7. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting, measuring, and/or monitoring strontium, its metabolites, and other biomarkers of exposure and effect to strontium. The intent is not to provide an exhaustive list of analytical methods. Rather, the intention is to identify well-established methods that are used as the standard methods of analysis. Many of the analytical methods used for environmental samples are the methods approved by federal agencies and organizations such as EPA and the National Institute for Occupational Safety and Health (NIOSH). Other methods presented in this chapter are those that are approved by groups such as the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA). Additionally, analytical methods are included that modify previously used methods to obtain lower detection limits and/or to improve accuracy and precision.

Its companion manual, the Draft Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) manual, robustly describes relevant analytical equipment and methods, and became available for public comment in July 2001 (MARLAP 2001).

7.1   BIOLOGICAL MATERIALS

Strontium can enter the human body through inhalation, ingestion, or penetration through the skin. Measurement of the quantities of radiostrontium in the body can be performed by two primary methods, *in vivo* measurements and *in vitro* measurements. These types of measurements are called bioassays. *In vivo* techniques measure the quantities of internally deposited radiostrontium directly using a whole body counter, while *in vitro* techniques permit estimation of internally deposited strontium by analysis of body fluids, excreta, or (in rare instances) tissues obtained through biopsy or postmortem tissue sectioning. Some of these analytical methods are summarized in Table 7-1.

7.1.1   Internal Strontium Measurements

In vivo (or direct) measurements of radioactive strontium in the body are made with radiation detector systems and associated electronics called whole body counters that measure radiation as it leaves the body from internally deposited radioactive strontium. This system measures the emission of gamma rays or x-rays from internally deposited radionuclides. These counters are insensitive to beta particles emitted

Table 7-1. Analytical Methods for Determining Strontium in Biological Samples

Sample matrix	Sample preparation	Analytical method	Detection limit	Percent recovery	Reference
Blood	Acidification with nitric acid; dilution; addition of La matrix modifier	GFAAS	0.13 mg/L	94.5–102.5	Burguera et al. 1999
Blood	Acid digestion; iron extraction; clean-up by ion exchange; thin film deposition	TRXF	0.04 µg/mL	No data	Prange et al. 1989
Blood	Acid digestion; dilution	ICP-AES	0.3 µg/L	113	NIOSH 1994; Piette et al. 1994
Blood serum	Dry ashing; neutron activation; chemical separation	TNA	0.02 µg/mL	75–90	Teree and Cohn 1966
Blood serum	Acidification and dilution	ICP-MS	No data	99	Muñiz et al. 1999
Bone	Acidification with nitric acid; dilution; addition of La matrix modifier.	GFAAS	0.13 mg/L	96.5–102.9	Burguera et al. 1999
Bone	Acid digestion	ICP-MS	6 µg/g dry weight	No data	Outridge et al. 1996
Bone ash	Acid dissolution; clean-up by coprecipitation and scavenging	β-GPC	No data	No data	Mutschke and Pribilla 1967
Hair	Ashed	PIXE	1 µg/g	No data	Clayton and Wooller 1985
Tissues	Acid digestion; dilution	ICP-AES	No data	113	NIOSH 1994
Tissues	Complexometric digestion in TMAH/EDTA matrix with heat	GFAAS	2.2 ng/g	99±4.2	D'Haese et al. 1996
Urine	Acidification with nitric acid; dilution; addition of La matrix modifier	GFAAS	0.13 mg/L	98.8–101.5	Burguera et al. 1999
Urine	Coprecipitation with calcium phosphate; sample wet ashed with nitric acid; extraction and separation on Crown ether loaded chromatographic column	LSC	7 dpm/L (0.82 Bq/L or 22 pCi/L)	95±5	Dietz et al. 1991
Urine	Wet ashed; precipitation with oxalate; acid dissolution; chemical extraction	LSC	0.6 pCi (22 mBq)	100	Kramer and Davies 1982

β-GPC (total radioactive strontium) = beta gas proportional counter; Bq = Becquerel; dpm = disintegrations per minute; EDTA = ethylenediamine tetraacetic acid; GFAAS (total strontium) = graphite furnace atomic absorption spectroscopy; ICP-AES (total strontium) = inductively coupled plasma atomic emission spectroscopy; ICP-MS (isotopic strontium composition) = inductively coupled plasma-mass spectrometry; La = Lanthanum; LSC (isotopic quanitification of ^{89}Sr and ^{90}Sr) = liquid scintillation counting; pCi = pico curies (10^{-12} curies); PIXE (total strontium) = proton induced x-ray emission; TMAH = tetramethylammonium hydroxide; TNA (total strontium) = thermal neutron activation and radiometric measurement; TRXF (total strontium) = total-reflection x-ray fluorescence

from radiostrontium; thus, the utility for radiostrontium is limited to high exposure measurements. *In vivo* assays are the most direct method of quantifying internally deposited radioactive materials. The determinations of ^{90}Sr levels are achieved by measuring, with a phoswich detector, the bremsstrahlung of the ^{90}Y beta rays (photons with energies ranging from 30 to 160 keV). The most commonly used detectors for measurement of ^{90}Y bremsstrahlung (i.e., electromagnetic radiation) by *in vivo* counting are sodium iodide or phoswich (NaI and CsI sandwich) (Tokareva et al. 2000). For whole-body counting, a scanning-bed geometry in a special shielding room is typically used. Although whole body counters may be used in many configurations, a chest counter is usually used for inhaled radioactive materials. *In vivo* analysis is widely used throughout the nuclear industry, both commercial and government, for quantifying levels of insoluble radioactive materials in the body (Kozheurov 1994).

In vivo counting systems are calibrated using tissue-equivalent phantoms. These phantoms have shapes similar to the human torso and are made of polystyrene or other tissue equivalent material. Standard radioactive strontium sources of known activity are inserted at locations where strontium would be expected to accumulate in a human body. Relationships are determined between the radioactive strontium activity measured by the detection system and the known activity in the phantom (Kozheurov 1994).

7.1.2   *In Vivo* and *In Vitro* Radiostrontium Measurements

In vitro radioactive strontium analyses are routinely performed in support of a personnel monitoring program or in cases where the size of an operation does not justify the cost of whole body counter facilities. These analyses are usually done on urine samples, but other types of body materials (e.g., feces or blood) may also be used. Urinalysis is effective for analysis of transportable or soluble strontium. Strontium may also be measured in fecal material using the same methods identified above for urinalyses, except that this matrix requires extensive preparation.

7.2   ENVIRONMENTAL SAMPLES

Two types of methods are commonly used for measurement of strontium and radiostrontium in environmental samples. The first is field surveys using portable survey instruments, and the second is analysis of samples procured in the field that are returned to the laboratory for quantification.

7.2.1   Field Measurements of Radiostrontium

Radiostrontium measurements in the field are typically qualitative in nature in that the instruments simply respond to beta emissions, regardless of their origin. However, the levels can be measured quantitatively if key parameters are known, such as the relative abundances of all beta-emitting isotopes present, the thickness of the layer being assessed, and the detection efficiency of the instrument for the type of surface being assessed. Measurements in the past have typically been made using portable, hand-held Geiger-Mueller or beta scintillation detectors equipped with a count rate meter, which detect beta radiation while discriminating against other forms of ionizing radiation in the same area. Survey instruments can provide a quick estimate or a measure of the level of activity that might be present. However, more accurate measurements of radioactive strontium may require that samples be taken for laboratory analyses.

7.2.2   Laboratory Analysis of Environmental Samples

Analytical methods for measuring strontium in environmental samples are summarized in Table 7-2. The available methods can be divided into two groups: chemical methods to determine the total mass of strontium in a sample and radiological methods to determine amounts of radioactive isotopes. Environmental media that have been tested for strontium include air filters, swipes, biota, water, soil, and others. A full range of laboratory analysis methods has been used to quantify the total strontium or its radioactive isotopes.

The chemical methods for detecting total strontium include spectrophotometry, fluorometry, kinetic phosphorescence, atomic absorption spectroscopy (e.g., flame and graphite furnaces), energy dispersive x-ray analysis (i.e., EDAX), x-ray fluorescence spectrometry, and inductively coupled plasma spectroscopy-atomic emission and mass spectrometry applications (i.e., ICP-AES and ICP-MS).

The quantity of radioactive strontium is typically determined by gas-flow proportional, liquid scintillation, and Cherenkov counting techniques (Scarpitta et al. 1999). The standard EPA analytical procedure to determine radiostrontium in water is Method 905.0, and several methods are permutations of this procedure. A stable strontium carrier is added to the water sample so that ^{89}Sr and ^{90}Sr are precipitated as insoluble carbonates. The sample then undergoes a preliminary counting that represents the total strontium activity ($^{89,\,90}$Sr) plus a small fraction of ^{90}Y that has grown in by radioactive decay.

Table 7-2. Analytical Methods for Determining Strontium in Environmental Samples

Sample matrix	Sample preparation	Analytical method	Sample detection limit	Percent recovery	References
Air	Particulate collection on cellulose filter; acid digestion	FAAS (Method D4185)	No data	No data	ATSM 1999
Water	Acid digestion	Spectrophotometric measurement (total strontium) (Method 911.03)	No data	No data	AOAC 1990
Water	Filtration; acid digestion; add matrix modifier	FAAS (Method D3920; 7780)	No data	No data	ASTM 1999; OSW 1992
Water	Wet acid digestion	ICP-AES (Method 200.15)	No data	No data	EMMI 2000a
Drinking, raw, and waste water	Wet acid digestion; addition of Sr carrier and precipitation as $SrCO_3$; extraction of Yttrium; precipitation of Yttrium oxalate.	β-GPC (Method 973.66; 7500-Sr)	No data	93–99	AOAC 1990; APHA 1992
Water	Complex EDTA; ion chromatography; precipitate Sr effluent fraction as $SrCO_3$	β-GPC (Method 008)	No data	No data	EMMI 2000b
Water (high Sr concentration)	Ion chromatography; dilution	β-GPC	No data	No data	EMMI 2000c, 2000d
Saline water	Dilution	FAAS (Method D3352)	No data	100–106	ASTM 1999
Soils and sediments	Digest organic matter; pyrosulfate fusion; dissolve condensed phosphates	β-GPC	No data	No data	EMMI 2000c, 2000d
Soils and sediments	Fuse with $NaOH$-Na_2CO_3; dissolve in acid; ion exchange	β-GPC (Method 008-S)	No data	No data	EMMI 2000b
Vegetation and food	Dry ash; complexation with EDTA; ion exchange chromatography; precipitate Sr effluent fraction as $SrCO_3$	β-GPC (Method 008-V)	No data	No data	EMMI 2000b
Milk	Complexation of Y in growth; extraction; precipitation as oxalate	β-GPC (Method 974.37)	No data	No data	AOAC 1990

[89]Sr and ^{90}Sr measured separately by measuring ^{90}Y in-growth

ß-GPC (total radioactive strontium) = beta gas proportional counter; EDTA = ethylenediamine tetraacetic acid; FAAS (total strontium) = flame atomic absorption spectroscopy; ICP-AES (total strontium) = inductively coupled plasma atomic emission spectroscopy

The ^{90}Y is allowed to reach equilibrium (e.g., approximately a 2-week period) and then is separated with stable yttrium-carrier as yttrium hydroxide (i.e., Y(OH)$_3$). The Y(OH)$_3$ precipitates are converted to the oxalate and the solid oxalate is beta counted in a low background gas-flow proportional counter. The ^{90}Sr concentration is determined from the ^{90}Y activity and the ^{89}Sr concentration by difference. Variations of the above method involve different techniques of selectively separating strontium from environmental samples. Using the various separation methods already described, Cherenkov counting, in conjunction with liquid scintillation, has also been use to detect ^{90}Sr by measuring the concentration of its progeny, ^{90}Y, in solution (Scarpitta et al. 1999).

Horwitz et al. (1991) developed an extraction chromatography technique in which strontium can be selectively separated from other interfering radionuclides such as alkaline and alkaline earth element ions. The technique uses an extraction column (e.g., Sr-resin) with a crown ether (4,4'(5')-bis(tert-butylcyclohexano)-18-crown-6) sorbed on an inert polymeric porous support. A sample with ^{90}Sr digested in concentrated nitric acid is diluted and loaded on the Sr-resin column in ~3 M nitric acid. Interfering elements are removed from the column with ~1 M nitric acid and strontium ions are subsequently eluted with a dilute acid solution. ^{90}Sr ions are then beta counted using a low background gas flow proportional counter or Cherenkov counting of ^{90}Y as previously discussed (Grahek et al. 1999; Torres et al. 2000, 2002). One disadvantage with this technique is some ions interfere with the strontium separation. For example, potassium diminishes the capacity of the Sr-resin column to retain strontium; lead also shows a very strong retention on the Sr-resin and irreversibly blocks Sr adsorption sites (Miró et al. 2002). Recently, improvements have been made to the extraction process using a wetting film technique, which has been shown to reduce ionic interferences (Miró et al. 2002).

7.3   ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of strontium is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (NTP), is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of strontium.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would

reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

7.3.1 Identification of Data Needs

Methods for Determining Biomarkers of Exposure and Effect.   Analytical methods with satisfactory sensitivity and precision are available to determine the levels of strontium in human tissues and body fluids. Strontium and radiostrontium are found in essentially all food, water, and air, so everyone is exposed to some levels. Recently, Sutherland et al. (2000a, 2000b) developed a molecular biological strategy to identify clustered lesions in DNA resulting from *in vitro* cellular exposure to gamma radiation. It is possible that this technique might be adapted to evaluate genetic damage in blood cells following exposure to radioactive strontium. This method, however, will not be specific for ^{90}Sr effects.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media.   Analytical methods with the required sensitivity and accuracy are available for quantification of strontium, both total and isotopic, in environmental matrices (Table 7-2). Knowledge of the levels of strontium in various environmental media, along with the appropriate modeling (see Chapters 3 and 5), can be used to evaluate potential human exposures through inhalation and ingestion pathways.

7.3.2 Ongoing Studies

No ongoing studies investigating new methods for detection and speciation of strontium or radiostrontium were identified in the Federal Research in Progress database (FEDRIP 2002).