A SIMPLE METHOD TO SCREEN RADIOSTRONTIUM IN WATER BY ION EXCHANGE CHROMATOGRAPHY

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OUTLINE

• Overview Radiostrontium Chemistry
• History of Artificial Radiostrontium Isotopes
• Radiostrontium in Environmental
• Method Rad 905.0
• A FERN Method for Drinking Water
• A FDA Method for Foods
• An Alternative New Methodological Study at FL BRC Health and Physics Laboratory
• Results and Comparisons
• Questions and Answers
ACKNOWLEDGEMENTS

DOH Mission to protect, promote and improve the health and safety of all people in Florida through integrated state, county, and community efforts.

Florida Bureau of Radiation Control Team:
Allen Moody and John Williamson

Department of Energy (MAPEP samples)

Waters (ERA samples)
RADIOLOGICAL EMERGENCY PREPAREDNESS & RESPONSE

MUST’VE BEEN EXPOSED TO LARGE DOSES OF RADIOACTIVE FALLOUT HYPE...

Dave Granlund © www.davegranlund.com

Alpha
Beta
Gamma
Neutron

paper
water
concrete
**Radiostrontium Chemistry**

![Periodic Table with annotations]

Cations alike: Magnesium, Calcium, Barium, Radium

(Mass Numbers in Parentheses are from the most stable of common isotopes.)

(Rare Earth Elements)

(Lanthamide Series)

(Actinide Series)
STRONTIUM (Sr) ISOTOPES AND RADIOACTIVITY

- Natural stable strontium isotopes
- Sr-87 as a progeny of primordial Rb-87 ($T_{1/2} = 4.88E+10$ years)
- < 4.2 mg/L in drinking water (25 mg/L limit)
- ~ 8 mg/L in ocean
- Radiostrontium isotopes (31 possible) from Sr-73 to Sr-107 with half-life between ns - years
- Sr-85 as gamma ray emitter
- Sr-89 and Sr-90 as beta particle emitters
- Limit of radiostrontium < 8 pCi/L drinking water
## Radioactivity of the Isotopes of Strontium

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-Life</th>
<th>Energy, $\beta$ keV</th>
<th>Mass for activity equal to 1Ci</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr-85</td>
<td>65 days</td>
<td>1065</td>
<td>28.2 $\mu$g</td>
</tr>
<tr>
<td>Sr-89</td>
<td>51 days</td>
<td>1495</td>
<td>36 $\mu$g</td>
</tr>
<tr>
<td>Sr-90</td>
<td>29 years</td>
<td>546</td>
<td>7 mg</td>
</tr>
<tr>
<td>Sr-91</td>
<td>10 hours</td>
<td>2699</td>
<td>0.3 $\mu$g</td>
</tr>
<tr>
<td>Sr-92</td>
<td>3 hours</td>
<td>1911</td>
<td>0.09 $\mu$g</td>
</tr>
<tr>
<td>Sr-94</td>
<td>75 seconds</td>
<td>3511</td>
<td>No data</td>
</tr>
</tbody>
</table>

Toxicological Profile for Strontium. 2004. Department of Health and Human Services. 1 Ci ~ 1 g Ra-226
RADIATION MILESTONES

- 1896: Radioactivity discovered by Becquerel and defined by Curie a year later
- 1899: Alpha, Beta, and Gamma particles named by Rutherford
- 1900s: Radiation therapy
- 1945: 1st atomic bomb tested
- 1954: 1st nuclear power plant operated (Obninsk, RUS)
- 1958: 1st nuclear-powered submarine (Nautilus, US)
- 2016: 450 nuclear power plants worldwide (99 in US)

https://en.wikipedia.org/wiki/Nuclear_power
NUCLEAR POWER AND RADIATION

• “There are more things on earth than are dreamt of in your philosophy.” Shakespeare in Hamlet (1600)
• “We knew the world would not be the same.” Oppenheimer in Manhattan atomic bomb project (1940s)
• Atomic forces as “The destroyer of worlds”
• 1g U ~ 2 tons oil ~ 3 tons of coal

THE BIRTH OF SYNTHETIC RADIOSTRONTIUM AND USE

- Radiostrontium a major fission by product at nuclear reactors
- Residue fallouts from atomic bombs, nuclear testing sites or meltdowns
- A fuel for radioisotope thermoelectric generator (RTG) and space craft
- Radiological therapy
- A Reference Standard for calibration in radiological laboratory
- Casino gambling misuses
- Radiological Dispersal Devices (RDD) or Dirty Bomb
- Used radioactive spent fuels and nuclear wastes (about 0.3% mass)
FISSION BYPRODUCTS OF URANIUM

$^{235}\text{U} + n \rightarrow ^{236}\text{U}$

$^{89}\text{Kr} + ^{144}\text{Ba} \rightarrow ^{89}\text{Rb}$

$^{89}\text{Sr} \rightarrow ^{89}\text{Y}$

$^{144}\text{La} \rightarrow ^{144}\text{Ce} \rightarrow ^{144}\text{Nd}$

$^{90}\text{Sr} + ^{144}\text{Xe}$

$^{140}\text{Xe}$

$^{137}\text{Cs}$

$^{131}\text{I}$

$^{96}\text{Rb}$

$^{89}\text{Y}$
YIELDS OF THERMAL FISSION BYPRODUCTS

Thermal Neutron Fission of U-235

$^{90}\text{Sr}$
$^{89}\text{Sr}$
$^{90}$Sr CONTAMINATED IN THE EARTH IN PBQ

1 Peta Bq = $10^{15}$ Bq = 2.7E+4 Ci ~ 27 Kg Ra-226
No data used for ground and underground from nuclear tests
RADIOACTIVE STRONTIUM IN ENVIRONMENTAL

- Radioactive material following prevailing winds
- Increased deposition rate due to rainfall
- Inhalation of radioactive materials
- Irradiation from deposited radioactive materials
- Deposition on water courses, crops, pastures, etc
- Ingestion of contaminated food or water
- Uptake by grazing animals and accumulation in their bodies

Florida Health
# Natural Radioactivity in the Body

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Activity in pCi</th>
<th>Activity in Bq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium(^a)</td>
<td>30</td>
<td>1.1</td>
</tr>
<tr>
<td>Thorium</td>
<td>3</td>
<td>0.11</td>
</tr>
<tr>
<td>Potassium-40</td>
<td>120000</td>
<td>4400</td>
</tr>
<tr>
<td>Radium</td>
<td>30</td>
<td>1.1</td>
</tr>
<tr>
<td>Carbon-14</td>
<td>400000</td>
<td>15000</td>
</tr>
<tr>
<td>Tritium</td>
<td>600</td>
<td>23</td>
</tr>
<tr>
<td>Polonium(^b)</td>
<td>1000</td>
<td>37</td>
</tr>
</tbody>
</table>

- \(^a\): higher numbers for cigarette consumptions
- \(^b\): smokeless tobacco products: 3.5-14.9 Bq/kg from Po-210
  
Radiostrontium Exposure and Adverse Health

- 1 μCi (~ 7 ng) of Sr-90 at 30 cm for skin dose rate of 732 mR/h or about 12 mR/min
- Expose to 1 μg 90Sr at 1 ft for 7 h ~ to 5 R
- Radiation field people (NRC): 50 mSv (5 rem/y)
- General Public (TEDE) 1 mSv (0.1rem) or 2 mR/h
- ACGIH (American Conference of Governmental Industrial Hygenists): 20 mSv for radiologist
- Acute radiation syndrome and late stochastic effect
- Leukemia
- Skeletal and bone marrow damages
- Cancers in young children
CASINO GAMBLING CARDS AND CHIPS
Sr-85 as gamma emitter, Sr-89 & Sr-90 as beta emitters
http://bestanimations.com/Military/Explosions/Explosions.html
http://slideplayer.com/slide/8970191/
$^{85}$STRONTIUM GAMMA RAY DECAY SCHEME

$^{85}$Sr → $^{85}$Rb

(T$_{1/2}$ = 65d)

γ (98.4%) 514 keV

S$_0$ (stable)
Sr-89 spray beta particles 10,600 time more than Sr-90
The Chernobyl accident released roughly 1000 PBq (10^{18} Bq) of strontium-89 into the atmosphere.
**90Strontium Decay Scheme**

- **90Sr**
  - $(T_{1/2} = 29\text{y})$
  - $\beta^-$
  - 546 keV

- **90Zr**
  - $(T_{1/2} = 64\text{h})$
  - $\beta^-$ (99.98%)
  - 2240 keV

- **90Y**
  - $(T_{1/2} = 64\text{h})$

- **So** (stable)
April 1986, the Chernobyl released roughly 10 PBq ($10^{16}$ Bq) of strontium-90 into the atmosphere.

March 2011, the Fukushima Daiichi released 0.1-1 PBq (0.36) of strontium-90 into the air and 2.2 PBq into the Pacific Ocean.

It takes hundreds of years for 1 PBq decayed to 1 Ci ($3.7E+10$ Bq).
A Secular Equilibrium between Sr-90 and Y-90

- 1st count after separation for Sr-90
- 2nd count about 2 weeks for calculating Sr-90 from Y-90
- Sr-90 or Y-90 analysis
YTTRIUM-90 INGROWN VS. SEPARATION TIME

Activity of Y-90 in Mixture

Error from 1st counting significant for Sr-90 analysis
RADIOSTRONTIUM ANALYTICAL CHEMISTRY

• Current method for Strontium in water: Rad 905.0 with MDA of 2 pCi/L.
• A traditional method for total radiostrontium analysis in water since 1980.
• A multiple steps chemical separation process and hazardous chemical involved.
• Using nitric acid concentrate to separation strontium in solution.
• Utilization sodium chromate, ammonia, acetic acid, for separation, neutralization and precipitation.
• Require a period of 2 weeks for yttrium ingrowths.

MDA: Minimum Detection Activity
SUMMARY OF METHOD RAD 905.0

Mixed-Nuclides

Chemical Separations
1. HNO₃ 16N (c)
2. Na₂CrO₄
3. NH₄OH

Eliminations
1. Calcium
2. Barium, Ra
3. Yttrium

- Carbonates
  - NaOH
  - Na₂CO₃

Gas Proportional Counter
- Cesium
- Iodide
- Potassium

http://www.epa.gov
PERMISSIBLE EXPOSURE LIMIT (PEL)

- Nitric acid: 2 ppm or 5 mg/m³ for 8h work (OSHA)
- Hydrochloric acid: 5 ppm or 7 mg/m³
- Acetic acid: 10 ppm or 25 mg/m³
- Ammonia hydroxide: 50 ppm or 35 mg/m³
- Na₂CrO₄: 5 μg/m³ (target lung, cancer reagent)
- American Conference of Governmental Industrial Hygienists (ACGIH) lower the numbers
DESIGN A NEW METHODOLOGICAL STUDY

• Specific separation for strontium
• High recovery
• Simple
• Interferences
• Rigid environments
• Hazardous chemicals
• Time
• Cost
• Recycle and Green Chemistry
A FERN METHOD ON Sr RESIN

- Total radiostrontium in drinking water
- Aim for rapid response analysis
- Environmental more friendly: utilize less hazardous chemicals
- Column chromatography separation application
- Using Sr-resin (Eichrom) available nowadays
- Employ vacuum box systems for separation
- Spiking a less amount of Sr-carrier in comparison to method Rad 905.0
- Require a period of 2-3 weeks for yttrium ingrowths

FERN: Food Emergency Response Network
**BASIC OF COLUMN CHROMATOGRAPHY**

• In 1906, Mikhail Tsvett, with 1st chromatography experiment observed pigments separation through a column

• Limestone as absorbance

• Ethanol and ether as solvents

• Chlorophylls, Xanthophylls and other isomers collected.

**Separation and purification mechanism:**

1. Analyte + Absorbance = An Analyte-Absorbance Formation

2. Analyte-Absorbance + Solvent = A solution of Analyte

3. Evaporation of solution of Analyte to obtain Analyte
A TYPICAL COLUMN CHROMATOGRAPHY PROCESS

Mixed-analytes → Mobile phase → Elution

Station phase → Collect analyte

Flow

Detector Signal

Chromatographic Retention Time
MECHANISM OF STRONTIUM RESIN SEPARATION
4,4'-(5')-DI-T-BUTYLCYCLOHEXANO 18-CROWN-6
A COMPLEX WITH CATIONS

Diluent: 1-octanol

A Donor-Receptor Complex Pair with K⁺

C.J. Pedersen: 18-Crown-6 Binding Constant with K⁺ is 10⁶M⁻¹
**FERN METHOD FOR DRINKING WATER**

- Rapid methodology for strontium analysis
- Recommendation for 5-8 mg of Sr per packed column
- Cation interferences: Ca$^{2+}$, Ba$^{2+}$, K$^+$, Cs$^+$, Pb$^{2+}$, Np$^{4+}$, Po$^{4+}$, Pu$^{4+}$
- Resin stability (32-86°F)
ACID DEPENDENCY FOR Sr RESIN I

www.eichrom.com
ACID DEPENDENCY FOR Sr RESIN II

www.eichrom.com
A SUMMARY OF FERN METHOD

Mixed-Nuclides

Sr-resin Column
1. HNO₃ 8N
2. HNO₃ 0.05N

Carbonates

NaOH → Na₂CO₃

Sr(NO₃)₂ → • Cesium
• Iodide
• Potassium

Separations
• Magnesium
• Calcium
• Barium, Ra

Gas Proportional Counter

http://www.eichrom.com
A FDA METHOD FOR FOODS ON DGA RESIN

- Analysis for Strontium-90 in food matrices
- Use wet ash with nitric acid and H₂O₂ in boiling solution
- Utilize DGA resin (Figure 1) to separate Strontium and Yttrium nuclides
- Liquid Scintillation application for counting of Y-90
- Require a secular equilibrium between Sr-90 & Y-90 before analysis (store sample for 2-3 weeks)

Donor-Receptor Complex Mechanism
R = normal alkyl chain or brain chain
SEPARATION OF CATIONS ON DGA RESIN I

Figure 5

SEPARATION OF CATIONS ON DGA RESIN II

Figure 6

SEPARATION OF CATIONS ON DGA RESIN III

Figure 7

SEPARATION OF Sr-90 AND Y-90 ON DGA RESIN IV

STRONTIUM RESIN vs. ION EXCHANGE RESIN

A. Strontium Resin Application
   - Strongly acidic concentration dependence
   - Vacuum box system
   - One time application
   - Reasonable cost
   - Less hazardous waste

B. Cation Exchange Resin Application
   - Affinity of cation to resin
   - Convenience column
   - Re-generable resin several times
   - Lower cost
   - Even less hazardous waste
AN ALTERNATIVE STUDY BY CATION EXCHANGE RESIN SEPARATION

Ion exchange mechanism forming an ionic complex polymer bound

Polystyrene bound complex

Resin bead pore size: a few nm to 20 nm
ELUTION OF CATIONS ON ION EXCHANGE RESIN

- Charge of ions
- Acidic strength dependency
- Flow of mobile phase
- Interference ions, hard water
- General order of cations by elution on cation exchange resin: monovalent ions, divalent ions, trivalent ions, tetravalent ions

- $\text{Hg}^2+ < \text{Li}^+ < \text{H}^+ < \text{Na}^+ < \text{K}^+ < \text{NH}_4^+ < \text{Cd}^{2+} < \text{Cs}^+ < \text{Ag}^+ < \text{Be}^2+ < \text{Ni}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+} < \text{Co}^{2+} < \text{Mg}^2+ < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+} < \text{Ra}^{2+} < \text{Pb}^{2+} < \text{Al}^{3+} < \text{Fe}^{3+} < \text{Y}^{3+} < \text{Pb}^{4+} < \text{Th}^{4+}$

- Chromatography separation techniques involved science and art
AN ION CHROMATOGRAM FROM A COLUMN

Concentration

1. Lithium (0.5 ppm)
2. Sodium (0.5 ppm)
3. Ammonium (0.8 ppm)
4. Potassium
5. Nickel (5 ppm)
6. Zinc (5 ppm)
7. Cobalt (5 ppm)
8. Magnesium (0.7 ppm)
9. Calcium (0.7 ppm)
A SCREENING METHODOLOGICAL STUDY FOR WATER

- Environmentally more friendly, utilize green chemistry, less hazardous chemicals

- Column chromatography separation application

- Using strong cation resins commercially available

- Conventional chromatography (normal atmosphere)

- Work with Sr-carrier (40 mg) for yield calculation, and work well with semi-hard water (up to 60 mg/L of calcium or magnesium ions) in contrast to Sr-resin methodologies (5-20 mg cations for a cartridge)

- Require a period of 2-3 weeks for yttrium ingrowths
A SUMMARY OF CATION EXCHANGE METHOD

Mixed-Nuclides

Cation exchange resin column

NaOH → Na$_2$CO$_3$ → Carbonates

• Cesium
• Iodide
• Potassium

Add Na$_2$CO$_3$ → H$^+$ diluted

Dry

Gas Proportional Counter

SrCO$_3$

Separations
• Magnesium
• Calcium
• Barium, Ra

http://www.fishersci.com/
RESULTS AND COMPARISONS

• Comparison between method Rad 905.0, a FERN method by strontium resin, and a study on ion exchange resin methodology

• Mixed-Analytes Proficiency Evaluation Program (MAPEP) samples from Department of Energy

• Analysis for total $^{90}\text{Sr}$ in mixed water samples, in vegetation samples, and in soil samples

• Trials utilized cation exchange resin for both $^{89}\text{Sr}$ and $^{90}\text{Sr}$ in Proficiency Testing study samples from Waters (ERA)

• Possible to develop a screening method by cation exchange chromatography
# Recovery Percentage for Sr-90 on Water Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method 905.0</th>
<th>Ion Exchange Method</th>
<th>Sr Resin Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>MaW28</td>
<td>103.32</td>
<td>105.26</td>
<td>No data</td>
</tr>
<tr>
<td>MaW32</td>
<td>95.46</td>
<td>97.05</td>
<td>98.62</td>
</tr>
<tr>
<td>MaW33</td>
<td>101.88</td>
<td>110.70</td>
<td>116.82</td>
</tr>
<tr>
<td>MaW34</td>
<td>100.34</td>
<td>96.21</td>
<td>No data</td>
</tr>
<tr>
<td>MaW35</td>
<td>100.00</td>
<td>100.00</td>
<td>No data</td>
</tr>
</tbody>
</table>

Mixed-analytes proficiency evaluation program (MAPEP) samples
## Recoveries of Sr-90 for Water Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical (percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MaW28</td>
<td>110</td>
</tr>
<tr>
<td>MaW32</td>
<td>90</td>
</tr>
<tr>
<td>MaW33</td>
<td>110</td>
</tr>
<tr>
<td>MaW34</td>
<td>100</td>
</tr>
<tr>
<td>MaW35</td>
<td>100</td>
</tr>
</tbody>
</table>

**Method 905.0**
- Ion Exchange Method
- Sr Resin Method
### Recovery Percentage for Sr-90 on Air Filters

**Sample** | **Method 905.0** | **Ion Exchange Method**
--- | --- | ---
RdF35 | 102.91 | 100.97

Mixed-analytes proficiency evaluation program (MAPEP) samples
# Recovery Percentage for Sr-90 on Vegetation Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method 905.0</th>
<th>Ion Exchange Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>RdV32</td>
<td>96.50</td>
<td>114.81</td>
</tr>
<tr>
<td>RdV35</td>
<td>53.75$^\delta$</td>
<td>76.44$^\varepsilon$</td>
</tr>
</tbody>
</table>

Mixed-analytes proficiency evaluation program (MAPEP) samples
$^\delta$ Dry ashed; $^\varepsilon$ Wet ashed
RECOVERY PERCENTAGE FOR Sr-90 ON SOIL SAMPLES

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method 905.0</th>
<th>Ion Exchange Method</th>
<th>Sr Resin Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>MaS33</td>
<td>98.12</td>
<td>95.45</td>
<td>105.91</td>
</tr>
</tbody>
</table>

Mixed-analytes proficiency evaluation program (MAPEP) samples
Recoveries of Strontium-90 for Different Matrices

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical (percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RdF35</td>
<td>40</td>
</tr>
<tr>
<td>RdV32</td>
<td>60</td>
</tr>
<tr>
<td>RdV35</td>
<td>80</td>
</tr>
<tr>
<td>MaS33</td>
<td>100</td>
</tr>
</tbody>
</table>

Methods:
- Method 905.0
- Ion Exchange Method
- Sr-Resin Method
# Recovery Percentage for Sr-89 on Water Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method 905.0</th>
<th>Ion Exchange Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>RAD 103</td>
<td>83.25</td>
<td>100.57</td>
</tr>
<tr>
<td>RAD 105</td>
<td>93.92</td>
<td>94.48</td>
</tr>
<tr>
<td>RAD 107</td>
<td>88.04</td>
<td>83.60</td>
</tr>
</tbody>
</table>

ERA Proficiency Testing Samples
RESULTS FOR ERA WATER SAMPLES I

Recoveries of Strontium-89

Theoretical (percentage)

Sample

Method 905.0
Ion Exchange Method

RAD 103
RAD 105
RAD 107
# Recovery Percentage for Sr-90 on Water Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method 905.0</th>
<th>Ion Exchange Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>RAD 103</td>
<td>106.66</td>
<td>104.04</td>
</tr>
<tr>
<td>RAD 105</td>
<td>91.79</td>
<td>108.07</td>
</tr>
<tr>
<td>RAD 107</td>
<td>101.43</td>
<td>100.02</td>
</tr>
</tbody>
</table>

ERa Proficiency Testing Samples
RESULTS FOR ERA WATER SAMPLES II

Recoveries of Strontium-90

Theoretical (percentage)

Sample

RAD 103  RAD 105  RAD 107

- Method 905.0
- Ion Exchange Method
STUDY ON HARD WATER MATRIX

- Well, surface, and saline waters as interferences
- Hard water samples range from 50 – 200 mg/L equivalence of Ca and Mg ions
- Spiked samples with Sr-90 standards (LCS) and analyzed by using ion exchange resin
- Column resin bed size ~ 0.5x6-8 inches
- Recoveries decreased when content of ions in hard water samples increase
- < 70% yields for hard water samples above 100mg/L
- Possible need to increase resin bed sizes for higher recoveries
SUMMARY AND FUTURE EXPLORATION

• A screening method for radiostrontium by cation exchange resin with the recovery within +/- 30 percent of theoretical value, not yet a confirmatory method for full scale analysis

• MDA for Sr-89 and Sr-90 detected at 2 pCi/L by cation exchange resin

• Other matrices, hard waters, foods

• Liquid scintillation counting application

• Other nuclides of interest

• Ra-226 & Ra-228 in water samples analyzed by gamma ray for 1 MAPEP and 4 ERA samples, all reported within +/- 30% theoretical values
QUESTIONS AND ANSWERS

Safety is no radiological accident.