Journal of Radioanalytical and Nuclear Chemistry, Vol. 269, No.1 (2006) 161–173

Determination of radiostrontium in environmental samples using sodium hydroxide for separation of strontium from calcium

L. Popov,[1]* X. Hou,[2] S. P. Nielsen,[2] Y. Yu,[2] R. Djingova,[3] I. Kuleff[3]

[1] *Kozloduy Nuclear Power Plant, Safety Department, Environmental Monitoring Division, BG-3321 Kozloduy, Bulgaria*
[2] *Risø National Laboratory, Department of Radiation Research, NUK-202, P.O. Box 49, DK-4000 Roskilde, Denmark*
[3] *Faculty of Chemistry, University of Sofia, blvd. James Bouchier, 1, BG-1164- Sofia, Bulgaria*

(Received January 16, 2006)

A method was developed to separate Sr from a large amount of Ca, based on the solubility difference of $Sr(OH)_2$ and $Ca(OH)_2$. If the determination of both ^{89}Sr and ^{90}Sr is required, then the separation of Sr from Ba is based on the difference in the solubility of Sr and Ba chlorides in HCl media. If only ^{90}Sr is to be analyzed by measuring ^{90}Y, the separation of Ba will be carried out by precipitation of Ba as $BaSO_4$. Cherenkov counting by a liquid scintillation spectrometer was used to measure radiostrontium and radioyttrium activities. Chemical yield of strontium was determined with ^{85}Sr-radioactive tracer. The analytical method has been successfully applied to the determination of ^{89}Sr and ^{90}Sr in different environmental materials, water, soil, sediments, milk, bones, grass, algae, ash from aerosol filters, etc. The analytical quality was checked by analyzing reference materials.

Introduction

Radiostrontium (^{89}Sr and ^{90}Sr) has been released to the environment by global fallout following atmospheric nuclear explosions, by nuclear waste discharges and fallout from the Chernobyl accident. Due to its short half-life ($T_{1/2} = 50.5$ d), ^{89}Sr quickly decays to undetectable levels, while ^{90}Sr is radiologically more dangerous because of its longer half-life ($T_{1/2} = 28.78$ y) and accumulation in bone tissue. Therefore the determination of radiostrontium is among the priorities in all instructions for the control of environmental contamination by radionuclides, during the last 50 years and is carried out in a huge number of laboratories all over the world.

Both ^{89}Sr and ^{90}Sr are pure β-emitters and the determination is done by direct measurement of ^{89}Sr and ^{90}Sr or by measuring the short-lived daughter ^{90}Y (pure β-emitter too) using a proportional counter or liquid scintillation analyzer, which requires previous chemical separation and pre-concentration. The separation of strontium from calcium, barium and radium in a large number of analyzed samples in radioecological, environmental and oceanographic studies, requires cost-effective and relatively simple procedures for the determination of radiostrontium. The separation of strontium from calcium, barium and radium is a rather time-consuming and expensive step in various analytical procedures for the determination of ^{90}Sr.

A general method for separation of Sr from Ca based on the insolubility of strontium nitrate in fuming nitric acid is still widely used since its first application in 1939.[1,2] For the analysis of samples with high calcium content, such as large volumes of seawater (~40 dm^3) or drinking water (~200 dm^3), soil or river and lake sediments (0.5 kg), milk (20 dm^3) etc., more than 2 dm^3 of fuming nitric acid has to be used. This is expensive, time-consuming, damaging for laboratory equipment, hazardous for the operators and the environment.

Many techniques for the separation of strontium from various matrices have been reported in recent years,[3–13] liquid-liquid extraction using a crown ether, liquid membrane extraction, extraction chromatography using Sr-Spec resin, ion-exchange and strontium rhodizonate and $CaHPO_4$ precipitation, etc. Unfortunately they cannot be used for the separation of strontium from large amounts of calcium and most of them cannot be applied for analysis of different types of environmental samples.

Strontium is usually separated from the isotopes of barium by $BaCrO_4$ precipitation, but the operation is difficult and time-consuming due to the critical control of pH of the solution and removal of the excess of chromium afterwards.[2]

CHEN at al.[3] developed a method for the determination of ^{90}Sr in water samples by separation of radiostrontium from calcium using precipitation of $Ca(OH)_2$ in alkaline solution.

The present paper reports the results on the further development and improvement of this method for the analysis of different type of environmental samples. The procedure proposed is easy, cheap, more safe than the methods using fuming HNO_3, and can be successfully applied to all major types of environmental samples.

Experimental

Reagents and equipment

All chemicals used were of analytical grade (Merck, Fluka). Hermle Z513 centrifuge (with 100, 250 and 500 cm^3 tubes) was used for separation of the precipitates. For measurement of the activity of radiostrontium and yttrium the Guardian (LKB Wallac,

0236–5731/USD 20.00

Akadémiai Kiadó, Budapest
Springer, Dordrecht

Finland) alpha/beta liquid scintillation spectrometer was used. For the determination of the chemical yield of yttrium the digital burette Titrex 2000 (Germany) was used.

Analytical procedure for determination of ^{89}Sr and ^{90}Sr

The proposed procedure is presented in Figs 1, 2 and 3. The initial step in this multiple procedure for the separation and isolation of radiostrontium from biomaterials (milk, bones, grass) and environmental samples (soil, sediments, and aerosol filters) is burning at 430–550 °C and addition of carrier (stable strontium). The detailed protocols are presented below.

The low concentration of radiostrontium in fresh and tap waters, in most cases asks for collecting huge volumes, 100 dm^3 or even 200 dm^3. This requires an appropriate sampling equipment as well as experience in the treatment of such huge sample.

Water (tap, waste, lake, sea, river, etc.): Filter 40 dm^3 (in a case of tap water, at least 50 dm^3) of the analyzed water. Add 14M HNO_3 to acidify the solution (pH 3–4). Add 2.5 g $Sr(NO_3)_2$ (~1000 mg Sr^{2+}-carrier) to the sample. Dissolve about 10–30 g $CaCl_2$ in 12M HCl and add it to the water sample. Add a known weight (m_{sample}) of ^{85}Sr yield tracer (~100–200 Bq) and stir for 5 minutes. Adjust pH ~10 with 6M NaOH. Add 0.7 kg dry Na_2CO_3 (if high calcium content is expected in the sample then the amount of the carbonate should be increased, the dry carbonate can also be dissolved in distilled water and then added to the sample). Stir for 20 minutes in order to dissolve Na_2CO_3 and to complete the carbonate precipitation. Check again pH (must be 8–10). Leave overnight.

Discard the supernatant. Collect the carbonate precipitate in a 2 dm^3 beaker, leave for 1 hour and discard the supernatant. Dissolve the precipitate with 6M HNO_3. Add 2–3 cm^3 25% H_2O_2 and heat for 1 hour the solution to boiling to decrease the volume (CO_2 should be completely gone). Cool the solution. Add 10 mg Fe^{3+}-carrier.

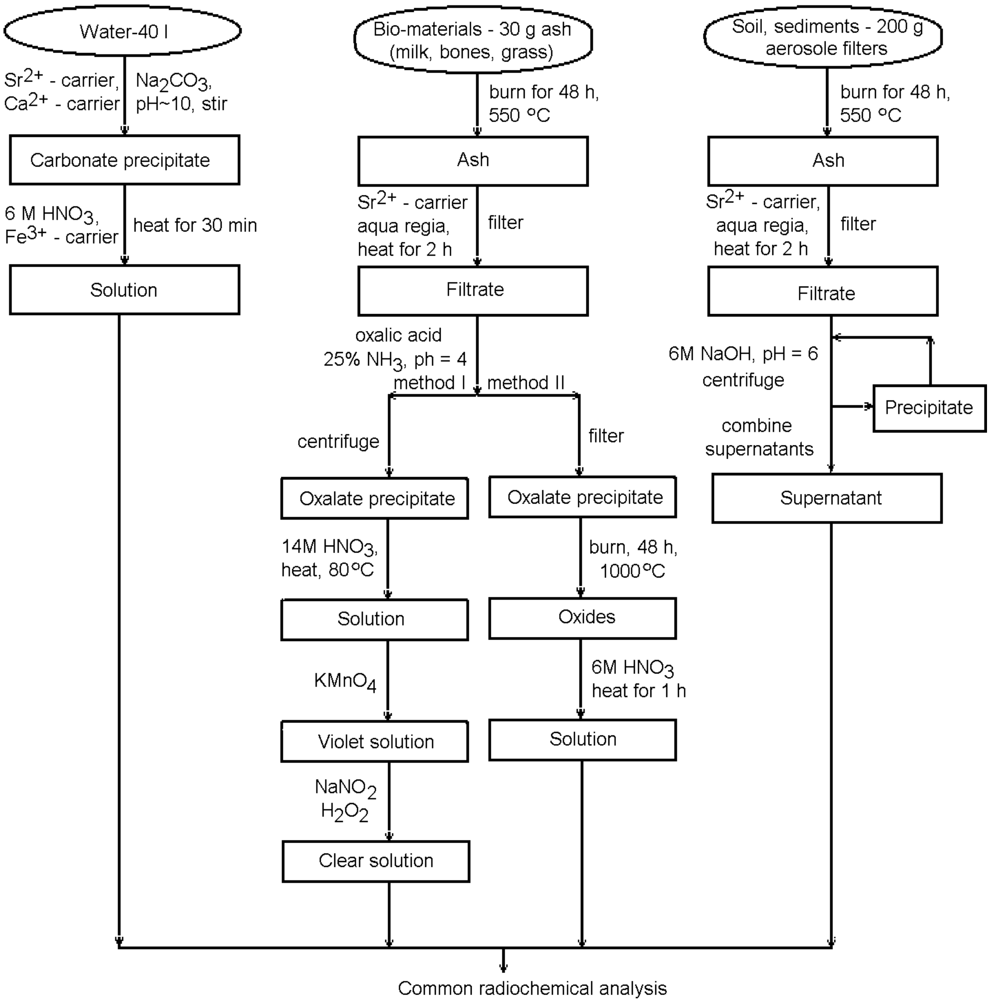

Fig. 1. Basic steps of radiostrontium (^{90}Sr and ^{89}Sr) analysis in environmental materials

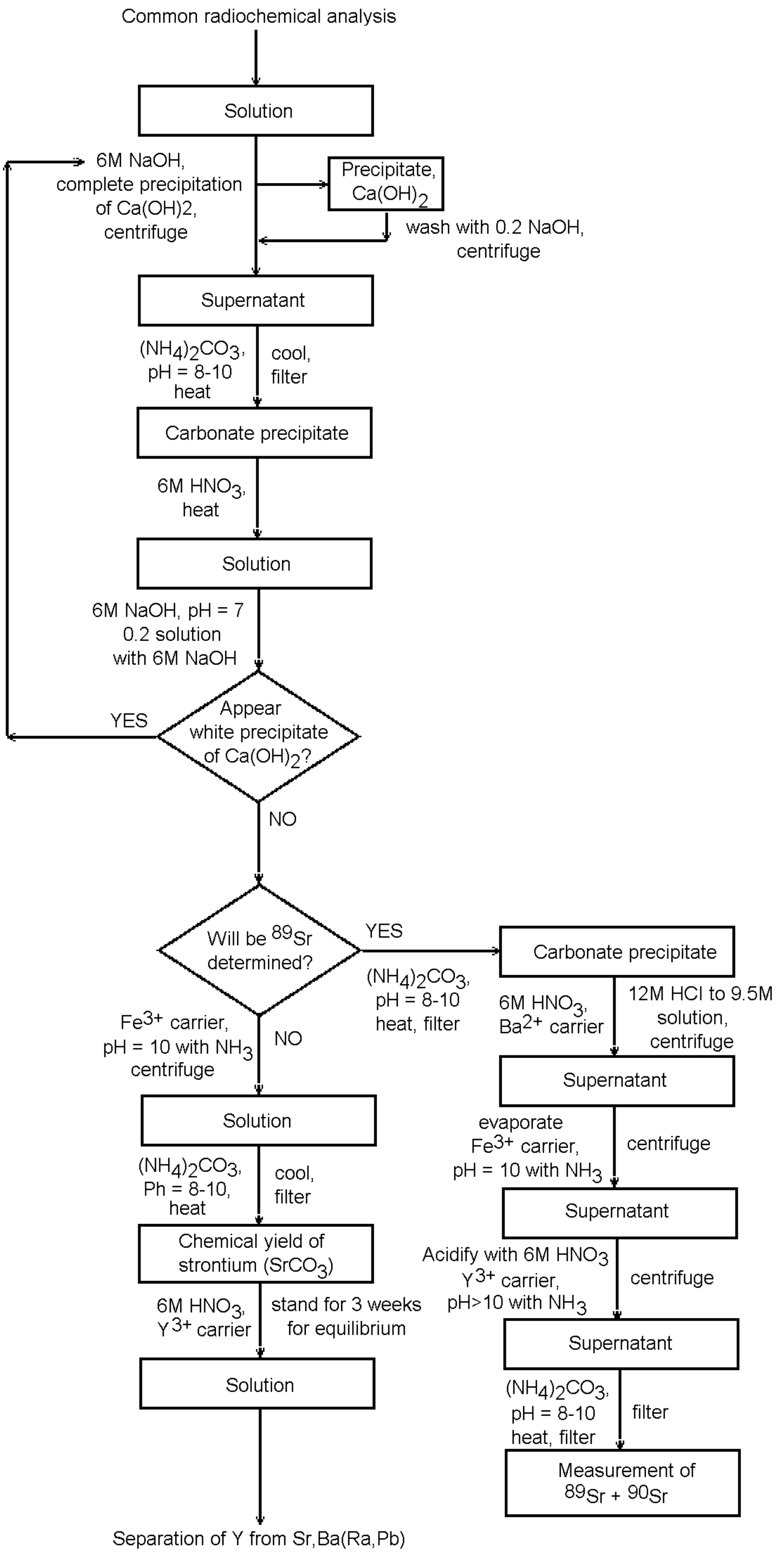

Fig. 2. Common radiochemical analysis of radiostrontium

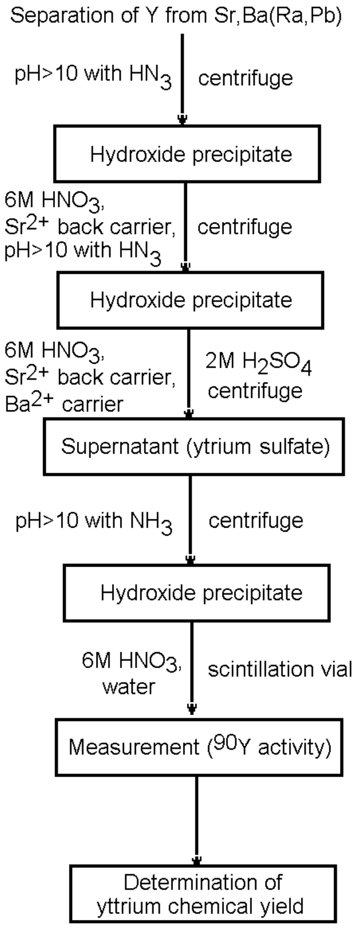

Fig. 3. Separation of yttrium from strontium and barium

If only ^{90}Sr is to be analyzed then continue with Section of separation of ^{90}Y, otherwise continue with the separation of ^{89}Sr/^{90}Sr.

Filter ash (aerosol or air precipitation), soil and bottom sediment samples: Transfer the filter ash (already burned at 430 °C for gamma-spectrometric measurement) or burned soil as well as river or lake sediment in a beaker. Add 2.5 g $Sr(NO_3)_2$ and a known weight (m_{sample}) of ^{85}Sr yield tracer (~100–200 Bq). Stir for 5 minutes. Cover with a watch glass and burn for 48 hours at 550 °C to destroy completely the organic material contained in the sample. If the color of the ash is not red-brown after ashing 10–20 mg Fe^{3+}-carrier has to be added.

Add 150–250 cm^3 aqua regia, 2–3 cm^3 25% H_2O_2 to the beaker, cover with a watch glass and heat for 2 hours at 250 °C. Add 200–300 cm^3 water, stir and filter through GF/A-filter. Wash the beaker and filter 4 times with 50 cm^3 0.2M warm HCl (measure ^{85}Sr-activity of the residue to check if it is below 3%). Transfer the solution to a centrifuge tube.

Add 6M NaOH to the centrifuge tube to adjust a pH 6 to form $Fe(OH)_3$. Centrifuge at 3000 rpm for 10 minutes and transfer the supernatant to 1 dm^3 beaker. Dissolve the iron hydroxide with 12M HCl and repeat the above step again until the ^{85}Sr-activity of the iron hydroxide precipitate is <4%. Combine the supernatants for further separation.

If only ^{90}Sr is to be analyzed then continue with Section of separation of ^{90}Y, otherwise continue with the separation of ^{89}Sr/^{90}Sr.

Biomaterial (milk, bones, grass, algae, etc.): Milk was first dried by evaporation; grass and algae were dried at 90 °C. The dried samples were burned at 430 °C for 72 hours. Transfer 30 g aliquot (or use the whole amount) of the ash to a porcelain crucible. Cover the crucible with a watch glass and burn for 48 hours at 550 °C to completely destroy the organic material contained in the sample. Transfer the ash to a 800 cm^3 beaker. Add 2.5 g $Sr(NO_3)_2$ (~1000 mg Sr^{2+}-carrier) and known weight (m_{sample}) of ^{85}Sr yield tracer (~100–200 Bq). Stir for 5 minutes. Add 150–250 cm^3 aqua regia, 2–3 cm^3 25% H_2O_2, cover with watch glass and heat for 2 hours at 250 °C. Add 200–300 cm^3 water, stir and filter through GF/A-filter. Wash the beaker and filter 4 times with 50 cm^3 0.2M warm HCl. Transfer the solution to a 1 dm^3 beaker.

Add oxalic acid to the filtrate (8 g per 100 cm^3 solution). Stir and heat to dissolve the oxalic acid. Add 25% NH_3 to adjust pH 4.5. In order to get rid of the oxalate anions, two methods were used**:** (1) burning the oxalate precipitate at 1000 °C, and (2) oxidizing the oxalate anions with $KMnO_4$.

(a) Filter the oxalate precipitate through ashless cellulose filter (white band). Check the solution for completeness of the precipitation with additional amount of oxalic acid and NH_3 to a pH of 4.5. Transfer the precipitate to a porcelain crucibe and dry it in an oven at 100 °C. Cover the crucibe and burn the precipitate in muffle furnace gradually at 800 °C-1000 °C for 48-96 hours.Transfer residue to an 800 cm^3 beaker, add 6M HNO_3 to dissolve the oxides. Add 1 cm^3 30% H_2O_2 to the beaker and stir, cover and heat for 30 minutes.

(b) Centrifuge at 3000 rpm for 10 minutes and discard the supernatant (first check if the precipitation is complete with additional amount of oxalic acid and ammonia to pH 4.5). Dissolve the oxalate precipitate in minimal amount of 14M HNO_3. Transfer the solution to a beaker. Heat the solution to 80–90 °C. Add a $KMnO_4$ with stirring to oxidize the oxalate anions to CO_2. Continue to add $KMnO_4$ with stirring until solution gets constant dark brown-black color and no bubbles of CO_2 appear. Add 1–2 g of $NaNO_2$ to reduce the excess $KMnO_4$ (dark color disappears completely). Transfer the solution to a centrifuge tube, add NaOH to pH 6, centrifuge at 3000 rpm for 10 minutes. Transfer the supernatant to a beaker.

Radiochemical separation of ^{90}Y

Adjust the solution to neutrality (pH 7) with 6M NaOH. Measure the volume of the solution, V_s. Add 6M NaOH (V_{NaOH}, cm^3) to reach a concentration of NaOH of 0.25M, following the equation:

$$V_{NaOH} = 0.0435 \cdot V_s \text{ cm}^3$$

Transfer the sample to a centrifuge tube and centrifuge at 3000 rpm for 10 minutes. Add several drops of 6M NaOH to check if the precipitation of Ca is complete. Transfer the supernatant to a beaker. Wash the precipitate in the centrifuge tubes with 0.2M NaOH and centrifuge. Add $(NH_4)_2CO_3$ (6 g per 100 cm^3 solution), heat the solution on a hotplate at 100 °C for 1 hour, cool and filter the solution through a glass-fiber filter (GF/A Whatman). Dissolve the precipitate with 6M HNO_3 and transfer the solution to a centrifuge tube. Add 2–3 cm^3 25% H_2O_2, and heat for 30 minutes. Repeat the above steps (separation of Sr from Ca) several times until no white precipitate of $Ca(OH)_2$ occurs.

Dissolve the precipitate in 6M HNO_3 and transfer the solution to a centrifuge tube. Add 5 mg Fe^{3+}-carrier and mix, then add 6M NaOH up to pH 10. Centrifuge at 3000 rpm for 10 minutes. Transfer the supernatant to a beaker. Add $(NH_4)_2CO_3$ (6 g per 100 cm^3 solution) to the solution. Stir and heat for 1 hour. Filter through glass-fiber filter paper (GF/A Whatman). Dissolve the precipitate with 6M HNO_3 and transfer the solution to a centrifuge tube. Measure the activity of ^{85}Sr tracer on gamma-spectrometer and calculate the final chemical yield of strontium.

Add 20 mg Y^{3+}-carrier and stir. Cover the tube with parafilm and leave the solution for 3 weeks for radioactive equilibrium between ^{90}Sr and ^{90}Y.

Add 25% NH_3 to adjust to pH>10, stir and heat for 5 minutes. Centrifuge at 3000 rpm for 10 minutes, discard the supernatant and dissolve the precipitate with 6M HNO_3. Add 5 mg Sr^{2+}-back carrier to the solution. Add 25% NH_3 and heat for 5 minutes. Centrifuge and discard the supernatant.

Dissolve the precipitate with 6M HNO_3. Add 10 mg Ba^{2+} and 5 mg Sr^{2+} holdback-carrier. Stir for 1–2 minutes. Add 2–3 cm^3 2M H_2SO_4 and stir to form $BaSO_4$. Centrifuge and transfer the supernatant to another centrifuge tube.

Add 25% NH_3 up to pH>10. Stir and heat for 5 minutes. Centrifuge and discard the supernatant. Record the date and time (t_0). Dissolve the precipitate with 2–3 cm^3 6M HNO_3. Transfer the solution to a 20 cm^3 plastic scintillation vial. Wash the centrifuge tube 3–4 times with 2–3 cm^3 distilled water of each. Add distilled water to the total volume of the solution in the scintillation vial of 20 cm^3.

Measure the activity of ^{90}Y by Cherenkov counting with liquid scintillation spectrometer.

After the measurement, the chemical yield of yttrium was determined using EDTA back titration (described below).

Radiochemical separation of ^{89}Sr/^{90}Sr

Adjust the solution to neutrality (pH 7) with 6M NaOH. Measure the volume of the solution, V_s. Add 6M NaOH (V_{NaOH}, cm^3) up to a concentration of NaOH of 0.25M, following the equation:

$$V_{NaOH} = 0.0435 \cdot V_s \text{ cm}^3$$

Transfer the sample to a centrifuge tube and centrifuge at 3000 rpm for 10 minutes. Add several drops of 6M NaOH to check if the precipitation of Ca is complete. Transfer the supernatant to a beaker. Wash the precipitate in the centrifuge tubes with 0.2M NaOH and centrifuge. Add $(NH_4)_2CO_3$ (6 g per 100 cm^3 solution) to the solution, heat the solution on hotplate at 100 °C for 1 hour, cool and filter the solution through a glass-fiber filter (GF/A Whatman). Dissolve the precipitate with 6M HNO_3 and transfer the solution to a centrifuge tube. Add 2–3 cm^3 25% H_2O_2, and heat for 30 minutes. Repeat the above steps (separation of Sr from Ca) several times until no white precipitate of $Ca(OH)_2$ occurs.

Dissolve the precipitate in 6M HNO_3 and transfer the solution to a centrifuge tube. Add 5 mg Fe^{3+}-carrier and mix. Add 6M NaOH to pH 10. Centrifuge at 3000 rpm for 10 minutes. Transfer the supernatant to a beaker. Add $(NH_4)_2CO_3$ (6 g per 100 cm^3 solution) to the solution. Stir and heat for 1 hour. Filter through glass-fiber filter paper (GF/A Whatman).

Dissolve the precipitate in 6M HNO_3 and transfer the solution to a centrifuge tube. Add 20 mg Ba^{2+}-carrier, measure the total volume of the solution, V_{sol} (cm^3). Add a small portion of concentrated 12M HCl acid (V_{HCl}, cm^3) to make concentration of HCl in the solution of 9.5M following the equation:

$$V_{\mathrm{HCl}} = 3.8 \cdot V_{sol}\ \mathrm{cm}^3$$

Stir, stand for 20 minutes to allow formation of $BaCl_2$, centrifuge at 3000 rpm for 10 minutes. Transfer the supernatant to another centrifuge tube. Add 20 mg Ba^{2+}, 4 cm^3 of 12M HCl, stir and stand for 20 minutes. Centrifuge at 3000 rpm for 10 minutes. Transfer the supernatant to a beaker and heat the solution to evaporate and to decrease the volume.

Add 10 mg Y^{3+}-holdback carrier and stir. Adjust to pH>10 with 25% NH_3. Record the date and time (t_0). Stir and heat for 5 minutes. Centrifuge at 3000 rpm for 10 minutes and transfer the supernatant to a beaker. Add $(NH_4)_2CO_3$ (6 g per 100 cm^3), stir and check pH to be 8–10. Heat for 30 minutes, cool and filter the carbonate precipitate through glass-fiber filter paper (GF/A Whatman). Dissolve the precipitate with 6M HNO_3 and transfer the solution to a plastic scintillation vial. Wash 2–3 times with 2–3 cm^3 distilled water and combine washings to the scintillation vial. Adjust with distilled water volume of the scintillation vial to be 20 cm^3.

Record date and time (t_1) and measure the radioactivity of ^{89}Sr+^{90}Sr by Cherenkov counting with a liquid scintillation spectrometer.

Recount the sample after 3–5 days (record current date and time, t_2) again by Cherenkov counting.

Measure the activity of ^{85}Sr-tracer on a gamma-spectrometer and calculate the final chemical yield of strontium. (Note: chemical yield of yttrium is 100%).

Determination of the chemical yield

The chemical yield of strontium is determined via gamma-spectrometric measurement of the activity of the radioactive tracer of ^{85}Sr (gamma-line with energy 514 keV).

The chemical yield of yttrium is determined using back titration of the EDTA with a solution of Zn^{2+}, following the procedure.

Transfer the content of measured yttrium source from a scintillation vial into an Erlenmeyer flask. Add 20.00 cm^3 0.02M EDTA solution and 2 cm^3 ammonia buffer with pH 10 (NH_4Cl/NH_4OH). Wash the flask with 20–30 cm^3 distilled water and heat for 15–20 minutes at 70–80 °C to dissolve yttrium oxalate. Add 3–4 drops of 2% (in ethanol) Eriochrom blackT. The solution becomes blue. The excess of EDTA is titrated with 0.02M Mg^{2+} solution and the chemical yield (%) is calculated by:

$$Y_Y = \frac{88.91.(V_{\mathrm{EDTA}} \cdot M_{\mathrm{EDTA}} - V_{\mathrm{Mg}_{2+}} .M_{\mathrm{Mg}_{2+}})}{m_{\mathrm{Y}^{3+}} - carrier} \times 100\%$$

where V_{EDTA}, $V_{\mathrm{Mg}^{2+}}$ is the volume of EDTA and Mg^{2+} solutions (cm^3), respectively, M_{EDTA}, $M_{\mathrm{Mg}^{2+}}$ is the molarity of EDTA and Mg^{2+} standard solutions (mol/dm^3), respectively, $m_{\mathrm{Y}^{3+}}$–*carrier* is the amount of the added Y^{3+}-carrier (mg).

Measurement and calculation of the results

Measurement of ^{90}Y-source and calculation of ^{90}Sr activity in the sample: The scintillation vial containing only ^{90}Y is counted using the calibrated liquid scintillation spectrometer in predefined and optimized energy windows with Cherenkov counting:[18]

$$A_{^{90}\mathrm{Sr}} = \frac{C - C_{\mathrm{bkg}}}{\varepsilon_{^{90}\mathrm{Y}} \cdot I_{\mathrm{Y}} \cdot D_t \cdot \eta_{\mathrm{Sr}} \cdot \eta_{\mathrm{Y}} \cdot V}\ \mathrm{Bq/dm^3}$$

where C is the gross count rate in the optimized energy window (cpm), C_{bkg} is the blank count rate in the same window (cpm), $\varepsilon_{^{90}\mathrm{Y}}$ is the efficiency of the liquid scintillation spectrometer for ^{90}Y (counts/Bq).

The I_{Y} ingrowth of ^{90}Y from ^{90}Sr is:

$$I_{\mathrm{Y}} = e^{-\frac{0.693 \cdot t_i}{t_{1/2}(\mathrm{Sr}-90)}} - e^{-\frac{0.693 \cdot t_i}{t_{1/2}(\mathrm{Y}-90)}}$$

where t_i is the time for ^{90}Y ingrowth (min), $t_{1/2}$(Sr-90) is the decay half-life of ^{90}Sr (15137280 min), $t_{1/2}$(Y-90) is the decay half-life of ^{90}Y (3846 min).

The D_t decay of ^{90}Y during the time of first yttrium hydroxide separation and the end of the measurement is:

$$D_{\mathrm{Y}} = e^{-\frac{0.693}{3846} \cdot (t_{Ysep} + t_m)}$$

where t_m is the measurement time (min), 3846 is the decay half-life of ^{90}Y (min), t_{Ysep} is the time between the first yttrium hydroxide precipitation and the beginning of the measurement (min), η_{Sr}, η_{Y} is the chemical yield of strontium and yttrium, respectively, and V is the volume (weight) of the sample (dm^3 or kg).

For the calculation of detection limit the approach by CURRIE[19] was applied. In this case the calculation of minimum detectable activity (MDA) can be done according to:

$$\mathrm{MDA}_{^{90}\mathrm{Sr}} = \frac{0.6\, u_c}{t_m \cdot \varepsilon_{^{90}\mathrm{Y}} \cdot I_{\mathrm{Y}} \cdot D_t . \eta_{\mathrm{Sr}} \cdot \eta_{\mathrm{Y}} \cdot V}$$

cpm/dm^3 or cpm/kg

where u_c is the combined standard uncertainty of the background (counts), the rest of the symbols have the same meaning as above.

Measurement of ^{89}Sr+^{90}Sr+^{90}Y source and calculation of ^{89}Sr and ^{90}Sr activity: The method proposed by CHANG et al.,[18] and Reference 20 was used for the measurement and calculation of ^{89}Sr and ^{90}Sr activity. The sample containing only purified (at time t_0) radiostrontium (^{89}Sr+^{90}Sr) is counted twice (t_1 and t_2) with liquid scintillation spectrometer by Cerenkov counting:

$$A_{t_0} = A_{{}^{90}\mathrm{Sr}} + A_{{}^{89}\mathrm{Sr}}$$

$$A_{t_1} = A_{{}^{90}\mathrm{Sr}}[e^{-\lambda_1(t_1-t_0)}] + A_{{}^{90}\mathrm{Sr}}[1-e^{-\lambda_2(t_1-t_0)}] + \\ + A_{{}^{89}\mathrm{Sr}}[e^{-\lambda_3(t_1-t_0)}]$$

$$A_{t_2} = A_{{}^{90}\mathrm{Sr}}[e^{-\lambda_1(t_2-t_0)}] + A_{{}^{90}\mathrm{Sr}}[1-e^{-\lambda_2(t_2-t_0)}] + \\ + A_{{}^{89}\mathrm{Sr}}[e^{-\lambda_3(t_2-t_0)}]$$

Expressing A_{t_1} and A_{t_2} from the last two equations as count rates C_{t_1} and C_{t_2} and solving them for $A_{\text{Sr-89}}$ and $A_{\text{Sr-90}}$ we get:

$$A_{{}^{89}\mathrm{Sr}} = \frac{\dfrac{C_{t_1} - C_{\mathrm{bkg}}}{\eta_{\mathrm{Sr}} \cdot V} - A_{{}^{90}\mathrm{Sr}} \cdot \varepsilon_{{}^{90}\mathrm{Sr}} \cdot e^{-\lambda_1 \cdot \Delta t_1} - A_{{}^{90}\mathrm{Sr}} \cdot \varepsilon_{{}^{90}\mathrm{Y}} + A_{{}^{90}\mathrm{Sr}} \cdot \varepsilon_{{}^{90}\mathrm{Y}} \cdot e^{-\lambda_2 \cdot \Delta t_1}}{\varepsilon_{{}^{89}\mathrm{Sr}} \cdot e^{-\lambda_3 \cdot \Delta t_1}}$$

$$A_{{}^{90}\mathrm{Sr}} = \frac{e^{-\lambda_3 \cdot \Delta t_1} \cdot (C_{t_2} - C_{\mathrm{bkg}}) - e^{-\lambda_3 \cdot \Delta t_2} \cdot (C_{t_1} - C_{\mathrm{bkg}})}{\eta_{\mathrm{Sr}} \cdot V\{\varepsilon_{{}^{90}\mathrm{Sr}}[e^{-\lambda_1 \cdot \Delta t_2} \cdot e^{-\lambda_3 \cdot \Delta t_1} - e^{-\lambda_1 \cdot \Delta t_1} \cdot e^{-\lambda_3 \cdot \Delta t_2}] + \varepsilon_{{}^{90}\mathrm{Y}}[e^{-\lambda_3 \cdot \Delta t_1} \cdot (1 - e^{-\lambda_2 \cdot \Delta t_2}) - e^{-\lambda_3 \cdot \Delta t_2} \cdot (1 - e^{-\lambda_2 \cdot \Delta t_1})]\}}$$

where C_{t_1} is the gross count rate in the optimized energy window during first measurement (cpm), C_{t_2} is the gross count rate in the optimized energy window during second measurement (cpm), C_{bkg} is the blank count rate in the same window (background sample = distilled water + 3 cm^3 6M HNO$_3$ + 10 mg Y^{3+}-carrier + 1000 mg Sr^{2+}-carrier + ^{85}Sr-tracer) (cpm), $\varepsilon_{{}^{90}\mathrm{Sr}}$, $\varepsilon_{{}^{90}\mathrm{Y}}$, $\varepsilon_{{}^{89}\mathrm{Sr}}$ is the efficiency of the liquid scintillation spectrometer for ^{90}Sr, ^{90}Y and ^{89}Sr, respectively, λ_1, λ_2, λ_3 is the radioactivity decay constant for ^{90}Sr, ^{90}Y and ^{89}Sr (min^{-1}), respecively, $\Delta t_1 = t_1 - t_0$, $\Delta t_2 = t_2 - t_0$ (min), η_{Sr} is the chemical yield of strontium, and V is the volume (or weight) of the sample (dm^3 or kg).

In cases when ^{89}Sr is absent from the sample, the last equation is simplified to:

$$A_{{}^{90}\mathrm{Sr}} = \frac{C_{t_2} - C_{t_1}}{\eta_{\mathrm{Sr}} \cdot V \cdot \varepsilon_{{}^{90}\mathrm{Y}}[e^{-\lambda_2 \cdot \Delta t_1} - e^{-\lambda_2 \cdot \Delta t_2}]}$$

Finally the calculated ^{89}Sr and ^{90}Sr specific activities are at moment t_0 (date and time of ^{90}Y separation). They should be corrected if necessary to a reference date (t_{ref}) by:

$$A_{{}^{89}\mathrm{Sr}}(t_{ref}) = A_{{}^{89}\mathrm{Sr}} \cdot e^{-\lambda_{{}^{89}\mathrm{Sr}} \cdot (t_0 - t_{ref})}$$

$$A_{{}^{90}\mathrm{Sr}}(t_{ref}) = A_{{}^{90}\mathrm{Sr}} \cdot e^{-\lambda_{{}^{90}\mathrm{Sr}} \cdot (t_0 - t_{ref})}$$

Minimum detectable activities (MDA) for ^{89}Sr and ^{90}Sr can be calculated by the following equations:

$$\mathrm{MDA}_{{}^{89}\mathrm{Sr}} = \frac{0.6\sqrt{t_m\{C_{\mathrm{bkg}} + A_{{}^{90}\mathrm{Sr}} \cdot \eta_{\mathrm{Sr}} \cdot V[\varepsilon_{{}^{90}\mathrm{Sr}} \cdot e^{-\lambda_1 \cdot \Delta t_1} + \varepsilon_{{}^{90}\mathrm{Y}}(1 - e^{-\lambda_2 \cdot \Delta t_1})]\}}}{t_m \cdot \varepsilon_{{}^{89}\mathrm{Y}} \cdot \eta_{\mathrm{Sr}} \cdot V \cdot e^{\lambda_3 \cdot \Delta t_1}}$$

$$\mathrm{MDA}_{{}^{90}\mathrm{Sr}} = \frac{0.6\sqrt{t_m(C_{\mathrm{bkg}} + A_{{}^{89}\mathrm{Sr}} \cdot \eta_{\mathrm{Sr}} \cdot V \cdot \varepsilon_{{}^{89}\mathrm{Sr}} \cdot e^{-\lambda_3 \cdot \Delta t_2})}}{t_m \cdot \varepsilon_{{}^{90}\mathrm{Y}} \cdot I_{\mathrm{Y}} \cdot \eta_{\mathrm{Sr}} \cdot V}$$

where the symbols have the same meaning as above.

Results and discussion

Sample preparation

An extremely important factor for the successful application of the proposed method for the separation of strontium from calcium is the sufficient quantity of calcium in the sample. Therefore, a known quantity of calcium is added to the water samples. Thus it is possible afterwards to precipitate and remove the hydroxides of calcium and other metallic ions (e.g., actinides and lanthanides).

The elimination of organic substances from the sample is very important for the analysis of environmental and biological materials. Therefore, attention should be paid to ashing the samples to complete decomposition of organic materials. (The color of the precipitate should become white.)

Radiochemical separation

One of the conditions for achieving high radiochemical yield of radiostrontium during the separation of calcium from strontium is heating of the solution to boiling which is necessary to digest the carbonate residue. In the analysis of biomaterials (e.g., bones) the high content of phosphates additionally hinders the oxalate precipitation of calcium/strontium and it is necessary to remove the oxalate before separation of calcium and strontium with NaOH. The experiments proved that high radiochemical yield and good separation could be achieved at pH 4.5. Only under these conditions the phosphates remain in the solution. If the separation is done at pH>5 (usually at pH 10) almost the entire quantity of strontium is bound as $Sr_3(PO_4)_2$, which afterwards co-precipitates with $Ca(OH)_2$. At pH<4 calcium and strontium cannot be precipitated as oxalates quantitatively. Therefore, it is important to keep pH of the solution exactly 4.5. This stage is of utmost importance for the whole procedure such problem does not exist because the phosphates remain in the solution as phosphoric acid.

The procedure for water samples was modified with the aim of avoiding the use of heating facility when first concentrating strontium/calcium as carbonates because it is impractical especially when analyzing large volumes of water (100–200 dm^3).[3] Instead of using $(NH_4)_2CO_3$ it was preferred to use of Na_2CO_3 and intensive stirring instead of heating.

It was observed that when a large amount of strontium carrier (1000 mg Sr^{2+}) is used and when calcium content is lower than the amount of strontium carrier then significant losses of strontium may occur during the separation of strontium from calcium. Such an effect was not observed when only 200 mg Sr^{2+}-carrier was used. If the concentration of NaOH is higher than 0.2M then it is possible to lose more than 70% of the strontium in the sample due to formation of precipitate of $Sr(OH)_2$. The dependency of strontium recovery (1000 mg Sr^{2+}-carrier) on the concentration of hydroxide anions in the solution is presented in Fig. 4. Washing the calcium/strontium precipitate with a solution of 0.2M NaOH may recover additional 30–60% of the strontium contained in the precipitate. Three washings of the strontium precipitate with 0.2M NaOH recover almost all strontium (even in high concentration of hydroxide anions).

A new approach was used to get rid of oxalate anions when analyzing biological samples. Although the oxalate precipitate can be burned to SrO/CaO at 1000 °C for 2–3 days, according to our experience this step is inconvenient and time consuming. Besides it can be a source of loss of strontium due to incomplete burning (especially when the amount of the oxalate precipitate is large). Oxalic acid can be oxidized only by very strong oxidizing agents such as $KMnO_4$ and Ce^{4+}. $KMnO_4$ was used which can serve as a visual indicator for the completeness of the oxidation and it is not expensive. The reaction is autocatalic but in the beginning heating of the solution to 80–90 °C is required. By adding $KMnO_4$ its excess is reduced to Mn^{2+} with $NaNO_2$. The Mn^{2+}-ions are removed as $Mn(OH)_2$ after precipitation with 6M NaOH at pH 6. Usually after 2 separations with NaOH all manganese is removed from the sample. Another 2–3 separations with NaOH are required to separate calcium from strontium.

Attention should be paid when using concentrated HCl to separate strontium from barium (radium, lead). Concentration of the solution should be made exactly 9.5M in order to prevent losses of strontium. For complete removal of barium (radium, lead) two separations with HCl are necessary.[3]

Experiments were carried out to determine how much calcium remains in the final precipitate of strontium carbonate and what error will occur if the chemical recovery of strontium is determined gravimetrically. The results are shown in Table 1. In order to separate as much calcium as possible after the first calcium separation it is necessary to work with lower volumes (volume of the solution ~50–100 cm^3). In this way the concentration of calcium is increased and the soluble product can be more easily reached. It can be calculated that ~1 mg of calcium will always remain in the sample when the concentration of NaOH is 0.2M and the volume of the sample is 70–80 cm^3. But while washing of calcium precipitate with 0.2M NaOH small amount of calcium is dissolved and that is why remaining calcium is above 1 mg. If the initial calcium content in the sample is low then 3 separations with NaOH are enough, otherwise 4 separations will be required. Use of large amount of strontium carrier (~1000 mg Sr^{2+}) prevents incidental losses of strontium on one hand and gives more accurate results for gravimetrical determination of the chemical yield of strontium, less than 5% error, similar to those using ^{85}Sr-tracer. Large strontium carrier on the other hand is a problem when analyzing both ^{89}Sr and ^{90}Sr with proportional gas-flow counter, then it is better to use smaller amount of strontium carrier (~200 mg Sr^{2+}) to avoid self-adsorption (when using gravimetrical determination of strontium recovery the error is less than 15%). Also if the sample contains certain amounts of stable strontium (for example soils and sediments contain ~100 ppm stable Sr) then negative error in determination of radiostrontium activity should be expected (due to high biased strontium recovery).

Chemical yield

More than 300 samples were analyzed and the results for chemical recoveries of strontium and yttrium are presented in Table 2 and Fig. 5. The average value of chemical yield of strontium is 76% and is higher for water, filter ash, soil and sediments, etc. When biological samples were analyzed the possibility of losses of strontium (between 5 and 30%) arose during filtration of the leached biomaterial due to absorption of strontium on the insoluble residue. Complete washing of the residue (3–5 times with 50–100 cm^3 warm HCl) was carried out in order to prevent substantial strontium loss at this initial step and strontium recovery increased from 70 to 90% for biological samples as well.

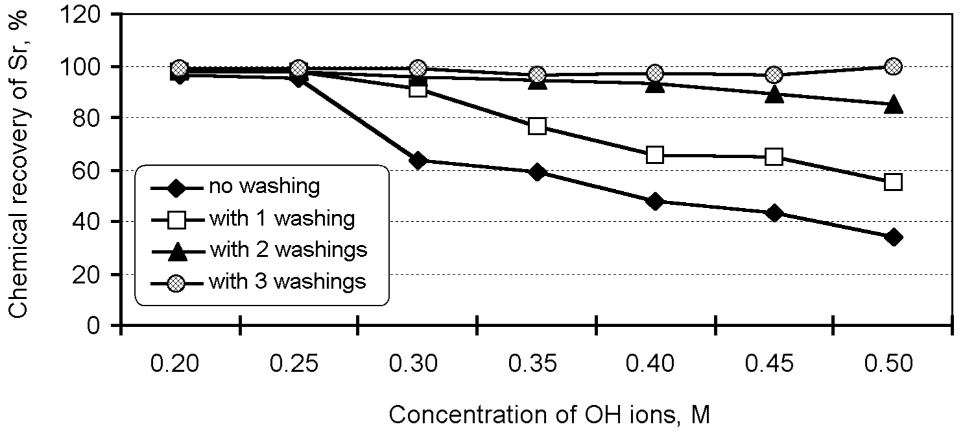

Fig. 4. Dependence of the chemical yield of strontium by the concentration of sodium hydroxide

Table 1. Amount of calcium in the separated strontium precipitate

Sample	Amount of Sr^{2+}, mg	Initial Ca^{2+} content, g	Number of separations with NaOH	Amount of Ca*, mg	Remained Ca/initial Ca, %	Chemical yield of Sr, %		Deviation (ICP-grav), %
						gravimetry	ICP-AES	
1	200	1.0	2	9.7	0.97	96.1	86.0	–10.1
2	200	2.5	3	8.4	0.34	71.7	59.5	–12.3
3	200	5.0	3	7.2	0.14	95.4	85.2	–10.2
4	200	10.0	3	11.9	0.12	98.0	87.4	–10.6
5	200	20.0	3	9.6	0.05	97.4	84.7	–12.7
Average:								–11.2
6	1000	1.0	3	3.4	0.34	94.1	90.8	–3.3
7	1000	2.5	3	5.8	0.23	88.2	85.3	–2.8
8	1000	5.0	3	8.9	0.18	84.2	81.6	–2.6
9	1000	10.0	4	14.5	0.15	81.2	78.0	–3.1
10	1000	20.0	4	9.6	0.05	85.5	84.1	–1.4
Average:								–2.6

* Determined using ICP-AES.

Table 2. Mean chemical yields of strontium and yttrium for different sample matrices

Sample type	Number of samples	Chemical yield of strontium, %	Chemical yield of yttrium, %
Water	91	83.6	86.0
Soil, sediments	39	75.3	87.6
Milk, bones, grass, etc.	52	67.0	88.8
Filter ash	70	74.8	87.6
Total:	252	76.4	87.5

Another loss of strontium, which was underestimated during the development of the procedure, was the step of dissolving strontium (calcium) carbonate precipitate in 6M HNO_3. Dissolving carbonates does not completely remove them from the solution and when later the solution is alkalinized with NaOH about 5–15% of strontium is precipitated as strontium carbonate and discarded with the precipitate of calcium hydroxide. Usually after 3–4 separations with NaOH more than 30–50% of the strontium can be lost. That is why heating the solution of dissolved strontium/calcium carbonate is always required to discard all carbonate anions.

In most cases iron content in soils and river/lake sediments is high (1–5 wt.% Fe) and typically large amounts of sample (200 or 1000 g) are required to determine environmental levels of ^{90}Sr. Usually in these samples calcium content is also high. If separation of Fe from Sr is carried out by hydroxide precipitation at pH 10 then chemical recovery of strontium is poor because of formation of iron and calcium hydroxides. To avoid this problem some authors use precipitation of Sr/Ca with oxalic acid where most iron remains in the solution, but this approach is more time-consuming. Good method to separate Fe from Sr/Ca is to use multiple (3–4) hydroxide precipitations at pH 5 to 6. For samples with low Fe content (or low weight) only 1–2 iron precipitations are enough.

Bone samples usually have high content of phosphates and they should be removed before separation of strontium from calcium. Oxalate precipitation of calcium/strontium at pH 4.5 solves the problem, because under these conditions phosphates remain in the solution as phosphoric acid.

After all improvements of the procedures chemical yields of strontium were increased for all kinds of sample matrices and chemical yield above 95% is now also possible.

The determination of the chemical yield of yttrium using back titration of yttrium is more accurate and faster method than the traditional gravimetrical determination of yttrium recovery such as $Y_2(C_2O_4)_3{\cdot}9H_2O$ or as Y_2O_3 (after burning the yttrium oxalate precipitate at 900 °C).

Measurement

For measurement of the activity of separated radiostrontium (^{89,90}Sr) Cherenkov counting with liquid scintillation spectrometer[18,20] was preferred as proposed by CHANG et al.[18] That method has lots of advantages compared to the traditional measurement with proportional counters. All beta-radionuclides with energies below 500 keV cannot be detected by Cherenkov counting and ^{85}Sr can be used as chemical yield determinant even when activities of ^{90}Sr are 100 times or more lower than that of ^{85}Sr. Chemical quench is absent and no scintillation cocktail is required. After ingrowth of ^{90}Y no separation and counting of the purified yttrium source is required as in the traditional proportional counting. Of course proportional counting can also be used with the described radiochemical procedures.

When ^{89}Sr is absent from the sample then separation and measurement of purified ^{90}Y by Cherenkov counting can be applied. Usually in that case efficiency is above 50%. However, after the measurement chemical yield of yttrium must be determined.

The detection limit of the measurement using Cherenkov counting with liquid scintillation spectrometer is very near to results, obtained by proportional counting as is presented in Table 3.

Although slightly higher the data in Table 3 demonstrates that measurement with Cherenkov counter with liquid scintillation spectrometer is much more convenient since it eliminates the self-absorption problems and permits the simultaneous determination of the chemical yield using ^{89}Sr as tracer, as well as the determination of radiostrontium when both ^{89}Sr and ^{90}Sr are present in the sample.

The exact evaluation of the detection limit (L_D)[19] when both ^{89}Sr and ^{90}Sr are present in the sample is impossible, because the L_D of one of the isotopes depends from the activity of the other. When the activity ratio ^{89}Sr/^{90}Sr (and vice versa) exceeds 40, then the simultaneous determination of strontium isotopes is problematic. Nevertheless, the determination of ^{89}Sr is easier when the activity of ^{90}Sr is higher, this being the normal case for environmental samples.

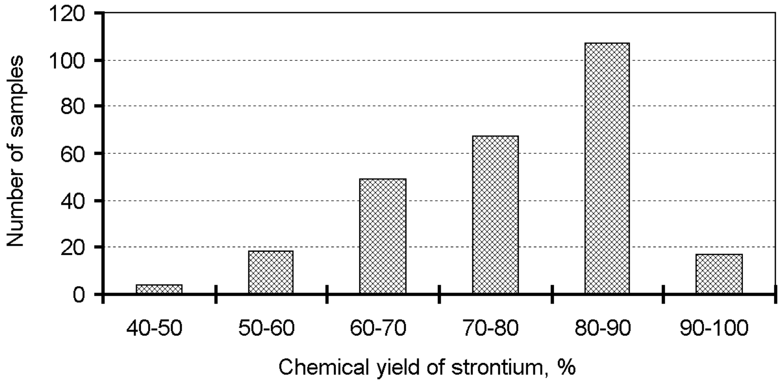

Fig. 5. Distribution of chemical yield of strontium

Table 3. Determination level of the proposed procedure when in the sample only ^{90}Sr present and the measurement is based on the registration of ^{90}Y

Sample	Sample size	LSC-Cherenkov*	Gas counting**
		L_D***	L_D***
Water	40 dm^3	0.6 mBq/dm^3	0.5 mBq/dm^3
Milk	10 dm^3	2.4 mBq/dm^3	2.1 mBq/dm^3
Soil, sediments	0.200 kg	0.12 Bq/kg	0.1 Bq/kg
Aerosol filter	70 000 m^3	$34 \cdot 10^{-6}$ Bq/m^3	$29 \cdot 10^{-6}$ Bq/m^3

* Background – 3 cpm; efficiency of registration – 0.55; time measurements – 200 min; yield of ^{90}Sr – 0.85; yield of ^{90}Y – 0.95.

** Background – 1.5 cpm; efficiency of registration – 0.45; time measurements – 200 min; yield of ^{90}Sr – 0.85; yield of ^{90}Y – 0.95.

*** L_D according Reference 19.

Table 4. Determination level of the proposed procedure for ^{90}Sr in water (sample size – 40 dm^3) when in the sample is ^{89}Sr and ^{90}Sr present in different ratios

Activity ratio	LSC-Cherenkov,* mBq/dm^3
0.01	0.47
0.1	1.14
1.0	3.48

* Background – 4 cpm; efficiency of registration – 0.5; time measurements – 200 min; yield of ^{90}Sr – 0.85.

The lowest L_D is achieved when only one of the strontium isotopes is present in the sample. The L_D values for ^{89}Sr, calculated the equations above correspond to the real experimental results when the measurement is done immediately after elimination of ^{90}Y. Simultaneously the L_D values for ^{90}Sr by the above equations are always higher when ^{90}Sr is present in the sample. Table 4 presents the results for L_D of ^{90}Sr at three different activity ratios for ^{89}Sr/^{90}Sr, which demonstrate well the possibilities of the proposed method.

The advantages of Cherenkov counting with liquid scintillation spectrometer of radiostrontium could be summarized as: (1) it is not necessary to determine the chemical yield for yttrium (it is every time 100%), and (2) the activity of yttrium does not change during the measurement.

Accuracy and precision

The accuracy and precision of the proposed procedure for the determination of radiostrontium were checked analyzing standard reference materials (SRM). The results are presented in Table 5. With the exception of 4 values (both ^{89}Sr and ^{90}Sr), all obtained results are in excellent agreement (SR<25%) according to SR-values and other 4 results are acceptable. Keeping in mind that the results presented in Table 5 are obtained by 5 chemists in one laboratory it may be concluded that the good accuracy and high precision of the proposed method are obtained and this is valid for analysis of water samples and environmental materials, soil, sediments, plants as well as for foodstuffs, milk, whey.

Table 5. Results from analysis of reference materials

Type of material	SRM	Nuclide	This work	$U_{c,x}$,[2]* %	Reference value, Bq/dm^3 or Bq/kg	Δ, %	SR,[3]* %	*Z*-score[4]*
Water	1M-2002, BfS (Germany)	^{90}Sr	0.80 ± 0.13[1]*	8.8	0.947 ± 0.14	–15.5	29.3	0.77
		^{89}Sr	2.20 ± 0.473	10.5	1.96 ± 0.40	+12.2	36.2	0.35
	2R-2002, BfS (Germany)	^{90}Sr	0.50 ± 0.08	8.0	0.545 ± 0.11	–8.3	22.9	0.33
	1M-2003, BfS (Germany) – N1	^{90}Sr	2.25 ± 0.13	3.1	2.64 ± 0.44	–14.8	20.1	0.85
		^{89}Sr	2.28 ± 0.12	2.6	2.99 ± 1.06	–23.7	27.8	0.67
	1M-2003, BfS (Germany) – N2	^{90}Sr	2.40 ± 0.25	5.4	2.64 ± 0.16	–9.1	18.9	0.81
	2R-2003, BfS (Germany)	^{90}Sr	0.36 ± 0.035	5.0	0.36 ± 0.09	0	10.0	0.103
	1M-2004, BfS (Germany)	^{90}Sr	2.40 ± 0.11	2.5	2.64 ± 0.32	–7.7	13.6	0.71
		^{89}Sr	1.62 ± 0.17	5.6	1.71 ± 0.63	–5.3	15.8	0.14
	2R-2004, BfS (Germany)	^{90}Sr	1.14 ± 0.21	9.6	1.15 ± 0.17	–0.9	20.0	0.04
Soil	Soil-6, IAEA (Austria)	^{90}Sr	28.6 ± 2.7	4.9	30.34 ± 1.87	–5.6	14.9	0.52
Sediment	Filter Schlamm-1999, BfS (Germany)	^{90}Sr	17.8 ± 1.7	5.1	16.1 ± 1.4	+10.6	21.7	0.77
	Sediment-375, IAEA (Austria)	^{90}Sr	117.7 ± 8.9	3.8	108 ± 3.0	+9.0	17.3	1.033
Milk	Milk-152, IAEA (Austria)	^{90}Sr	7.29 ± 0.75	2.6	7.70 ± 0.33	–5.3	10.3	0.50
	Milk-321, IAEA (Austria)	^{90}Sr	2.88 ± 0.41	7.3	3.30 ± 0.07	–12.7	25.5	2.37
Whey	Whey-154, IAEA (Austria)	^{90}Sr	5.77 ± 0.68	5.9	6.9 ± 0.5	–16.3	27.7	1.34
Clover	Clover-156, IAEA (Austria)	^{90}Sr	13.3 ± 1.5	5.6	14.8 ± 0.73	–10.2	20.3	0.68

[1]* Combined standard uncertainty (u_c);

[2]* Relative combined standard uncertainty ($u_{c,x}$);

[3]* According to Reference 21 $SR = \frac{|C_x - C_w| + 2\mathrm{SD}}{C_w} \times 100$ where C_x is the experimental value, C_w is the true value, SD is the standard deviation of C_x.

when SR≤25% = excellent agreement between experimental value and certificate value;

25%<SR≤50% = acceptable; SR>50% = unacceptable.

[4]* *Z*-score = $\frac{|x_{exp} - x_{ref}|}{\sqrt{u_{exp}^2 + u_{ref}^2}}$ where X_{exp} is the experimental value, X_{ref} is the reference value, U_{exp} is the uncertainty of the experimental value, U_{ref} is the uncertainty of reference material.

Acceptance level: Z-score < 3.

Table 6. Approximate price (in Euro) only for the step of separation of strontium from calcium*

Sample	With 6M NaOH	With fuming HNO_3
Soil – 200 g	0.2	30
Soil – 1000 g	0.4	150
Sea water – 40 dm^3	0.4	300
Tap water – 200 dm^3	0.3	100
Milk – 10 dm^3	0.3	90

* Evaluation was made according to the quantities needed for the separation of radiostrontium from calcium using prices for NaOH and fuming HNO_3 (see, e.g., Reference 22).

One of the advantages of the proposed method is the relatively low cost in comparison to methods using fuming HNO_3. This is demonstrated by the data in Table 6, where the approximate prices only for the step of separation of strontium from calcium with fuming nitric acid and with NaOH for different matrices are shown. Besides if fuming nitric acid is used then the cost strongly depends on the calcium content of the sample. This problem is solved if sodium hydroxide is used instead.

Conclusions

The advantages of the presented method compared to other analytical methods for the determination of radiostrontium are: all kinds of environmental materials can be analyzed (robustness); good accuracy; good precision (high chemical yields); strontium can be separated from a large content of calcium. In comparison to the methods using fuming nitric acid the present one is safer for the laboratory staff, laboratory equipment and the environment, and cheaper.

*

Authors would like to thank to Dr. Q. CHEN (Risø National Laboratory, Roskilde, Denmark) for his constructive remarks, ideas and encouragement during the whole time of the development of the procedures.

One of the authors (LP) would like to express his thanks to the IAEA for financial support during his training fellowship in Risø National Laboratory, Department of Radiation Research, Roskilde, Denmark as well as to the staff of the Environmental Monitoring Division at NPP "Kozloduy" and especially to G. MIHAJLOVA, I. HRISTOVA, P. DIMITROVA and S. IVANOVA for their technical support in the experimental work.

References

1. C. LIEBER, Naturwiss., 27 (1939) 421.
2. IAEA, Reference Method for Marine Radioactivity Studies, IAEA Technical Report Series No. 118, International Atomic Energy Agency, Vienna, 1970.
3. Q. CHEN, X. HOU, Y. YU, H. DAHLGAARD, S. P. NIELSEN, Anal. Chim. Acta, 466 (2002) 109.
4. E. P. HORWIEZ, M. T. DIETZ, D. E. FISHER, Solvent Extr. Ion Exch., 8 (1990) 557.
5. M. PIMPL, J. Radioanal. Nucl. Chem., 194 (1995) 311.
6. C. W. LEE, K. H. HONG, M. H. LEE, Y. H. CHO, G. S. CHOI, Y. W. CHOI, S. H. MOON, J. Radioanal. Nucl. Chem., 243 (2000) 767.
7. E. P. HORWIEZ, M. T. DIETZ, D. E. FISHER, Anal. Chem., 63 (1991) 522.
8. F. GOUTELAND, R. NAZARD, C. BOCQUET, N. COQUENLORGE, P. LETESSIER, D. CALMET, Appl. Radiation Isotopes, 53 (2000) 145.
9. M. HEILGEIST, J. Radioanal. Nucl. Chem., 245 (2000) 249.
10. F. DOBINSON, Nature, 183 (1959) 674.
11. N. A. MYERS, Nature, 183 (1959) 1807.
12. J. COBB, P. WARWICK, R. C. CARPENTER, R. T. MORRISON, Sci. Total Environ., 173/174 (1995) 179.
13. R. STELLA, T. G. VALENTINI, L. MAGGI, J. Radioanal. Nucl. Chem., 161 (1992) 413.
14. H. V. WEISS, W. H. SHIPMAN, Anal. Chem., 29 (1957) 1764.
15. F. PATTI, A. HERNANDEZ, Anal. Chim. Acta, 55 (1971) 325.
16. E. J. BARATTA, F. E. KNOWLES Jr., Anal. Chem., 43 (1971) 1138.
17. M. D. ERICKSON, N. A. CHIECO, HASL-300, http://www.eml.doe.gov/publications/, 1997.
18. T. M. CHANG, S. C. CHEN, J. Y. KING, S. J. WANG, J. Radioanal. Nucl. Chem., 204 (1996) 339.
19. L. A. CURRIE, Anal. Chem., 40 (1968) 586.
20. Handbook of Radioactivity Analysis, M. F. L'ANNUNZIATA (Ed.), Academic Press, Elsevier Science, 2003.
21. E. MCFARREN, R. LISHKA, J. PARKER, Anal. Chem., 42 (1970) 358.
22. Laboratory Chemicals and Analytical Reagents, Fluka, Riedel-de Haën, 2005/2006.