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Determination of ^{90}Sr Accumulation in Human Teeth

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The accumulation of ^{90}Sr in decayed or exfoliated human teeth was investigated by ultra low level beta counting. Fuming nitric acid and the necessary carriers and reagents were used for dissolving the samples, and the separation and purification of ^{90}Sr. The Ca contents of samples were determined by flame atomic absorption spectrometry with Zeeman-effect background correction. A mixture of K and La used as a matrix modifier was found to be preferable for the determination of Ca in samples. The optimum concentration and concentration ratio of K and La on the absorbance of Ca in the NIST certified reference material, bone ash 1400 solution were determined. The reliability of the measurements was tested by analyzing ^{90}Sr in the IAEA certified reference material, animal bone, and Ca in bone ash 1400, by adding a K + La mixture. Recoveries are greater than 95% and relative standard deviations are lower than 10% . The detection limits of ^{90}Sr and Ca are 0.9 Bq/kg sample and 12.3 μg/L, respectively.

Key Words: Tooth, ^{90}Sr, ^{90}Y, Calcium, Flame atomic absorption spectrometer

Introduction

The presence of ^{90}Sr in environmental and biological samples is mainly due to atmospheric nuclear weapons testing and nuclear accidents[1]. This artificially produced radionuclide has received considerable attention in studies of the transfer of fallout fission products from the environment to human beings because of its persistence in the environment and its long term retention in teeth and bones once it is ingested[1,2]. ^{90}Sr has long physical and biological half-lives, 28.6 and 49.3 years, respectively[1]. Without monitoring the presence of radioactive isotopes such as ^{90}Sr in the human body, no definite assessment of the health effects of exposure to man-made radioactivity can be made[3]. ^{90}Sr is also commonly regarded as the most hazardous long lived nuclear fission product because of its high yield, relatively high solubility and similarity in behavior to the essential nutrient and bone constituent Ca. Since ^{90}Sr becomes bound up in the skeleton instead of Ca, and it is a potential cause of bone cancer and damage to blood forming tissue[2]. For this reason, ^{90}Sr has been a principal subject for environmental monitoring and radioecological research[1]. It would therefore be of interest to learn the possible extent of contamination of teeth by ^{90}Sr.

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Ca is the most abundant mineral in the body, and the bones contain about 99% of the body's Ca. In addition to its major function in building and maintaining bone and teeth, Ca is also important in much of the body's enzyme activity[3]. One factor that plays an important role in the ^{90}Sr/Ca ratio in human bone and teeth is the primary source of dietary Ca. The population receives its Ca mainly from cereals, legumes, vegetables, milk and milk products. The cow has been shown to be an efficient discriminator between Sr and Ca. As a result, a higher Sr/Ca ratio will be observed in human bone and teeth when dietary Ca is derived directly from plants than when derived from other dairy foods[2].

Since ^{90}Sr and its daughter product ^{90}Y are pure beta-emitters, their activity in environmental samples can only be determined after the isolation of Sr from other elements and interfering β-emitting radionuclides[4]. One important step in ^{90}Sr analysis is the separation of Sr from large amounts of Ca. For this purpose the different solubilities of Sr and calcium nitrate in fuming nitric acid are frequently used[4]. Although this method is time consuming, it is accurate and safe. The fuming nitric acid method has been applied to various samples for isolation of ^{90}Sr from other interfering nuclides[5−10].

The aim of the present work was to measure ^{90}Sr activity and Ca contents in human teeth in order to obtain a database in Turkey and to document ^{90}Sr activity levels. For this purpose, fuming nitric acid and the necessary carriers and reagents were used for the separation and purification of ^{90}Sr from other elements. ^{90}Sr activities and Ca contents in tooth samples were determined. The activity of ^{90}Sr, Bq per kg Ca for a sample was obtained.

Experimental

Instrumentation

A WPC 9550 model ultra low level alpha/beta counting instrument (Proton Instrument Corp.) equipped with an ultra thin window gas flow proportional detector and a 10% CH_4+ 90% Ar (w/w) gas mixture was used for the determination of ^{90}Sr activity from the activity of the daughter ^{90}Y.

All Ca absorption measurements were performed using a Hitachi model 180/80 flame atomic absorption spectrometer (F-AAS) equipped with a Zeeman-effect background corrector and an automatic data processor. An acetylene-air flame was used in F-AAS. A Hitachi Ca hollow cathode lamp operated at 7.5 mA was used for all measurements. The resonance line was set to 422.7 nm and a slit width of 1.3 nm was used.

Reagents and solutions

All reagents were of analytical-reagent grade. All solutions were prepared with deionized water obtained by using an ultrapure water system (Barnstead, P/N-1161, $\geq$ 18 MΩ cm^{-1}).

All reagents and carriers were produced by Merck. Fuming nitric acid (96-100% , w/w), acetic acid (6 M), ammonium acetate (25% , w/w), oxalic acid (8% , w/w), sodium chromate (30% , w/w), ammonia (6 M), methyl red indicator (0.1% , w/w), hydrogen peroxide (35% , w/w) and nitric acid (concentrated, 7 M, 3.5 M and 1.0 M) reagents were used. Sr^{2+} (10 mg/mL from Sr $(NO_3)_2$), Y^{3+} (10 mg/mL from $Y(NO_3)_3.6H_2O$), Ba^{2+} (10 mg/mL from $Ba(NO_3)_2$), Fe^{3+} (2.5 mg/mL from $Fe(NO_3)_3.9H_2O$) carriers and K^+ (5 mg/mL from KNO_3) solution were prepared by dissolving in a deionized water and HNO_3 mixture.

Furthermore, 1 mg/mL Ca and 10% m/v La (26.6% m/v $LaCl_3.7H_2O$) stock standard solutions (BDH Chemicals) were used. Working standard solutions were freshly prepared by dilution of stock standard solutions to the desired concentrations in 0.2% HNO_3 as diluent before the measurements.

Sample collection and preparation

Thirty tooth samples (all of which required extraction for orthodontic reasons) were collected from the Dental Faculty of Ankara University. The age range of the adult humans concerned was from 17 to 61, and they were from 8 different cities in Turkey. Eighteen were males and the others females. IAEA certified reference material, animal bone (IAEA-A-12), was used.

After drying at 110 °C for 2 h, the teeth and animal bone were ashed in a muffle furnace at 800 °C for 8 h. The samples were ground and dried again at 110 °C. The analyses of samples were performed by taking aliquots (0.2-4.0 g) from the dried samples. The samples were moistened by adding a small volume of 0.5 M HNO_3. After adding a Sr solution as a carrier, the sample was dissolved in fuming nitric acid[5,8–10]. When the fuming nitric acid concentration decreased to 75% by mass during the dissolution, a white $Sr(NO_3)_2$ precipitation was obtained by mixing in an ice bath. This was separated from Ca and other elements, except for Ba, Pb and Ra by centrifugation. The Ca solution was transferred into a 50 mL volumetric flask, diluted with deionized water to the mark and kept until the determination of Ca by F-AAS. $Sr(NO_3)_2$ precipitate was dissolved in deionized water and neutralized with ammonia. A Ba carrier was added, and then Na_2CrO_4 buffered with an acetate-acetic acid buffer was introduced and heated, and Ra, Ba and Pb were removed as chromate precipitates by centrifugation [5,8]. The solution was made basic with ammonia and coagulated on a hot water bath by the addition of solid $(NH_4)_2CO_3$ [8]. After centrifugation, the solution was discharged and the precipitate containing ^{90}Sr, was dissolved in HNO_3 [5,8]. After adding hydrogen peroxide and an Fe-carrier to precipitate any remaining fission products[5], the solution was heated on a water bath and made basic with ammonia. After centrifugation, the residue was rejected and the centrifugate was acidified with HNO_3. A Y carrier was added to promote the complete precipitation of ^{90}Y[5]. The solution was left to stand for 21 days for build up of the ^{90}Y daughter and to reach continuous ^{90}Sr-^{90}Y equilibrium [5,8]. Y was precipitated by adding 0.5-2.0 mL of concentrated ammonia [5,8]. After centrifugation, solution was transferred to another tube and the precipitate of Y was dissolved in 6 M HNO_3. The process of Y precipitation was repeated twice. After dissolving the Y precipitate, 10 mL of 8% oxalic acid solution was added to the solution and heated on a water bath for 15 min, then filtered, and the precipitate was dried at 110 ^{o}C for 2 h. From the weight of $Y_2(C_2O_4)_3.9H_2O$ precipitate, the chemical yield of Y was determined.

Solid $(NH_4)_2CO_3$ was added to the collected solutions from the Y precipitation and $SrCO_3$ was precipitated. After filtration, the precipitate was dried at 110 ^{o}C until constant weight. From the weight of $SrCO_3$, the chemical yield of Sr was determined.

Decomposition of certified reference material

The bone ash 1400 certified reference material taken from the National Institute of Standards and Technology (NIST) was dissolved according to the method described in a previous study[11]. A portion (0.33 g) of the sample was accurately weighed into a 50 mL acid-cleaned PTFE beaker and 3 mL of 7 M nitric acid was added. The beaker was covered with a PTFE cover and heated on a hot plate at 120 °C for 2 h. After cooling to room temperature, 2 mL of concentrated HNO_3 and 2 mL of hydrogen peroxide were added. The beaker

was heated at 100 °C for 1 h, and then the temperature was gradually raised to 130 °C until the complete decomposition of the sample was achieved. If this was not completed, a further 2 mL of concentrated HNO_3 and 1 mL of hydrogen peroxide were added and the above procedure was repeated to dissolve the residue. The resulting solution (nearly 2 mL) was transferred to a 50 mL calibrated flask by washing the interior surface of the beaker 3 times with 1 M HNO_3 and diluting to the mark with deionized water.

Results and discussion

Counting of samples

The samples, animal bone and backgrounds were counted for 60,000 seconds. The error associated with the background measurements is about 1% or less[3]. The background range was 0.012-0.014 counts per second (cps). The efficiency of the counting was established by using a calibrated solution of ^{90}Sr/^{90}Y (3.849 kBq = 0.1040 μCi; mass of solution is 1.00817 g in 1 mL V-Vial; density is 0.9996 g/mL at 20 °C) obtained from NIST and diluted to 3.849 Bq with deionized water. It was ensured that the ^{90}Y was in equilibrium with its parent ^{90}Sr in the solution. The counting efficiency of the instrument was 45.0 ± 0.5% .

^{90}Sr activity in a sample was calculated by the following equation as described in previous works[8,10,12].

^{90}Y=^{90}Sr=A f / (Sr Y E M), Bq/kg sample ash

Where A is the absolute count rates of ^{90}Y (cps) obtained by subtracting the background count from sample counting, f is the time correction factor for ^{90}Y (f = $1/e^{-\lambda t}$, λ = 0.693/64.4 h, 64.4 is the half-life of ^{90}Y and t is the time from precipitation to the half of counting in hours). Sr and Y are the chemical yields of Sr and Y, respectively. Chemical yields for both Sr and Y were obtained gravimetrically. Chemical yields ranged from 75% to 88% for Sr and from 94% to 98% for Y. E is the counting efficiency of the instrument to ^{90}Y standard and M is the weight of the sample (kg).

Optimization of calcium determination

The effects of concentration and concentration ratio of K, La and K + La modifier mixture on the absorbance values of Ca in bone ash-1400 solution were investigated. Ca (12.5 μg/mL) obtained from the bone ash solution by diluting and appropriate concentrations of K (0-5.0 mg/mL), La (0-4.0 mg/mL) or K (0-5.0 mg/mL) + La (0-4.0 mg/mL) were added to each 10 mL volumetric flask and diluted to the mark with deionized water. While the concentration of Ca (1.25 μg/mL) in each solution was kept constant, the concentrations of K, La and K + La modifier solutions were varied as described. Absorbance values of Ca obtained against concentration and concentration ratio of K, La and K + La modifier mixture were plotted and are shown in Figure 1. The optimum concentrations of K and La, and the concentration ratio of K/La were 0.8 mg/mL K, 0.6 mg/mL La and 0.8/0.6 (mg/mL K/ mg/mL La), respectively.

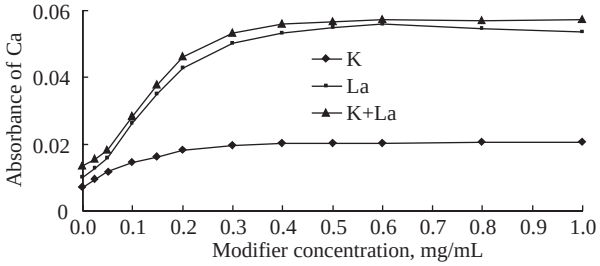

Figure 1. Effect of concentration and concentration ratio of K and La on Ca absorbance.

Analytical quality validation

^{90}Sr in animal bone (A-12) using fuming nitric acid, and Ca in bone ash-1400 using the K + La mixture were determined in order to verify the accuracy of the proposed methods. The recovery studies for ^{90}Sr and Ca are given in Table 1. The values for ^{90}Sr and Ca were within the recommended confidence intervals of reference materials. A sample with minimum detectable ^{90}Sr activity and background were counted for 60,000 seconds. By using the chemical yields of Y and Sr carriers and the counting efficiency, the limit of detection was calculated as 0.9 Bq/kg sample within a 3σ-level statistical certainty[6,12]. The reliability of the method for the analysis of Ca was checked using working standard solutions and bone ash solution. The accuracy and precision of the method were also tested by analyzing bone ash containing 38.18 ± 0.13% Ca, 0.684 ± 0.013% Mg, 17.91 ± 0.10% P and 660 ± 27 μg/g Fe as major elements. Higher recovery values for Ca (100%) and a lower detection limit (12.3 μg/L, 3σ-criterion) were obtained by adding a K + La mixture to the bone ash solutions. When the K + La mixture was not used, the limit of detection was 38.6 μg/L. By adding K + La to the solutions, such effects become negligible and the accuracy and precision of the method are satisfactory. The concentrations of Ca in samples were determined using calibration graphs prepared with standard Ca solutions.

Table 1. Recovery studies for ^{90}Sr and Ca in certified reference materials.

Element determined	Reference material	Modifier	Concentrations: Certified value	Concentrations: Found*, $\overline{X}\pm$ ts/$\sqrt{n}$	Recovery, %
^{90}Sr	Animal bone		54.4 (46.3 - 59.2) (Bq/kg)	52.2 ± 3.1	96
Ca	Bone ash	No	38.18 ± 0.13 (%)	34.9 ± 2.4	91
		K		35.7 ± 1.8	94
		La		37.5 ± 1.1	98
		K + La		38.3 ± 0.4	100

*An average of 4 determinations for ^{90}Sr; Mean of 16 replicate measurements of Ca in the sample solution with a 95% confidence level.

Application

An optimum concentration ratio of the recommended K + La modifier mixture that provided higher absorbance values for Ca was applied to the determination of Ca in tooth samples to prevent flame ionization and the effect of phosphate interference on the Ca determination, respectively[8]. ^{90}Sr activities and Ca

contents were determined in adult tooth samples originating from 8 different regions of Turkey. Ca concentrations and ^{90}Sr activity per kg Ca (^{90}Sr, Bq/kg Ca) for the same tooth are given in Table 2. The Ca concentration in the samples varied between 34.1 and 46.9% by mass. The activity of ^{90}Sr per kg sample ash was also calculated. The concentration of ^{90}Sr in each tooth (Bq ^{90}Sr/kg Ca) was different.

Table 2. ^{90}Sr activity and amount of Ca in human teeth.

Sample No.	Age in years	Region	Sex[a]	Ca % [b]	^{90}Sr, Bq kg^{-1} Ca,d.w.
1	42	Ankara	F	36.9 ± 0.3	45 ± 1
2	31	Çorum	F	42.0 ± 0.4	14 ± 0.4
3	59	Konya	F	39.0 ± 0.3	2.9 ± 0.1
4	45	Kırşehir	F	36.7 ± 0.4	64 ± 2
5	30	Ankara	F	34.3 ± 0.3	9.3 ± 0.4
6	27	Malatya	M	38.5 ± 0.3	180 ± 6
7	45	Çorum	M	37.8 ± 0.3	171 ± 5
8	25	Ankara	M	38.0 ± 0.3	151 ± 5
9	61	Ankara	M	38.2 ± 0.4	75 ± 3
10	49	Ankara	F	45.5 ± 0.4	740 ± 3
11	51	Ankara	M	41.3 ± 0.3	7.8 ± 0.4
12	39	Kırıkkale	M	44.3 ± 0.3	163 ± 5
13	41	Ankara	M	46.9 ± 0.4	65 ± 2
14	40	Ankara	M	44.4 ± 0.4	411 ± 14
15	26	Kırşehir	M	35.8 ± 0.3	52 ± 2
16	17	Kırşehir	F	36.2 ± 0.3	217 ± 5
17	29	Ankara	F	37.1 ± 0.4	566 ± 14
18	24	Kırıkkale	M	34.1 ± 0.3	729 ± 25
19	33	Zonguldak	M	35.5 ± 0.3	161 ± 5
20	35	Yozgat	F	37.3 ± 0.3	336 ± 12
21	41	Ankara	M	37.4 ± 0.3	168 ± 4
22	39	Kırıkkale	M	37.0 ± 0.3	60 ± 2
23	47	Malatya	M	39.8 ± 0.2	75 ± 2
24	37	Ankara	M	36.2 ± 0.4	76 ± 2
25	42	Kırıkkale	M	37.1 ± 0.3	167 ± 4
26	61	Ankara	F	36.6 ± 0.2	210 ± 5
27	38	Ankara	M	37.4 ± 0.3	370 ± 9
28	28	Ankara	F	38.4 ± 0.3	52 ± 2
29	26	Çorum	M	39.5 ± 0.3	43 ± 1
30	24	Çorum	F	37.8 ± 0.3	29 ± 1

[a]M: Male, F: Female.
[b]Mean of 15 replicate measurements of a sample solution with a 95% confidence level, $\overline{X} \pm ts/\sqrt{n}$.

According to the Radiation and Public Health Project (RPHP), adult teeth have been analyzed and the expected average RPHP level of ^{90}Sr activity per kg Ca ranged roughly between 37 and 74 Bq/kg Ca in 1970-1994. The highest values obtained by the RPHP are about 370 Bq ^{90}Sr/kg Ca[3]. The maximum permissible body burden recommended by the International Commission on Radiological Protection (ICRP) is 74 kBq per body weight[2]. ^{90}Sr, Bq/kg Ca values against age are given in Figure 2. As can be seen in Table 2 and Figure 2, ^{90}Sr activity levels in adult uptake against age are variable. Four of the results obtained are higher than 370 Bq ^{90}Sr/ kg Ca[3], but they are lower than the value recommended by the ICRP[2]. The main source of ^{90}Sr contamination in biological and environmental samples is nuclear weapons testing and

nuclear accidents such as the Chernobyl incident [1,13]. The global variation in ^{90}Sr activity levels in teeth and bone may be related to dietary levels[2]. The variations in ^{90}Sr activity may also suggest differences in human dietary intake, such as plants, the regions and where people live. Moreover, the geographic origin of plants, food and the type of water consumed (public water, well water, or bottled water) are also factors in determining the ^{90}Sr content in teeth[3].

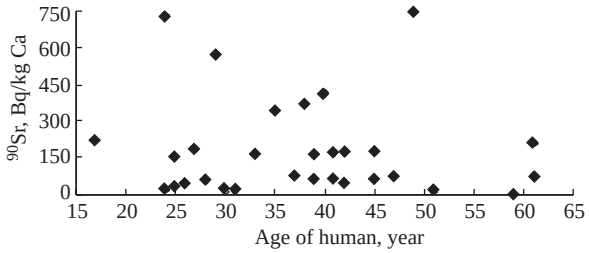

Figure 2. ^{90}Sr activity per kg Ca versus age, year.

Conclusion

The results of the ^{90}Sr activity per kg Ca were compared with the RPHP and ICRP results mentioned above. This would seem to indicate that the body burden has never reached levels that might reasonably be expected to cause damage to human beings.

It is clear that many more thousands of teeth must be analyzed to obtain full account of many factors, such as proximity, ground water flows, wind patterns, and dietary and ethnic differences. Regional fallout radiation measurements should also be performed. Nevertheless, because of the radiological toxicity of ^{90}Sr, studies will continue to assess the long term behavior and consequences of ^{90}Sr released into the environment. The procedure can be used for determination of low level ^{90}Sr in environmental and biological samples.

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