DETERMINATION OF LOW-LEVEL $^{90}$Sr IN ENVIRONMENTAL MATERIALS: A NOVEL APPROACH TO THE CLASSICAL METHOD

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A method was developed for the separation of strontium from large amounts of calcium which does not depend on fuming nitric acid. A sample in the form of mixed carbonates or oxides is stirred into concentrated nitric acid in the proportion 1:7 w/v. Strontium forms insoluble nitrates while calcium remains in the solution. Two re-precipitation steps combined with an acetone wash yield a very pure strontium salt which is suitable for gravimetric determination of recovery. The method, devised originally for $^{90}$Sr assay in sea water, can also be applied to solid samples which present analytical problems due to their high calcium content.

INTRODUCTION

Recent activity levels of $^{90}$Sr in environmental materials are so low that large samples must be processed to ensure meaningful data. Typically, several hundred grams of solids and tens to hundreds of liters of water are needed for a single analysis.

Such large samples bring into the solution huge amounts of foreign ions which interfere with strontium determination and must be removed at the early stages of an analysis. Calcium presents a special problem because it follows strontium in most chemical reactions.

Separation of these elements can be effected in many ways. The oldest and the most popular are methods based on the selective leaching of calcium nitrate from mixed anhydrous salts with organic solvents, and methods exploiting the difference in solubility of calcium and strontium nitrates in concentrated nitric acid (1-3). The latter have become an integral part of many radiochemical procedures (4, 5) because they are very selective, can be scaled-up to handle large amounts of material, and offer excellent decontamination from many interfering elements, including radioactive ones (excepting radium and lead isotopes). They have, however, one serious disadvantage in that they require fuming nitric acid. This acid has a bad reputation in laboratories as it gives off noxious and offensive fumes, burns the skin, is very corrosive, and presents a fire hazard.

Many methods have been proposed which offer milder separation conditions, such as ion-exchange (6, 7) and solvent extraction of the daughter $^{90}$Y (8, 9). They do not appear to be replacing those based on fuming nitric acid, however, as they lack the desired versatility and are more complex.
A survey of IAEA's intercomparison exercises has revealed that two out of three participants still give preference to the methods utilizing fuming acid.

We have developed a method which, while not using fuming nitric acid, retains all the advantages resulting from its use. It yields, in addition, very pure strontium salts which can be weighted for recovery determination. Dangerous manipulations with concentrated acids such as evaporation, filtration, and centrifugation have been eliminated and other analytical steps have been simplified for ease of performance, economy of materials, and time saving.

![Calcium-strontium separation flowsheet](image)

Figure 1. Calcium-strontium separation flowsheet. "m" and "n" are masses of mixed carbonates and strontium nitrate, resp.
EXPERIMENTAL

Regents:

Only two reagents are needed to separate strontium from calcium: concentrated nitric acid and acetone. The concentration of acid is not critical as long as it is no lower than 65% by weight. The acetone should contain no water. Analytical-grade reagents from freshly opened bottles can be used without additional preparations. Strontium carrier solution (100 mg Sr²⁺ cm⁻³) is prepared by dissolving 241.5 g Sr(NO₃)₂ or 303.4 g SrCl₂·6H₂O in water and adjusting the volume to 1 dm³. The concentration should be checked gravimetrically using the same method as for the samples. Oxalic acid, concentrated ammonia liquor, saturated ammonium or sodium carbonate solution, 8M HNO₃, 0.3M BaCl₂, 0.3M Na₂CrO₄, standardized yttrium solution (10 mg Y³⁺ cm⁻³), unstandardized iron carrier (10 mg Fe³⁺ cm⁻³), dilute ammonia and nitric acid solutions, and phenol red indicator solution are used at various stages of the analysis. Normal precautions should be taken to minimize the reagent blank.

Equipment:

A low-level beta counter is the only instrument which is required, apart from an oven, a muffle furnace, an analytical balance, hot plates, and magnetic stirrers, all of which are normally available in chemical laboratories. Laboratory glassware is standard.

Procedure:

The sample must be in the form of a dry carbonate or oxide powder and may contain up to 2 g of stable strontium carrier (1 g is the recommended amount).

Weigh the carbonates to the first decimal place. Select a glass beaker of an appropriate size and weigh it to the second decimal place. Pour into the beaker concentrated HNO₃ whose volume (cm³) equals seven times the weight of mixed carbonates (g). Add the carbonate to the acid while stirring the contents of the beaker with a glass rod. As soon as the precipitate settles, draw off the supernatant as completely as possible and discard it. Wash the residue with three consecutive portions of acetone and thoroughly remove the liquids by aspiration. The volume of acetone is not critical, but it should be large enough to enable complete removal of the calcium-bearing acid liquor. Thirty to fifty cm³ for the first wash and fifteen to twenty cm³ for the remainder is recommended.

Gently warm the beaker with strontium nitrate crystals to expel the residue acetone, and weigh it. Dissolve the salts in a minimum volume of distilled water. The right volume, in cm³, is obtained by multiplying the weight of strontium nitrate by a factor of 1.5. Add dropwise, while swirling vigorously, 2 cm³ conc. HNO₃ and then, faster, the remaining volume. The total volume of acid equals ten times the volume of water used for dissolving the strontium salts. Proceed with the sample as described earlier, using smaller volumes of acetone. If the washing solutions were drawn off to the last drop, two washings may be sufficient; if not - three washings are recommended. Repeat the dissolution/reprecipitation steps as described above and bring the strontium nitrate to dryness at 150°C. Cool the beaker in a dessicator to the ambient temperature and weigh it. Calculate the approximate
strontium content by multiplying the weight of Sr(NO₃)₂ by a factor of 0.4140. The separation flowsheet is shown in Figure 1.

The strontium nitrate is virtually free of calcium but may contain traces of lead, barium, and radium as well as small amounts of common elements such as iron and other hydrolysable ions. The latter are scavenged on iron hydrous oxides while the former are co-precipitated with barium chromate at pH 5.5, as described in common radiochemical procedures (4, 5).

Strontium is precipitated from the purified solution as a carbonate. Sufficient volume of saturated ammonium carbonate or sodium carbonate solution is added to the hot solution of strontium to ensure complete precipitation (10 cm³ is the recommended volume). The weight of dry SrCO₃ multiplied by a factor of 0.5935 gives the strontium content of the sample.

RESULTS AND DISCUSSION

Pretreatment of Samples:

The way in which samples can be reduced to a carbonate powder depends on their nature and the quantity of material being handled. Detailed procedures for the preparation of various materials for radiochemical analyses are given in Reference 4 while a survey of methods applicable to materials of marine origin can be found in Reference 5.

We give preference to methods which use oxalic acid for group separation of alkaline earth elements as they yield precipitates which settle rapidly, are easy to collect by filtration, are relatively free from other cations, and ensure good recoveries. Our routine method of ⁹⁰Sr determination in sea water includes precipitation of oxalates with oxalic acid and ammonia at pH 6 ± 0.5. The amount of oxalic acid is estimated from the experimentally established formula:

$$H_2C_2O_4 \cdot H_2O(g) = 0.4 \text{ VS},$$

where V is water volume (dm³) and S is salinity (%0). For 10 dm³ Baltic water samples of low salinity (S = 5-20 %0) spiked with 1 g Sr²⁺ the loss of the carrier due to incomplete precipitation does not exceed 10 percent.

For samples which dissolve nearly completely in nitric acid - bones, shells, carbonates, fertilizers, etc. - the preliminary group separation of alkaline earth elements does not seem to be necessary in the light of a test performed on the reference bone sample A-12 (Table 1). It appears that a sufficient degree of equilibration is attained between the strontium contained in samples and that introduced as a carrier at the stage of Ca-Sr separation. Although this phenomenon may only result from mechanical homogenization of the independently formed Sr(NO₃)₂ crystals, that does not matter as long as there are no mechanical losses of the solid phase at the first cycle of washing. True equilibration occurs when the solid phase is dissolved in water for subsequent purification. When more experimental evidence is gathered to better document this finding it will yield a considerable time saving in routine assay of such materials for ⁹⁰Sr.
Table 1
Results of $^{90}\text{Sr}$ measurements on IAEA reference sample A-12 (animal bone). Sample size 20 g dw, carrier 1 g Sr$^{2+}$

<table>
<thead>
<tr>
<th>Method</th>
<th>Carrier Recovery %</th>
<th>$^{90}\text{Sr}$ content mBq g$^{-1}$</th>
<th>$\pm 1\sigma$ mBq g$^{-1}$</th>
<th>Confidence limits (0.05) mBq g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>91.2</td>
<td>51</td>
<td>2</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>81.1</td>
<td>49</td>
<td>2</td>
<td>---</td>
</tr>
<tr>
<td>Certified value</td>
<td></td>
<td>55</td>
<td>---</td>
<td>46 - 59</td>
</tr>
</tbody>
</table>

$*$Propagated random uncertainty (does not include possible calibration bias).

Method 1: ashed sample was introduced into conc. HNO$_3$ (140 cm$^3$); after 0.5 h stirring, the strontium carrier was added (10 cm$^3$ aqueous solution) and stirring was continued for another 0.5 h, then processed as described in the text.

Method 2: ashed sample was dissolved in dil. HNO$_3$, Sr carrier was added and oxalates were precipitated using oxalic acid and ammonia (pH ~5). Precipitate was converted to carbonates at 550$^\circ$ C, the powder was introduced into 140 cm$^3$ conc. HNO$_3$, then continued as in the procedure.

Size of Sr Carrier:

There are unavoidable losses of strontium occurring in the course of an analysis. As most methods for $^{90}\text{Sr}$ determination require complex treatment combining several separation/purification steps, the chances of losses are compounded. The addition of stable strontium carrier helps reduce these losses and, as far as $^{90}\text{Sr}$ is concerned, the amount is not critical. However, it should be kept within a reasonable range as the scale of analytical operations is dependent on it to some degree. We consider one gram of strontium an optimum amount for the following reasons: analytical operations on solid phases, such as decantation, filtration, washing, drying, and weighing, can be performed comfortably and accurately, mechanical losses due to aspiration of supernatants are relatively small as is the consumption of reagents, and all operations can be done in small-size vessels, which help reduce the blank. As one gram of strontium largely exceeds the natural strontium contents of the samples being analyzed, the contribution of the latter can often be neglected, or can be estimated approximately, without committing an appreciable error.

Sample-to-acid ratio:

In classical separation schemes strontium nitrate is precipitated from solutions containing more than 70% of nitric acid in order to reduce its loss by solubility. From the data given in Table 2 it would appear that such conditions are preferable. However, with increasing concentrations of nitric acid, solubilities of other salts also diminish, as can be seen in Table 3.

Table 2
Solubility of strontium nitrate in nitric acid at $t = 25^\circ$C (10)

<table>
<thead>
<tr>
<th>HNO$_3$ (wt %)</th>
<th>48</th>
<th>52</th>
<th>58</th>
<th>63</th>
<th>67</th>
<th>72</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr(NO$_3$)$_2$ (mg Sr dm$^{-3}$)</td>
<td>2000</td>
<td>1200</td>
<td>440</td>
<td>163</td>
<td>58</td>
<td>17</td>
<td>3.3</td>
<td>1.1</td>
</tr>
</tbody>
</table>
The results of an experiment are given in Reference 10 in which strontium nitrate was precipitated with fuming nitric acid in the presence of calcium ions (concentrations were not reported). The results were as follows:

<table>
<thead>
<tr>
<th>HNO₃ Wt %</th>
<th>% Sr in ppt.</th>
<th>% Ca on Sr ppt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>100 ± 1.7</td>
<td>51 ± 3.2</td>
</tr>
<tr>
<td>70</td>
<td>98 ± 1.4</td>
<td>11 ± 2.3</td>
</tr>
<tr>
<td>60</td>
<td>81 ± 4.2</td>
<td>2.6 ± 1.0</td>
</tr>
</tbody>
</table>

This data along with that in Table 3, clearly indicates that when higher concentrations of nitric acid are chosen for Ca-Sr separation larger volumes are needed to retain the calcium in the solution. It is also evident, that if strontium recovery is to be determined gravimetrically, the separation cycle must be repeated several times in order to obtain strontium nitrate of adequate purity. Usually, three to five precipitations with fuming nitric acid are recommended (4).

Conversely, when precipitation is made from less concentrated acid, the strontium salt contains fewer impurities and may require fewer purification cycles. The reaction can be run in a smaller volume of acid due to a higher solubility of calcium nitrate in dilute solutions, thereby reducing volume-dependent strontium losses. A suppression of Sr(NO₃)₂ solubility in concentrated solutions of Ca(NO₃)₂ can also be anticipated as a result of the action of mass.

In order to check the latter assumption, a series of experiments were made, in which anhydrous calcium and strontium nitrates were shaken with nitric acid solutions of different concentrations. The equilibrium concentrations of calcium and strontium were determined gravimetrically and by atomic absorption spectrometry. The results, shown in Figures 2 and 3, indicate that whereas solubility relationships for calcium and strontium nitrates alone follow the same pattern as described earlier (10-12), the solubility of strontium nitrate in acid, saturated with respect to calcium nitrate, is much lower compared to that in nitric acid alone. The difference was threefold in undiluted conc. HNO₃ (15.15M) and fivefold in 12.45M HNO₃.
It was concluded from these experiments that, to minimize strontium losses, the separation of strontium nitrate should be made in solutions which are nearly saturated with respect to calcium nitrate. Such solutions are, however, difficult to prepare and handle. Solutions which can be obtained by bringing mixed carbonate powder and concentrated nitric acid into contact appear more promising. Such a system was studied in more detail, and the results are presented in Table 4.
As can be seen, the proportions of nitric acid and mixed carbonates can vary by a wide range without producing larger strontium losses due to solubility (Figure 4). The observed effect is a combination of several processes acting in opposite directions. The losses are trivial compared to the initial amount of Sr added as a carrier and any proportion is considered acceptable. We have arbitrarily chosen a proportion of 1 to 7 because it is convenient to manipulate with smaller volumes. Further reduction of the ratio is impractical because the increased viscosity makes further operations more difficult.
Table 4

<table>
<thead>
<tr>
<th>CaCO₃:HNO₃ w/v ratio</th>
<th>Concentration of Ca(NO₃)₂ g dm⁻³</th>
<th>% saturation</th>
<th>HNO₃ M</th>
<th>Solubility of Sr(NO₃)₂ mg Sr dm⁻³</th>
<th>Sr⁺ mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:70</td>
<td>23.4</td>
<td>12</td>
<td>14.9</td>
<td>20.1</td>
<td>14.1</td>
</tr>
<tr>
<td>1:35</td>
<td>46.8</td>
<td>22</td>
<td>14.6</td>
<td>22.5</td>
<td>7.9</td>
</tr>
<tr>
<td>1:23.3</td>
<td>70.3</td>
<td>30</td>
<td>14.3</td>
<td>24.8</td>
<td>5.8</td>
</tr>
<tr>
<td>1:17.5</td>
<td>93.7</td>
<td>35</td>
<td>14.0</td>
<td>26.9</td>
<td>4.7</td>
</tr>
<tr>
<td>1:14</td>
<td>117</td>
<td>40</td>
<td>13.7</td>
<td>29.1</td>
<td>4.1</td>
</tr>
<tr>
<td>1:11.7</td>
<td>140</td>
<td>44</td>
<td>13.4</td>
<td>32.3</td>
<td>3.8</td>
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<tr>
<td>1:10</td>
<td>164</td>
<td>47</td>
<td>13.2</td>
<td>35.2</td>
<td>3.5</td>
</tr>
<tr>
<td>1:8.75</td>
<td>187</td>
<td>49</td>
<td>12.9</td>
<td>39.3</td>
<td>3.4</td>
</tr>
<tr>
<td>1:7.78</td>
<td>211</td>
<td>52</td>
<td>12.6</td>
<td>42.9</td>
<td>3.3</td>
</tr>
<tr>
<td>1:7</td>
<td>234</td>
<td>54</td>
<td>12.3</td>
<td>46.5</td>
<td>3.3</td>
</tr>
</tbody>
</table>

*Sr** denotes the amount of strontium that remains in solution in equilibrium with the solid phase when 10 g of CaCO₃ is reacted with concentrated HNO₃ in proportions as indicated.

Figure 4. Solubility of Sr(NO₃)₂ in solutions obtained by mixing CaCO₃ and conc. HNO₃ in proportions as given in Table 4.
Washing Procedure:

The proper choice of washing solvent is important as it determines the purity of the strontium salts and the speed with which the separation operations can be made. The solvent should readily dissolve calcium nitrate without causing an appreciable loss of strontium nitrate, should mix well with the mother liquor, and should be easily removable in the crystalline phase. Nitric acid is not a good choice because the crystals of strontium nitrate settle slowly due to its high density and viscosity, and because its removal requires a prolonged heating. Absolute ethanol and acetone can be used interchangeably instead as both solvents possess the desired qualities. We have chosen acetone because its boiling point is lower compared to that of ethanol (56°C vs. 78°C) which facilitates the drying procedure. Acetone reacts vigorously with concentrated HNO₃ upon a prolonged contact, but normal washing operations - as described in the procedure - carry no risk whatsoever.

Calcium Removal and Strontium Losses:

The first separation step, followed by an acetone wash, removes about 99% of the initial calcium content. When strontium recovery is determined by instrumental methods, this single operation is sufficient. For gravimetric yield determination and for a more complete removal of interfering radionuclides further treatment may be needed. We have performed up to three dissolution-precipitation cycles on a series of seawater samples (in addition to the main separation step) to see how calcium ions are distributed between the solid and liquid phases after each cycle. In Table 5 a few examples are given illustrating the efficiency of cleansing operations. From this data it can be seen that only one additional cycle is needed to produce a high purity salt. In routine analyses, two dissolution-reprecipitation cycles are recommended to leave a necessary safety margin. Our experience, based on a detailed analysis of strontium salts isolated from 31 samples of mixed carbonates, has convinced us that >99% purity is readily attained by following the described procedure. In all but one case the amount of calcium in strontium salts was found to be under 1 percent (0.2% on the average). The stoichiometric composition of the final SrCO₃ preparations were confirmed by acidimetric titration and comparing the results with those obtained by gravimetry. Again, the results were consistent to better than 1 percent in all but one case.

Table 5
Purification efficiency for mixed carbonates isolated from 50 dm³ seawater samples to which 1 g Sr²⁺ carrier was added

<table>
<thead>
<tr>
<th>Mass of carbonates (g)</th>
<th>Initial content (mg)</th>
<th>Calcium in post-crystallization liquids (mg)</th>
<th>Strontium recovered (mg)</th>
<th>Calcium in strontium salt (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca</td>
<td>Sr</td>
<td>II</td>
<td>III</td>
</tr>
<tr>
<td>4.43</td>
<td>1300</td>
<td>700</td>
<td>16</td>
<td>0.5</td>
</tr>
<tr>
<td>31.24</td>
<td>12100</td>
<td>800</td>
<td>17</td>
<td>0.6</td>
</tr>
<tr>
<td>42.00</td>
<td>16200</td>
<td>1100</td>
<td>16</td>
<td>0.5</td>
</tr>
<tr>
<td>46.86</td>
<td>17800</td>
<td>1200</td>
<td>24</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Strontium losses due to solubility can be estimated approximately from solubility curves. In practice these losses are four times higher, as determined by analyses of a liquid phase overlying Sr(NO₃)₂ (0.19 - 0.31 vs. 0.04 - 0.08 mg Sr cm⁻³), and may result from an incompletely established equilibrium between liquid and solid phases and the presence of tiny crystals suspended in the sampled portions of the liquid. By contrast, organic solvents used for washing the solid phase do not cause appreciable losses of strontium. In skilled hands overall losses of strontium do not exceed 4 - 10 percent for the whole separation procedure.

CONCLUSIONS

The described method does away with the fuming nitric acid, thereby greatly improved working conditions in terms of safety and health hazards. It is very simple, requires minimum reagents and equipment, and can be applied in modestly equipped laboratories. Losses are small and predictable and chemical recovery can be determined by simple weighing due to the purity of the final strontium preparations. It is particularly suited to routine work where large samples are required throughout.

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REFERENCES