 2 mL Sr Resin cartridge with 5 mL 8M HNO_3.

(5) Load sample at 1-2 mL/min, collecting eluate (^{90}Y-fraction).

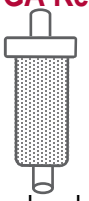
(6) Rinse c-tube with 5 mL 8M HNO_3.

(7) Add tube rinse to column. Elute, collecting eluate (^{90}Y fraction).

Method appropriate for high ^{90}Sr/^{89}Sr ratios or ^{90}Sr confirmation. Potential for 1-3% Sr break-through, limits application for high ^{89}Sr/^{90}Sr ratios.

C. Sr/^{90}Y Separation (DGA Resin)

DGA Resin, Normal
2 mL cartridge



(1) Dissolve Sr Residue from planchet used for total $^{89/90}$Sr measurement with 5 mL 8M HNO_3. (Or acidify Cerenkov sample to 8M HNO_3.)

(2) Transfer dissolved residue to 15mL c-tube.

(3) Rinse planchet with 5 mL 8M HNO_3. Add to 15 mL c-tube.

(4) Precondition 2 mL DGA Resin cartridge with 5 mL 8M HNO_3.

(5) Load sample at 1-2 mL/min.

(6) Rinse c-tube with 5 mL 8M HNO_3.

(7) Add tube rinse to cartridge.

(8) Rinse DGA with 15 mL 0.1M HNO_3.

(9) Save (4) to (8) as Sr fraction.

(10) Strip ^{90}Y with 10 mL 0.1M HCl.

Preferred method for high ^{89}Sr/^{90}Sr ratios. Additional rinses may be required for direct determination of ^{90}Sr via ^{90}Y, see AN-1414.

ICP-MS (^{90}Sr only) ^{90}Sr may be determined by inductively coupled plasma-mass spectrometry (ICP-MS) following separation on Sr Resin (Figure 1A). However, due to the relatively short half-life of ^{90}Sr, **application to low level environmental analyses will be limited** by the available mass spectrometry technology and concentration chemistries. Recent publications suggest detection limits of ~1Bq/g are possible. However the achievable detection limit will depend on several factors, including sample type, sample size, and the age and type of MS instrument available [1]. **Radiometric techniques will allow lower detection limits** for ^{90}Sr and the ability to also determine ^{89}Sr.

Accurate measurement of strontium chemical yield as ^{88}Sr by ICP-MS has very little chance for impact by **isobaric interferences** (^{87}Rb-H$^+$, which should be effectively removed by Sr Resin Separation). ^{90}Zr is the only significant isobaric interference for ^{90}Sr measurement. Separation chemistries should be tailored to ensure complete removal of zirconium (rinsing with 3M HNO_3-0.05M oxalic acid for Sr Resin separations). Determination of ^{90}Sr by ICP-MS **greatly simplifies the calculation of ^{90}Sr activity**, which can be complicated in radiometric detection techniques by the ingrowth of ^{90}Y and the decay of ^{89}Sr.

ICP-MS and **ICP-AES** (atomic emission spectrometry) are also very effective tools for the determination of **strontium chemical yield** when using radiometric detection methods for ^{89}Sr and ^{90}Sr. ICP-MS and ICP-AES will often give more precise chemical yield data than gravimetric techniques, while also allowing the use of **less Sr carrier** (<1 mg vs 4-10 mg stable Sr). Many environmental samples (soils, brines, sea water and some ground waters) may contain significant levels of stable strontium. Pre-anlysis of these samples by ICP-MS or ICP-AES for **native Sr** content may be necessary to adjust the amount of stable Sr yield monitor added and to ensure accurate measurement of the Sr yield throughout the separation process.

Total $^{89/90}$Sr In instances where **^{90}Sr is the only radiostrontium isotope** likely to be present or where total ^{89}Sr + ^{90}Sr determination is desired, radiostrontium may be determined by liquid scintillation counting or gas flow proportional counting following separation on Sr Resin (Figure 1A). **Confirmation of ^{90}Sr** activity will require **discrimination from ^{89}Sr** through two count methods and calculations [2], ingrowth and separation of ^{90}Y (Figure 1B or 1C) [4,5] or selective ^{89}Sr/^{90}Y measurement(s) using Cerenkov counting [3].

^{90}Sr by Direct Recovery of ^{90}Y In the analysis of debris from decommissioning of older facilities or other instances where **^{90}Sr is likely to be present in the absence of short-lived fission products** (^{91}Y, ^{89}Sr, etc.) and where **^{90}Y is in equilibrium with ^{90}Sr**, ^{90}Sr may be determined by liquid scintillation, gas flow proportional counting, or Cerenkov counting following the direct **separation of ^{90}Y on DGA Resin** (Figure 1C) [6]. The **very high retention of ^{90}Y** on DGA resin allows recovery of ^{90}Y from **difficult matrices, large sample volumes, and/or samples with high native Sr content** that may prove problematic using the isolation of Sr on Sr Resin. However, the presence of fresh fission products, such as **^{91}Y and rare earth radionuclides**, will cause **significant positive bias** in the ^{90}Sr determination performed using this method. Stable yttrium carrier yield can be measured by ICP-MS or ICP-AES.

Two Count Method Total $^{89/90}$Sr can be measured in an **initial count** using GFPC or LSC following separation on Sr Resin (Figure 1A). Following a period of **ingrowth for ^{90}Y**, the samples can be **counted again**, and individual ^{89}Sr and ^{90}Sr activities calculated by **solving a series of equations** related to the decay of ^{89}Sr and the ingrowth of ^{90}Y (two count method) [2]. Ideally, the **initial count** is performed **as quickly as possible** following the separation on Sr Resin to minimize ^{90}Y ingrowth. The **second count** is ideally performed **after 1-2 weeks of ^{90}Y ingrowth**. Computational methods for resolving the ^{89}Sr and ^{90}Sr activities are outlined in Appendix B of reference [2].

Cerenkov vs LSC The beta emission of **^{90}Sr is below the threshold for efficient measurement by Cerenkov counting** (LSC without addition of cocktail). **^{89}Sr may be determined by Cerenkov counting** immediately following separation of radiostrontium on Sr Resin (Figure 1A). **^{90}Y will also be efficiently measured by Cerenkov counting**.

Counting of ^{89}Sr by Cerenkov counting is **less efficient than by liquid scintillation** (LSC). However, the lower counting efficiency is partially offset by the **lower background** observed in Cerenkov counting. Furthermore, Cerenkov counting **eliminates interferences** from many low energy beta emitters that may cause bias in measurements made by LSC or GFPC. Additionally, Cerenkov counting **does not require the addition of cocktail**, offering cost savings in waste disposal and reagent costs. Cerenkov counting **does not suffer from quenching** which can occur in liquid scintillation.

Counting ^{89}Sr by Cerenkov or total $^{89/90}$Sr by GFPC as a first measurement leaves open the option to separate ^{90}Y from the strontium fraction for further confirmation of ^{90}Sr or discrimination of ^{89}Sr/^{90}Sr. Counting the strontium fraction by LSC limits any further separation on the sample due to the addition of the LSC cocktail, leaving the two count method as the only viable ^{89}Sr/^{90}Sr discrimination option after LSC measurements of $^{89/90}$Sr, unless the sample is split prior to LSC.

^{89}Sr by Cerenkov, $^{89/90}$Sr by LSC Counting (Rapid $^{89/90}$Sr) ^{89}Sr is determined by Cerenkov counting immediately following separation of radiostrontium on Sr Resin (Figure 1A) [3]. After the addition of LSC cocktail, ^{90}Sr may then be determined by measuring total radiostrontium (^{89}Sr + ^{90}Sr) by standard liquid scintillation counting and calculating the difference (total radiostrontium - ^{89}Sr), taking into account ingrowth of ^{90}Y and decay of ^{89}Sr during counting.

This approach **may not be appropriate for samples that require long count times** to meet data quality objectives or for samples with low ratios of ^{89}Sr/^{90}Sr, due to interference from ^{90}Y ingrowth. However, this method can be used very effectively to **rapidly determine ^{89}Sr and ^{90}Sr** in samples containing relatively high amounts of radiostrontium in the **immediate aftermath of a release of fresh fission products**.

When utilizing Cerenkov and/or liquid scintillation counting, chemical yield of Sr throughout the separation process is most effectively measured via stable strontium carrier by taking a small aliquot of the separated strontium fraction for analysis by ICP-MS or ICP-AES. Recovery by ^{85}Sr gamma emission is not recommended, due to interference with the measurement of total radiostrontium by liquid scintillation counting.

DGA vs Sr Resin for ^{90}Y Separation For samples with expected high ratios of ^{89}Sr/^{90}Sr, using DGA to selectively retain ^{90}Y (Figure 1C) is recommended, as the Sr can be effectively rinsed from the column, while ^{90}Y recovery remains strongly adsorbed (k' Y on DGA >>1000). In high ^{89}Sr/^{90}Sr samples, small breakthrough of strontium from separation on Sr Resin (Figure 1B) into the ^{90}Y fraction (k' Sr only ~100 on Sr Resin) can lead to high bias of the ^{90}Sr measurement and a corresponding low bias of the ^{89}Sr.

^{89}Sr by Cerenkov, ^{90}Y by Cerenkov Following Ingrowth and Separation ^{89}Sr is measured by Cerenkov counting following separation of strontium on Sr Resin (Figure 1A). ^{90}Sr may then be determined by waiting 1-14 days for ^{90}Y ingrowth, acidifying the Cerenkov counted sample with HNO_3, separating the ^{90}Y using Sr Resin (Figure 1B) or DGA Resin (Figure 1C), and measuring ^{90}Y by Cerenkov counting.

This method is **not as rapid as the Cerenkov/LSC rapid $^{89/90}$Sr method**, due to the ^{90}Y ingrowth period. However, due to the separation of pure ^{90}Y from strontium and other beta emitting nuclides with high decontamination factors, this method **may provide more accurate and sensitive measurements** for samples with **high ^{89}Sr/^{90}Sr or ^{90}Sr/^{89}Sr ratios**. The chemical yield of Sr may be measured via stable strontium carrier by taking a small aliquot of the separated strontium fraction for analysis by ICP-MS or ICP-AES or by ^{85}Sr gamma emission. Yttrium yields may also be tracked using stable Y and measurement by ICP-MS or ICP-AES.

$^{89/90}$Sr by GFPC, ^{90}Y by GFPC Following Ingrowth and Separation Total $^{89/90}$Sr can be measured effectively using low background gas flow proportional counting (GFPC) following separation of strontium on Sr Resin (Figure 1A) [4,5]. Prior to measurement by GFPC, purified strontium fractions are dried onto cupped planchets or precipitated as carbonates or phosphates and collected on filter paper (and dried). Immediate counts of the purified strontium fractions yield the total radiostrontium (^{89}Sr + ^{90}Sr). Following the initial count for total radiostrontium and a period of ^{90}Y ingrowth, the dried sample can be dissolved from the planchet or filter using HNO_3, and additional separations performed to isolate ^{90}Y from the strontium fraction using Sr Resin (Figure 1B) or DGA Resin (Figure 1C). ^{90}Y can then be measured by GFPC after evaporation on a stainless steel planchet or collection of an YF_3 precipitate on a filter. ^{90}Sr activity can be calculated using the measured ^{90}Y activity and the period of ingrowth from the initial separation. ^{89}Sr activity can be calculating by difference (total radiostrontium - ^{90}Sr).

When using GFPC, strontium chemical yield may be determined via stable strontium using ICP-MS, ICP-AES or gravimetric methods. Additionally, multiple drawer GFPC systems allow for the **simultaneous counting** of multiple samples, an option which is normally not available for Cerenkov or LSC.

References

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6) Maxwell, S.L.; Culligan, B.K.; Hutchinson, J.B.; Utsey, R.C.; McAlister, D.R.; "Rapid Determination of ^{90}Sr in Seawater Samples," *J. Radional. Nucl. Chem.*, 303, 709-717 (2015).