

Extraction of radiostrontium from the mixture of radionuclides in urine using dicarbolyde of cobalt

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The radiostrontium extraction from urine following the extraction of radiocesium was investigated. The polyhedral complex of the type $H^+[(\pi-(3)-1,2-C_2B_9H_{11})_2Co^-]$, further referred to as dicarbolyde- H^+ , in nitrobenzene was used for extraction. The influence of nitric acid and poly(ethylene glycol) concentration upon the yield of radiostrontium extraction was examined. The poly(ethylene glycol) hydrophobizing supports the extraction of strontium cations into nitrobenzene.

Distribution ratios of microamounts of ^{90}Sr and ^{89}Sr were determined in the system nitrobenzene—dicarbolyde- H^+ —nitric acid solution, or nondiluted urine and urine diluted 5 to 20 times with distilled water, respectively. Distribution ratios of some other fission and activated radionuclides were determined under conditions suitable for radiostrontium extraction.

The selective and quick procedure for quantitative analysis of radiostrontium in urine was suggested. By this procedure the activity of 3.7 Bq dm^{-3} can be determined.

Была исследована последующая экстракция радиостронция после изоляции ^{137}Cs из моча. Для экстракции использовалось комплексное соединение типа $H^+[(\pi-(3)-1,2-C_2B_9H_{11})_2Co^-]$, в дальнейшем называемое дикарболоид- H^+ , в нитробензоле. Было исследовано влияние концентрации азотной кислоты и полиэтиленгликоля на выход экстракции радиостронция. Полиэтиленгликоль гидрофобизирует катионы стронция и этим стимулирует их экстракцию в органическую фазу.

Были определены коэффициенты распределения для микроколичества ^{90}Sr и ^{89}Sr в системе нитробензол—дикарболоид- H^+ —азотная кислота, или моча неразбавленного и моча разбавленного 5—20кратно дистиллированной водой. Были определены коэффициенты распределения некоторых продуктов расщепления и активированных радионуклидов при условиях благоприятных для экстракции радиостронция.

Был предложен селективный, быстрый метод для количественного определения радиостронция в моче. Минимально определяемое количество радиостронция достигает величины 3.7 Bq dm^{-3} .

The most tedious operation in radiostrontium determination is to concentrate it from the biological material, to isolate and separate the radionuclide from radiochemical impurities. For this purpose the methods of precipitation [1—4], ion exchange [5—7], and extraction [8—11] are frequently used. Extraction procedures are especially of advantage due to their speed and high selectivity.

It was shown [12—14] that dicarbolides of transition metals possess high selectivity towards caesium, while the extraction of radiostrontium is not significant. Dicarbolides of cobalt were used for separation of caesium from the mineralizates of biological tissues [15—17], contaminated excreta [18], and milk [19].

Štefek *et al.* [20] demonstrated that poly(ethylene glycol) strongly increases the extraction of microamounts of strontium into nitrobenzene, when univalent hydrophobic anion of dicarbolide- H^+ was used. The magnitude of synergic effect over 10^3 creates good conditions for the extraction of strontium after previous extraction of caesium. As both radionuclides belong to the most significant components of fission mixture and the extraction of other fission and activated radionuclides using dicarbolide- H^+ appears to be low, the conditions for a selective and quantitative separation of radiostrontium from contaminated excreta were investigated in this work.

Dicarbolide- H^+ with high stability constant of its complex anion, fully dissociated and stable also in a high acidic media [21], together with poly(ethylene glycol) of the mean relative molecular mass 300 was used for this purpose.

Experimental

The following radionuclides were used: (^{90}Sr - ^{90}Y)-nitrate, ^{89}Sr -chloride, ^{22}Na -chloride, ^{86}Rb -chloride, (^{95}Zr - ^{95}Nb)-oxalate, ^{133}Ba -chloride, all from ROTOP (GDR), (^{106}Ru - ^{106}Rh)-nitrate, ^{137}Cs -chloride, ^{144}Ce -chloride, all from IZOTOP (USSR), ^{60}Co -chloride and ^{65}Zn -chloride from METRONEX (Poland). All the radionuclides were carrier-free or with negligible amount of carrier. Standard solutions were prepared in the range of concentration 1—100 MBq cm^{-3} . The amount of radiochemical impurities was below 1%. Pipetting was performed by constriction pipettes.

Radionuclides ^{90}Sr and ^{90}Y were prepared from the ^{90}Sr - ^{90}Y mixture by extraction of ^{90}Sr into nitrobenzene using 10^{-2} M dicarbolide- H^+ , 0.1% (v/v) (further only in %) poly(ethylene glycol) 300, further referred to as PEG 300, and 0.1 M nitric acid in an aqueous phase. ^{90}Sr was purified by double scrubbing with 0.1 M- HNO_3 containing 0.1% PEG 300. Equal volumes of organic and aqueous phase were used. ^{90}Y remains quantitatively in an aqueous phase, also after double extraction of ^{90}Sr .

The extraction agent dicarbolide- Cs^+ was in the form of orange powder practically insoluble in water. Dicarbolide- H^+ was prepared from its caesium salt being dissolved in nitrobenzene by shaking twice for 30 min with equal volume of 1 M nitric acid. The other concentrations of extractant were prepared by dilution with nitrobenzene.

Human urine collected from several individuals diluted with distilled water or nitric acid

respectively, was used. The concentration of nitric acid in aqueous solutions was determined by titration with NaOH and with phenolphthalein as indicator.

Various concentrations of PEG 300 solutions were prepared by dilution of 1% stock solutions ($2.2 \times 10^{-2} \text{ mol dm}^{-3}$) of PEG 300 with 0.1 M nitric acid, as well as by further dilution of 1% PEG in nondiluted urine and diluted urine by nitric acid solution, by urine and distilled water, in volume ratios of 1 : 4, 1 : 9, and 1 : 19.

The extraction was done at a phase ratio 1 : 1, by shaking for 10 min. The activity of ^{90}Sr in 1 cm^3 of both phases was measured:

— in a well-type scintillation crystal NaI(Tl) connected to NZQ 717 T laboratory measuring set (Tesla, Přemyslení, CSSR) after (1 month) attainment of radioactive equilibrium. The activity of daughter ^{90}Y was measured. The other gamma emitters were measured in this way as well;

— in a liquid scintillation cocktail with spectrometer Tri-Carb Mod. 3390 (USA), immediately after the extraction and reextraction of ^{90}Sr into aqueous phase was finished. ^{90}Sr was reextracted from nitrobenzene into the equal volume of 0.1 M nitric acid containing $5 \times 10^{-4} \text{ M}$ barium nitrate. 1 cm^3 of aqueous phase was added to 15 cm^3 of precooled Bray scintillation solution [22] and activity of beta emitter ^{90}Sr was measured. Distribution ratio was calculated as

$$D = \frac{\text{activity of organic phase}}{\text{activity of aqueous phase}}$$

Results and discussion

Under conditions suitable for extraction of ^{137}Cs ($D = 10^3$ for 10^{-2} M dicarbolyde- H^+ and 0.1 M-HNO_3), the extraction of ^{90}Sr is very low, as can be seen from Table 1. The extraction of ^{90}Sr strongly increases with decreasing nitric acid concentration, and the distribution ratio reaches a magnitude of 350 in 10^{-3} M-HNO_3 . The same course is shown also for the most of other radionuclides.

Table 1

Changes of ^{90}Sr distribution ratio with nitric acid concentration in aqueous solutions
Extraction with 10^{-2} M dicarbolyde- H^+

[HNO_3] mol dm^{-3}	$D^{90}\text{Sr}$
10^{-3}	350.0
10^{-2}	8.95
10^{-1}	0.085
0.5	0.008
1.0	0.001

However, it was found out that hydrophobization of ion associates with poly(ethylene glycol) supports the passage of Sr into organic phase [13, 20]. The changes of distribution ratio of ^{90}Sr , ^{90}Y , and ^{89}Sr with the concentration of PEG in aqueous solution at 10^{-2} M dicarbolide- H^+ showed that with increasing concentration of PEG the distribution ratio increased by about 3 orders of magnitude and reached the maximum value in 0.25% PEG as seen from Table 2. The distribution ratio of yttrium reached the maximum at the same concentration of PEG, but its value was much lower.

Table 2

Changes of radiostrontium and radioyttrium distribution ratio with poly(ethylene glycol) concentration in 0.1 M nitric acid
Extraction with 10^{-2} M dicarbolide- H^+ in nitrobenzene, activity of radionuclides measured by scintillation crystal NaI(Tl) or by liquid scintillation spectrometric method (LSSM)

[PEG] v/v %	LSSM $D^{90}\text{Sr}$	NaI(Tl) $D^{89}\text{Sr}$	NaI(Tl) $D^{90}\text{Y}$
1.0	276	264	0.063
0.1	603	628	0.092*
10^{-2}	250	251	0.011
10^{-3}	29.1	24.9	0.009
10^{-4}	2.7	2.6	0.007
10^{-5}	0.3	0.3	0.004
0	0.1	0.1	0.003

*PEG 0.25%.

No significant differences between distribution ratios of ^{89}Sr and ^{90}Sr were found. Results in Tables 3 and 4 give evidence that the maximum value of the distribution ratio has been reached at different PEG concentrations depending on dicarbolide- H^+ concentration used in experiments. The highest distribution ratio with 10^{-2} M dicarbolide- H^+ in nitrobenzene was reached at 0.25% concentration of PEG in aqueous phase. When 10^{-1} M dicarbolide- H^+ was used, the maximum of the distribution ratio lay in the range from 1 to 2.5% PEG and its value was about 50 times higher.

Results in Table 3 show that the distribution ratio of Sr, extracted from diluted urine or water respectively, was by about 2 to 3 orders of magnitude higher than in the case of extraction from nondiluted urine. The top value of the distribution ratio lay in all cases at 0.25% PEG concentration. Corresponding conclusions can be drawn from the results in Table 4, showing distribution ratios of ^{90}Sr extracted with

Table 3

Changes of ^{89}Sr distribution ratio with poly(ethylene glycol) concentration using 0.1 M nitric acid in aqueous phase

Extraction with 10^{-2} M dicarbolide- H^+ from aqueous solutions, from urine diluted 1 : 9 by water and from nondiluted urine

[PEG]	$D^{89\text{Sr}}$			
	v/v %	Water	Diluted urine	Nondiluted urine
1.0		264	26.4	0.24
0.5		422	30.9	0.30
0.25		628	41.8	0.41
10^{-1}		474	31.4	0.25
10^{-2}		251	20.9	0.14
10^{-4}		2.6	0.2	0.04
0		0.1	0.03	0.01

Table 4

Changes of ^{89}Sr distribution ratio with poly(ethylene glycol) concentration using 0.1 M nitric acid in diluted (1 : 9) and nondiluted urine

Extraction with 0.1 M dicarbolide- H^+

[PEG]	$D^{89\text{Sr}}$		
	v/v %	Diluted urine	Nondiluted urine
5.0		1308	8.6
2.5		1390	12.5
1.0		1408	40.5
0.25		1080	30.4
10^{-1}		749	14.9
10^{-2}		384	8.6
10^{-4}		30.6	5.4
0		10.5	0.6

10^{-1} M dicarbolide- H^+ from nondiluted urine and the urine diluted with 0.1 M- HNO_3 with various PEG concentrations in aqueous phase.

Both, dilution of urine and nitric acid concentration have shown a significant influence on Sr extraction. Effect of these factors on distribution ratio of Sr is given in Tables 5 and 6. Table 5 shows the quick increase of the distribution ratio of Sr with the dilution of urine and with decreasing nitric acid concentration using

Table 5

Effect of urine dilution and nitric acid concentration on the value of ^{89}Sr distribution ratio
Extraction with 10^{-2} M dicarbolide- H^+ in nitrobenzene at 0.25% PEG in aqueous phase

Dilution Urine : Water	D^{89}_{Sr} at nitric acid in mol dm $^{-3}$				
	0.0	10^{-2}	10^{-1}	0.5	1.0
1 : 0	0.86	0.5	0.4	0.28	0.23
1 : 4	11.6	10.6	9.15	5.25	2.14
1 : 9	38.8	47.9	41.8	24.4	5.21
1 : 19	82.7	55.7	45.6	27.2	9.56
0 : 1	1302	715	628	350	22.3

Table 6

Effect of urine dilution and nitric acid concentration on the value of ^{89}Sr distribution ratio
Extraction with 0.1 M dicarbolide- H^+ in nitrobenzene using 1% PEG in aqueous phase

Dilution Urine : Water	D^{89}_{Sr} at nitric acid in mol dm $^{-3}$		
	0.1	0.5	1.0
1 : 0	40.8	22.4	19.9
1 : 4	623	408	190
1 : 9	1408	800	391
1 : 19	1903	1705	681
0 : 1	2020	1800	1201

10^{-2} mol dm $^{-3}$ concentration of extractant. In Table 6 are given similar dependences for extraction of Sr by 10^{-1} M dicarbolide- H^+ in the presence of 1% PEG and at various concentrations of nitric acid in diluted and nondiluted urine and water. The values of distribution ratios suitable for selective extraction of radiostrontium after selective extraction of ^{137}Cs are of order of 10. The corresponding extraction conditions, as are shown in Table 5, for extraction using 10^{-2} M dicarbolide- H^+ and 0.25% PEG are in the range from (0.1 to 0.5) M- HNO_3 for the urine diluted 10–20 times. For extraction of Sr from nondiluted urine the proper conditions are 10^{-1} M dicarbolide- H^+ , (0.1–0.5) M- HNO_3 , and 1% PEG. Distribution ratios of the other contaminants under these experimental conditions are given in Table 7.

Table 7

Values of distribution ratios of some fission and activated radionuclides at proper conditions for radiostrontium extraction

Radionuclide	Distribution ratio of radionuclides at conditions:			
	Urine : Water 1 : 19 10^{-1} M dicarbolide- H^+ 10^{-1} M- HNO_3 1% PEG	Urine : Water 1 : 19 10^{-2} M dicarbolide- H^+ 10^{-1} M- HNO_3 0.25% PEG	Urine : Water 1 : 19 10^{-2} M dicarbolide- H^+ 5×10^{-1} M- HNO_3 0.25% PEG	Distilled water 10^{-2} M dicarbolide- H^+ 5×10^{-1} M- HNO_3 0.25% PEG
^{22}Na	2.35	0.169	0.063	0.109
^{45}Ca	5.11	0.073	0.043	0.512
^{60}Co	4.99	0.060	0.012	0.025
^{65}Zn	4.75	0.059	0.017	0.024
^{89}Sr	1903	45.6	27.2	350
^{90}Y	58.6	0.21	0.030	0.030
^{95}Zr	0.121	0.025	0.005	0.015
^{106}Ru	0.135	0.013	0.006	0.015
^{137}Cs	506	18.7	5.64	9.21
^{133}Ba	—	263	155	1856
^{144}Ce	224	0.276	0.014	0.061
^{86}Rb	120	5.45	1.19	3.82

According to these data it is clear that radiostrontium can be extracted directly from excreta, after caesium has been extracted, when a proper amount of PEG is added. The radiochemical purity of isolated Sr depends on both, the quality and quantity of the other contaminants in the radioisotope mixture, and on the number of extraction and scrubbing processes used during the course of analysis. The most simple procedure is required for the analysis of the old fission products mixture.

Finally, it can be stated that the consecutive extraction of radiostrontium following extraction of radiocaesium from urine contaminated by a mixture of fission products and activated radionuclides is very selective, quick and reaches a high yield.

Radiostrontium isolation following caesium separation from a mixture of contaminating radionuclides may be performed as follows:

— to dilute urine 10—20 times, to adjust the nitric acid concentration from 0.1 to 0.5 M, to add the carrier (CsCl, less than 10^{-4} mol dm⁻³), to extract ¹³⁷Cs with 10^{-2} M dicarbollide-H⁺ in nitrobenzene (if Rb radionuclides are present, they will be also partly extracted);

— after caesium extraction to add poly(ethylene glycol) 300 (final concentration in aqueous phase has to be 0.25%), to extract radiostrontium at the phase ratio from 1 : 1 to 1 : 10 by shaking for 5 min with 10^{-2} M dicarbollide-H⁺ in nitrobenzene from the urine diluted by 0.5 M-HNO₃ without adding a carrier. The extraction yield of radiostrontium is higher than 99%. The amount of other contaminants may be decreased to less than 1% by double scrubbing with 0.5 M-HNO₃ containing 0.5% PEG, at phase ratio 1 : 1. Scrubbing does not practically decrease the yield of radiostrontium as seen from Table 7.

The total time of performing the complete radiochemical analysis is less than 30 min. The measuring of the activity of ⁸⁹Sr may be performed directly using a well-type scintillation crystal NaI(Tl). The activity of ⁹⁰Sr after its reextraction from the organic phase may be measured using the liquid scintillation technique.

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References

1. Gedeonov, L. I. and Ivanova, L. M., *Radiokhimicheskii analiz objektov vneshnei sredy*. Moskovskoe otdelenie ob'yedinyenykh gosudarstvennykh izdatelstv, Moscow, 1972.
2. Blume, W., *Report SZS-2*. Staatliche Zentrale für Strahlenschutz, Berlin, 1966.
3. Beneš, J. and Herchl, M., *Jad. Energ.* 17, 55 (1971).
4. *Quick Methods for Radiochemical Analysis*. Technical Reports Series No. 95, IAEA, Vienna, 1969.
5. Čechvala, L. and Petrášová, M., *Chem. Listy* 70, 1296 (1976).
6. Millard, N. E. and El-Atrash, A. M., *Egypt. J. Chem.* 16, 173 (1975).

7. Barrata, E. J., *Anal. Chem.* 57, 37 (1974).
8. Rehak, W. and Feddersen, B., *Report SZS-2*, p. 17. Staatliche Zentrale für Strahlenschutz, Berlin, 1973.
9. Testa, C., Delle, R., and Site, A., *J. Radioanal. Chem.* 34, 121 (1976).
10. Barrata, E. J. and Reavey, T. C., *J. Agr. Food Chem.* 17, 1337 (1969).
11. Kyrš, M., Rais, J., Selucký, P., and Kadlecová, L., *J. Radioanal. Chem.* 29, 15 (1976).
12. Hawthorne, M. F., *Pure Appl. Chem.* 29, 547 (1972).
13. Selucký, P. and Kyrš, M., *J. Inorg. Nucl. Chem.* 38, 1744 (1976).
14. Ščasnár, V. and Koprda, V., *Radiochem. Radioanal. Lett.* 34, 23 (1978).
15. Koprda, V. and Ščasnár, V., *J. Radioanal. Chem.* 51, 245 (1979).
16. Ščasnár, V. and Koprda, V., *Radiochem. Radioanal. Lett.* 39, 75 (1979).
17. Koprda, V. and Ščasnár, V., *Chem. Zvesti* 34, 480 (1980).
18. Ščasnár, V. and Koprda, V., *J. Radioanal. Chem.* 59, 389 (1980).
19. Koprda, V. and Ščasnár, V., *Radiochem. Radioanal. Lett.* 44, 349 (1980).
20. Štefek, M., Kyrš, M., and Rais, J., *Zh. Anal. Khim.* 31, 1364 (1976).
21. Rais, J., Selucký, P., and Kyrš, M., *J. Inorg. Nucl. Chem.* 38, 1378 (1976).
22. Bray, G. A., *Anal. Biochem.* 1, 279 (1960).

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