Isolation of ^{137}Cs from biological material contaminated by a mixture of radionuclides

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The efficiency of isolation of ^{137}Cs from biological material by extraction using cobalt dicarbolide-H^+ was compared with the absorption on ferrocyanides of cobalt(II), copper(II), and on ammonium molybdophosphate (AMP). Extraction of ^{137}Cs appeared to be the best among the investigated procedures. The subject of examination was the influence of preanalytical treatment of biological sample upon the yield of isolation of ^{137}Cs by the extraction using dicarbolides of cobalt(II) and its influence upon the decontamination efficiency of isolation procedure. Analyses were made of tissue samples with *in vivo* incorporated radionuclides ^{137}Cs, ^{60}Co, ^{65}Zn, ^{95}Zr, ^{106}Ru, and ^{144}Ce on the one hand diluted in mineral acid only, and on the other hand mineralized by both the wet and dry method; the influence of the degree of biological material mineralization upon the quantity of the extracted amount of ^{137}Cs was revealed. The examination was made of the suitability of the individual isolation procedures for ^{137}Cs from a mixture of radionuclides, their activity ratio being within the range of 1 to 100 times of ^{137}Cs activity.

Была сравнена эффективность изоляции ^{137}Cs из биологических материалов экстракцией с дикарболлидом кобальта с его абсорбцией на осадках ферроцианидов кобальта и меди и фосфомолибдата аммония. Экстракция дикарболлидом-H^+ оказалась наиболее подходящей с точки зрения селективности. Было исследовано влияние предварительной обработки биологического образца на выход экстракции ^{137}Cs дикарболлидом кобальта и ее влияние на фактор очистки. Проанализированы образцы тканей, которые содержали радионуклиды ^{137}Cs, ^{60}Co, ^{65}Zn, ^{95}Zr, ^{106}Ru и ^{144}Ce после *in vivo* инкорпорации. Демонстрируется влияние растворения в минеральной кислоте и минерализации мокрым и сухим способом на выход ^{137}Cs. Была исследована пригодность отдельных способов изоляции ^{137}Cs из смеси радионуклидов при 1—100-кратном избытке их активности.

Besides the radiometric assessment of radionuclides by amplitude analysis of their gamma radiation, the isolation of radionuclide from the mixture we are dealing with, used to be frequently a more suitable alternative, mainly depending

on the quantitative and qualitative characteristics of a mixture of radionuclides. Isolation of ^{137}Cs from biological, *in vivo* contaminated material, containing even 100-fold excess of the other radionuclides appeared to be nearly quantitative. A simple extraction and double scrubbing was used for isolation. The amount of contaminating radionuclides in purified extracts was far less than 5% of extracted ^{137}Cs. The transfer of radionuclides into the solution by wet mineralization is made by using oxidation agents in liquid phase, as a rule nitric acid [1], perchloric acid or sulfuric acid [2]; sometimes the technique of oxidation by peroxyl radicals with catalytic influence of Fe^{2+} ions is applied [3].

A dry mineralization procedure consists of preliminary drying of biological tissues and their subsequent burning at the temperature 350—700°C [1, 4, 5]. The choice of suitable temperature conditions at burning is orientated chiefly upon preventing retention of the radionuclide in carbonized mineralizate.

For radiocaesium concentration from mineralizates or aqueous solutions, frequent use is made of ferrocyanide of transition metals [6, 7], or ammonium molybdophosphate [8, 9] and lately also polyhedral complexes derived from transition metals and carboranes [10] which possess high selectivity towards caesium and have numerous advantages in comparison with the other extraction agents [11, 12]. These compounds extract mainly weakly hydrated ions of alkali metals as ion associates, whereas extraction of strongly hydrated polyvalent ions into nitrobenzene is far less significant [13, 14]. The polyhedral complex of the type H^+ [π-(3)-1,2-$C_2B_9H_{11}$]$_2Co^-$ further referred to as dicarbolide-H^+ (and its chlorinated derivative H^+ ($C_4B_{18}H_{15}Cl_7Co^-$) further referred to as Cl-dicarbolide-H^+) are fully dissociated in nitrobenzene and the stability constant of complex anion is so high that the dissociation of component need not be considered [11]. Both agents may be used with advantage for isolation of ^{137}Cs from a mixture of radionuclides after the biological material mineralization. Suitable conditions were selected under which alkali metals are not extracted significantly. The conditions were verified, under which high decontamination efficiency of isolation of ^{137}Cs from ^{106}Ru and ^{95}Zr [14] is achieved, changing the acidity of aqueous phase.

In this paper a comparison is made of efficiency of ^{137}Cs isolation from a mixture of radionuclides by extraction using dicarbolide-H^+ with other currently used procedures. Simultaneously, the influence of preanalytical treatment of sample of biological material upon the yield of isolation was investigated.

Experimental

All the used chemical agents were of anal. grade. The dicarbolide-Cs^+ and Cl-dicarbolide-Cs^+ were in the form of yellow or orange powder, practically insoluble in water (provided by courtesy of J. Rais, Institute of Nuclear Research, Řež near Prague).

The following radionuclide solutions were used: ^{51}Cr-chloride, ^{60}Co-chloride, ^{65}Zn-chloride, all from Metronex (Poland), ^{95}Zr-oxalate from Rotop (GDR), ^{106}Ru-nitrate, ^{137}Cs-chloride, ^{144}Ce-chloride, all from Izotop (USSR). All the radionuclides were carrier-free or with negligible amount of carrier. The radiochemical purity of radionuclides used was over 99.9%, for ^{137}Cs 99.65%, according to certificates. The isotopic contamination of ^{137}Cs by ^{134}Cs was 0.34%. For study of the effect of back isotopic carriers on the ion-exchange adsorption of radionuclides on the precipitates were used $ZrOCl_2 \cdot 5H_2O$ and $CeCl_3 \cdot 6H_2O$ and CsCl in 0.1 M concentration. Standard solutions were prepared in the range of 10—100 MBq cm^{-3}. Pipetting of exact quantities of standard solutions for the preparation of radioisotope mixture was performed by constriction pipettes.

To compare the efficiency of isolation of ^{137}Cs from a mixture of radionuclides ^{51}Cr, ^{60}Co, ^{65}Zn, ^{95}Zr, ^{106}Ru, ^{137}Cs, ^{144}Ce, by coprecipitation with ferrocyanide of cobalt(II) and copper(II), with ammonium molybdophosphate and by extraction using dicarbolide-H$^+$, the radionuclide mixtures were prepared. Into the mixture of radionuclides ^{51}Cr, ^{60}Co, ^{65}Zn, ^{95}Zr, ^{106}Ru, and ^{144}Ce, each in quantity of 37 kBq, ^{137}Cs was added in a quantity of 0.37 kBq, 3.7 kBq, and 37 kBq. The ratios of activity of ^{137}Cs to the individual radionuclides were: 1 : 100, 1 : 10, and 1 : 1. The samples of volume 20 cm^3 in 1.4 M-HNO_3 were used for isolation of ^{137}Cs by ferrocyanide of copper(II) and the samples of the same volume in 2.8 M-HNO_3 were used for the isolation of ^{137}Cs by ferrocyanide of cobalt(II) and AMP. For the extraction by dicarbolide-H$^+$ 2 cm^3 of stock solutions of radionuclides in 1 M nitric acid were used.

Other model samples of radionuclides in solutions of nitric acid were prepared from stock solutions of radionuclides, their activity amounting from 10 to 100 kBq and concentration of nitric acid from 5×10^{-3} to 10^{-2} M, filled up to 10 cm^3 by distilled water.

The samples of biological material with *in vivo* incorporated fission and activated radionuclides were prepared by administration of a mixture of radionuclides intravenously into the ear vein of a 30 kg pig that had received intravenously ^{137}Cs in a quantity of 37 MBq 14 days ago. The injection solution contained the following amounts of radionuclides: ^{51}Cr — 2.77 MBq, ^{59}Fe — 2.13 MBq, ^{106}Ru — 0.456 MBq, ^{65}Zn — 5.55 MBq, ^{60}Co — 1.83 MBq, ^{95}Zr — 4.07 MBq, and ^{144}Ce — 6.53 MBq. Two hours after the administration of the radionuclides the animal was slaughtered and samples of the following organ tissues were taken: lungs, spleen, liver, kidney, heart, and muscle (musculus gastrocnemius). The tissue samples after performing radiometric analysis, were kept in a deep frozen state till the preanalytical processing and the radiochemical analysis was made.

A relative activity of the solid phase was measured after isolation of ^{137}Cs, or the aliquot of 1 cm^3 of organic phase after extraction using dicarbolides.

For a single radionuclide, the measurement was performed using a well-type NaI(Tl) scintillation crystal connected to an NZQ 717T laboratory measuring set (Tesla, Přemyšlení, Czechoslovakia) in the region of gamma peak, with a counting error less than 2% and a counting efficiency of 35% for ^{137}Cs.

In the case of a mixture of radionuclides, the measurement was performed using a germanium—lithium drifted semiconductor detector of 32 cm^3 volume connected to an NTA 1024 multichannel pulse-height analyzer (Orion, Hungary) with preamplifier JS-3B (Institute of Nuclear Research, Řež near Prague, Czechoslovakia) connected to an XY-writer NE 230 (EMG, Hungary) and a numeric printer NZ 891 (EMG, Hungary) with

a counting error less than 2% and counting efficiency of 0.6% for ^{137}Cs. The other multichannel amplitude analyzer set used in this work consists of the semiconductor detector Ge(Li) (Institute of Nuclear Research, Řež near Prague, Czechoslovakia) of 74 cm^3 volume, with the preamplifier (Cannbera, USA), the pulse-height analyzer ST-400 DM (Victoreen, USA), and XY-writer NE 230 (EMG, Hungary). Etalones and standard solutions (Institute for Development, Production and Use of Radioisotopes (ÚVVVR), Czechoslovakia) were used for energy calibration and absolute activity calculation of measured samples.

Ferrocyanide of copper(II) and ferrocyanide of cobalt(II) were prepared by stirring 20 cm^3 of 0.1 M nitric acid with 6 cm^3 of 0.1 M copper(II) nitrate or cobalt(II) nitrate and 2 cm^3 of 0.1 M ferrocyanide of sodium for 10 min. The precipitate was separated by centrifugation with laboratory centrifuge K 23 (Janetzki, GDR) at 528 G. The amount of dry precipitate was 68 mg for ferrocyanide of copper(II) and 66 mg for ferrocyanide of cobalt(II).

Ammonium molybdophosphate was prepared by stirring 7 cm^3 of 6% w/v ammonium nitrate solution (71.4 g ammonium nitrate and 134 cm^3 concentrated nitric acid filled up to 1000 cm^3 by distilled water) with 3 cm^3 of 10% w/v ammonium molybdate and 1 cm^3 of 0.7% w/v dihydroammonium phosphate (3.62 g of dihydroammonium phosphate in 500 cm^3 of water) for 20 min in a water bath at 80°C. The precipitate was washed 3 times with hot distilled water and separated by centrifugation at 528 G. The amount of dry precipitate was 118 mg.

Dicarbolide-H^+ as well as Cl-dicarbolide-H^+ were converted into their acidic forms from 10^{-2} or 3×10^{-1} M solutions of their caesium salt forms in nitrobenzene by shaking them twice in 30 min with the equal volume of 2 M nitric acid containing 15% v/v of propyl alcohol and then shaking them 8 times with the equal volume of 1 M nitric acid. More than 99% of extractant has been converted into an acidic form. The other concentrations of extractant were prepared by dilution with nitrobenzene.

The mineralization of organic tissues in a dry way was made after the preceding dissolution of the 20—60 g tissue sample in 20 cm^3 of concentrated nitric acid in a boiling water bath. The sample was evaporated and burned at the temperature of 350°C for 6 h. The mineralization was supported in 1 h intervals by small shares of concentrated HNO_3 and H_2O_2 (30%). The mineralizate was then dissolved in 6 M nitric acid and diluted by distilled water to the final concentration of nitric acid (1 M). The concentration of nitric acid was determined by volumetric titration with sodium hydroxide and phenolphthalein as indicator.

Comparing the efficiency of isolation of ^{137}Cs from biological material after mineralization a part of tissues with incorporated radionuclides had been simply dissolved in 20 cm^3 of HNO_3 (65%), and after evaporation to approximately 1—2 cm^3, the solution was diluted so as to achieve 1 M nitric acid concentration. Organic substances not decomposed yet in this case, interfere with the determination of nitric acid by titration on phenolphthalein, so after further dilution of solution aliquots the concentration of nitric acid was determined by pH-meter OP-205 (Radelkis, Budapest) with glass-silver chloride electrode.

The effect of multiple repeating of mineralization cycle on the yield of ^{137}Cs isolation by extraction using dicarbolide-H^+ was verified by mineralization of 1.6 g of muscle tissue with *in vivo* incorporated ^{137}Cs after its dissolution in 1.6 cm^3 of concentrated HNO_3 on boiling water bath, and evaporation to dryness. The mineralization consists of repeating the following procedure: dissolution of the tissue in 1 cm^3 of nitric acid, evaporation almost to

dry state on a boiling water bath (repeated 3 times), dilution by distilled water to the volume of 10 cm^3, taking 2 cm^3 for extraction and concentration of the rest on the boiling water bath. This procedure was repeated 6 times. Nitric acid concentration in the analyzed solution was measured by glass-silver chloride electrode after a proper dilution. In the course of extraction steps repeated after each mineralization cycle, the concentration of biological tissue in mineralizate was decreasing due to analytical sampling from original concentration 0.16 g cm^{-3} to 0.04 g cm^{-3} in the last extraction.

Isolation of ^{137}Cs by precipitates of ferrocyanide of cobalt(II), ferrocyanide of copper(II), and ammonium molybdophosphate was performed as follows: 10 cm^3 of analyzed solution was added to a fresh precipitate and the suspension was intensively stirred for 10 min. The precipitates were separated in polyethylene test tube at 528 G. The solid and liquid phase were analyzed by gamma spectrometry.

Isolation of ^{137}Cs by dicarbolide-H^+ and Cl-dicarbolide-H^+ in nitrobenzene was made at a phase ratio of 1:1, the volume of phase being 2—15 cm^3, by shaking for 10 min. The radionuclides in the aqueous and organic phase were analyzed before and after the separation process.

Results and discussion

The efficiency of ^{137}Cs separations from some fission and activated radionuclides, by ferrocyanide of cobalt(II), ferrocyanide of copper(II), ammonium molyb-

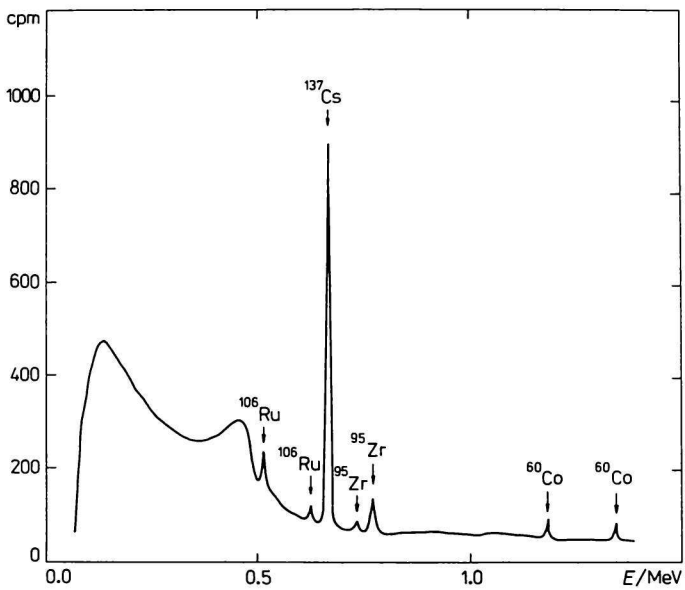

Fig. 1. Gamma spectrogram of radionuclides separated by ferrocyanide of copper(II). Individual amounts of radionuclides in aqueous phase were the same as amount of ^{137}Cs.

dophosphate and by extraction using dicarbolide-H^+, from mixtures of radionuclides in nitric acid—water solutions has been studied. In model samples the activity of ^{137}Cs to other individual radionuclides in the mixture was at the ratio of 1 : 100, 1 : 10, and 1 : 1.

The efficiency of separation process was evaluated by gamma spectrometry.

Figs. 1—3 give the gamma spectra of radionuclides isolated by precipitates of the ferrocyanides and ammonium molybdophosphate from the aqueous phase containing ^{137}Cs is the same quantity as the other radionuclides. In Fig. 4 there are the

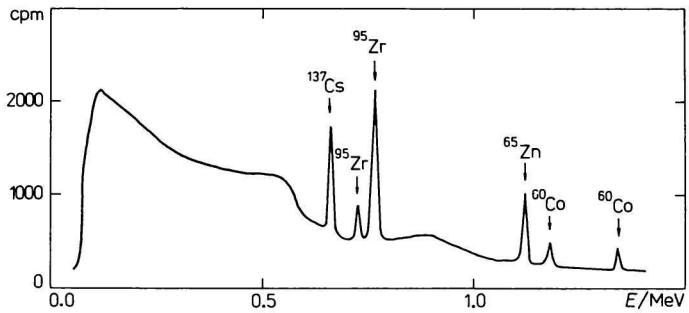

Fig. 2. Gamma spectrogram of radionuclides separated by ferrocyanide of cobalt(II).

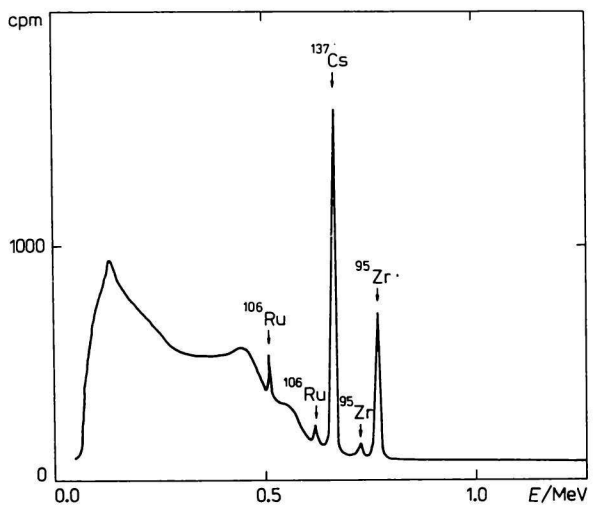

Fig. 3. Gamma spectrogram of radionuclides separated by ammonium molybdophosphate.

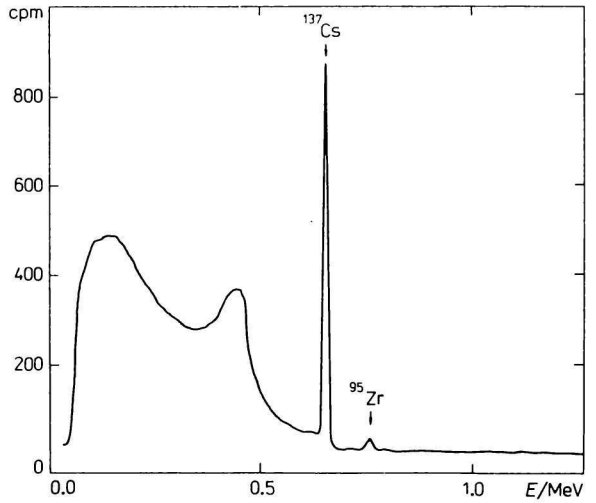

Fig. 4. Amounts of radionuclides in organic phase extracted by 10^{-2} M dicarbolide-H^+ from aqueous solution with ^{137}Cs activity equal to the activity of other individual radionuclides.

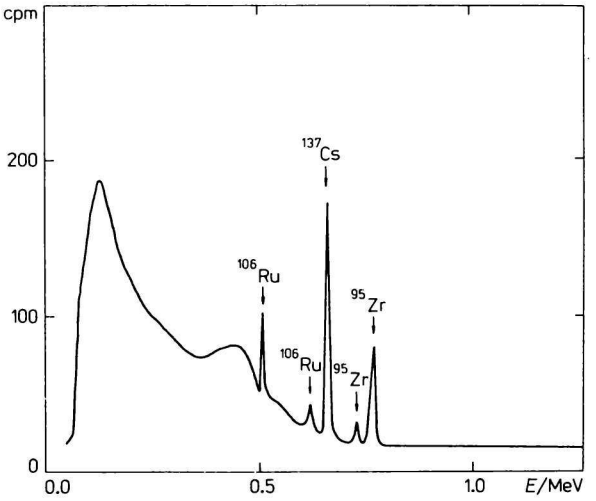

Fig. 5. Radionuclide gamma spectra in organic phase after extraction by 10^{-2} M dicarbolide-H^+ from aqueous phase with original activity ratio of ^{137}Cs to other radionuclides 1 : 10.

gamma spectra of the radionuclides in the organic phase after their extraction by dicarbolide-H^+ at quantity of ^{137}Cs to the individual radionuclides in the aqueous phase at the ratio 1 : 1, in Fig. 5 at the ratio 1 : 10, and in Fig. 6 at the ratio 1 : 100.

Figs. 4—6 show that the isolation of ^{137}Cs by dicarbolide-H^+ is rather selective also at a 100-fold excess of the other radionuclides in aqueous phase in contrast to

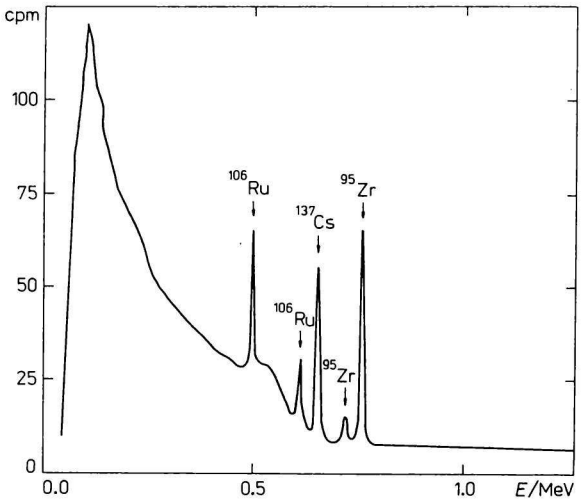

Fig. 6. Radionuclide gamma spectra in organic phase after extraction by 10^{-2} M dicarbolide-H^+ from aqueous phase with original activity ratio of ^{137}Cs to other radionuclides 1 : 100.

the isolation of ^{137}Cs by the precipitates (Figs. 1—3), which retain considerable quantities of the other fission and activated radionuclides already at mutually comparable quantities with ^{137}Cs in the aqueous sample. The experiments at other, above-mentioned ratios of radionuclide quantities showed that the greater is the ratio between the other radionuclides and ^{137}Cs in the aqueous solution, the greater are the relative quantities of contaminants of isolated ^{137}Cs absorbed on precipitates. Together with ^{137}Cs considerable quantities of ^{60}Co, ^{65}Zn, ^{95}Zr, and ^{106}Ru were retained on precipitates. The comparison shows that ammonium molybdophosphate appears to be more selective than ferrocyanide of copper(II) and the latter seems to be more selective than ferrocyanide of cobalt(II). In general, however, the selectivity of ^{137}Cs isolation by the precipitates is rather low and could be used mainly for separation of ^{137}Cs from samples where it is the dominating radionuclide. Extraction of ^{137}Cs by dicarbolide-H^+ showed to be the most selective, but the extraction yield of the solution is a little lower when compared with the other methods. Decreasing the acidity of aqueous phase (Fig. 7) the yield may be increased, but there is a partial increase of Zr and Ru coextraction, too. As evident from Fig. 6, Cs may be isolated from a radionuclide mixture also at hundredfold surplus of the other radionuclides with high yield. Amounts $<2\%$ of ^{95}Zr and $<1\%$ of ^{106}Ru are extracted, the other radiochemical impurities are extracted in amounts far less than 1%.

The distribution ratio in the course of multiple extraction of ^{137}Cs using dicarbolide-H^+ remains constant up to very low concentrations as seen from Table 1 where are the values of distribution ratio for the same sample at the

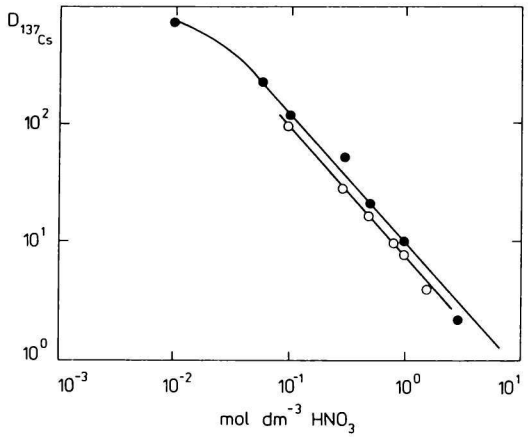

Fig. 7. Dependence of ^{137}Cs distribution ratio on concentration of nitric acid in aqueous phase at the extraction of ^{137}Cs by dicarbolide-H^+ in nitrobenzene.
● 10^{-2} M dicarbolide-H^+; ○ 8×10^{-3} M Cl-dicarbolide-H^+.

Table 1

Successive extraction of ^{137}Cs by 10^{-2} M dicarbolide-H^+ in nitrobenzene from 1 M nitric acid

Extraction No.	Distribution ratio $D_{^{137}Cs}$	Individual extraction yield %	Total extraction yield %
1	10.1	91.0	91
2	9.4	8.13	99.13
3	8.8	0.78	99.91
4	9.3	0.08	99.99

repeating extraction by equal volume of organic phase. It is evident that the total extraction yield of ^{137}Cs grows quickly already at the value of ^{137}Cs distribution ratio about 10 in 1 M-HNO_3. The extraction of radiochemical impurities due to nearly constant amount of contaminants remains practically unchanged in each extraction step so that the total quantity of impurities in collected extracts after the n-th extraction step may be considered to be the n-fold amount of contaminants at a single extraction.

In routine use it seems to be of higher advantage to extract the solution at lower acidity of aqueous solution and to scrub impurities by 1 M nitric acid, than to extract ^{137}Cs repeatedly from the strong acidic aqueous solutions and not to scrub the other contaminants.

Should the amount of radiochemical impurities of isolated ^{137}Cs bé less than 5%, one extraction step seems to be sufficient at the ratio of activities of ^{137}Cs to the individual other radionuclides 1 : 1, the extraction step and single scrubbing at the

ratio 1 : 10, and the double extraction with two or three scrubbings with 0.5—1.0 M nitric acid at the ratio about 1 : 100. Under these conditions the error of nonspectrometric, single radiometric determination of ^{137}Cs in the sample is only several per cent, taking into account the decrease of extraction yield with the scrubbing procedures (x% of the value of ^{137}Cs in each case of extraction or scrubbing procedure by 1 M nitric acid).

As it was shown, extraction of ^{137}Cs by dicarbolide-H^+ may be used for nonspectrometric, radiometric determination of isolated ^{137}Cs also for samples in which the activities of other individual radionuclides are of amount greater than 100 times the quantity of ^{137}Cs.

With the aim to investigate the efficiency of the individual isolation procedures for ^{137}Cs from samples of organ tissues with *in vivo* incorporated radionuclides, the samples of biological tissues were prepared by administration of a mixture of radionuclides to a 30 kg pig. In Table 2 are the fractions of activities of *in vivo* incorporated radionuclides from the administered quantities, in the tissues of individual organs, the samples of which were analyzed by multichannel gamma spectrometry.

The gamma spectrograms of the samples of the individual organ tissues showed substantial differences in distribution of radionuclides between parenchymatous organs and muscle tissue. From Table 2 it is evident that the highest concentration of ^{137}Cs was found in muscle, which on the other hand is the only tissue in which the other radionuclides are not retained in a significant quantity. ^{137}Cs is usually the dominant contaminant in muscle and often also in other organ tissues.

As a preanalytical treatment of organ tissues we used mineralization in a dry way and/or a dissolution in a hot concentrated nitric acid. ^{137}Cs was extracted from 1 M nitric acid solution of mineralizate by 2.2×10^{-2} M Cl-dicarbolide-H^+ in nitrobenzene. The distribution ratio of ^{137}Cs from the aqueous solution is 46.2 and the expected extraction yield is 97.8%. The extraction yield of ^{137}Cs from mineralizates of organ tissues is shown in Table 3. It turned out that the total quantity of

Table 2

Fraction of administered activity of radionuclides in organ tissues of pig (in %)

Body organ	^{51}Cr	^{60}Co	^{65}Zn	^{95}Zr	^{106}Ru	^{137}Cs	^{144}Ce
Lungs	7.2	24.8	4.8	89.7	21.1	1.6	44.0
Liver	—	23.4	60.4	—	7.8	10.6	0.9
Kidney	—	3.7	2.1	—	2.1	1.7	—
Spleen	—	0.6	1.1	0.1	—	0.1	0.1
Heart	—	0.6	0.6	—	0.6	1.3	—
Muscle	—	—	—	—	—	51.0	—
Blood	0.9	18.3	2.1	8.3	16.6	1.4	—

coextracted contaminants is less than 5% of activity of extracted ^{137}Cs, whereby in general, the mineralization in a dry way assures higher extraction yields than mineralization in nitric acid only.

The efficiency of mineralization procedure in the wet way was verified with the muscle tissue containing *in vivo* incorporated ^{137}Cs. The single mineralization cycle was repeated several times with the same sample. The results given in Table 4 show that the distribution ratio of ^{137}Cs being extracted by dicarbolide-H^+ in nitrobenzene was increasing gradually according to the number of mineralization cycles (double amount of nitric acid over the weight of biological material was used) and from after the sixth cycle it remained practically unchanged. It turned out that in order to achieve consequent muscle tissue mineralization it is necessary to add concentrated HNO_3 portionwise up to the total quantity of 12 times the weight of mineralized tissue. The simple dissolution of tissue sample in concentrated HNO_3 on a hot water bath, to the end of foam forming, results in achieving low distribution ratio of ^{137}Cs (Table 4), mainly as a consequence of insufficient decomposition of organic substances.

The adequate necessary quantities of mineralization agent are evident also from Table 5 showing the changes of distribution ratio of ^{137}Cs depending on the sample mass of biological material after the simple dissolution of muscle tissue in 1 cm^3 of concentrated HNO_3 and after extraction of ^{137}Cs using 10^{-2} M dicarbolide-H^+ in nitrobenzene. The concentration of nitric acid in the aqueous phase before extraction was 0.16 M for the sample with 2 g of muscle tissue dissolved.

The value of the distribution ratio for ^{137}Cs being extracted from 0.5 M-HNO_3 would amount to 0.57, *i.e.* it would be lower than the value of distribution ratio shown in Table 4 for the equal amounts of tissue and solvent, which indicate a negative influence of quantity of nondecomposed organic substances on the value of distribution ratio. More clearly this effect can be shown on the values of distribution ratio given in Table 5 documenting that a 20-fold increase of mass ratio of concentrated HNO_3 used for dissolving a biological material causes a 4-fold increase of distribution ratio.

After a complete mineralization of 10 g of muscle with *in vivo* incorporated ^{137}Cs we obtained the value of the distribution ratio equal to 8.32 extracting ^{137}Cs from a solution of 0.54 M nitric acid by 10^{-2} M Cl-dicarbolide-H^+ and the value of extraction yield reached 94.8%; similarly, by complete mineralization of 2.8 g of muscle after 15 mineralization cycles we obtained the value of $D = 132$ extracting ^{137}Cs from the 0.028 M nitric acid by dicarbolide-H^+, and the extraction yield was practically 100%.

The decreasing influence of nondecomposed and dissolved substances of biological sample with increasing ratio of phases upon the value of ^{137}Cs distribution ratio is shown in the lower part of Table 5. It is evident that the higher is the relative amount of organic phase the higher value is acquired by the distribution ratio.

Table 3. Extraction yield of ^{137}Cs from organ tissues with *in vivo* incorporated fission and activated radionuclides determined by gamma spectrometry
Extraction after mineralization in dry or wet way by dicarbolide-H^+ in nitrobenzene

Organ tissue	Amount of sample [g] mineralized by		Substance concentration in mineralizate		Extraction yield %		Coextracted impurities %
	dry way	wet way	dry way	wet way	dry way	wet way	
Lungs	18.25	19.00	0.100	0.214	101.9	96.0	<1.3 ^{106}Ru
Liver	34.10	32.45	0.171	0.590	98.0	71.7	<2.5 ^{95}Zr
Kidney	44.19	58.88	0.719	0.393	100.0	52.0	<1.0 ^{65}Zn
Spleen	33.89	25.07	0.403	0.270	96.3	67.8	
Heart	38.37	32.20	0.518	0.239	94.5	74.8	

Table 4. Effect of repeating of single mineralization cycle on the change of ^{137}Cs distribution ratio
Extraction by 10^{-2} M dicarbolide-H^+ in nitrobenzene from solution of muscle tissue

Fraction of ^{137}Cs taken to analysis	Number of mineralization cycles	Nitric acid concentration in aqueous phase M	Distribution ratio $D_{137_{Cs}}$	$D_{137_{Cs}}$ corresponding to extraction from 0.5 M nitric acid
0.200	Single dilution in concentrated nitric acid	0.28	1.7	0.9
0.160	*1*	0.35	3.1	2.0
0.128	*2*	0.96	4.0	8.7
0.102	*3*	1.41	7.5	11.9
0.082	*4*	0.44	20.4	17.1
0.065	*5*	1.10	9.0	22.0
0.052	*6*	1.55	9.8	35.4
—	Water—nitric acid solution	0.50	11.8	25.7

Table 5

Effect of tissue amount mineralized by constant volume of concentrated nitric acid on the value of ^{137}Cs distribution ratio by extraction with 10^{-2} M dicarbolide-H^+

Tissue amount g	Distribution ratio $D_{137_{Cs}}$	Phase ratio organic : aqueous	Nitric acid concentration M
0.12	8.3	1:1	0.88
0.52	8.1	1:1	0.65
1.05	5.1	1:1	0.30
1.48	3.2	1:1	0.35
2.03	2.1	1:1	0.18
2.03	3.0	2:1	0.18
2.03	3.6	3:1	0.18
2.03	4.0	4:1	0.18

Table 6

Changes of distribution ratio of ^{137}Cs by extraction with dicarbolide-H^+ from solutions of muscle tissue dissolved in nitric acid amount proportional to the amount of analyzed tissue

Muscle tissue amount g	Amount of concentrated nitric acid cm^3	Amount of water added cm^3	Final nitric acid concentration before extraction mol dm^{-3}	$D_{137_{Cs}}$
0.53	0.5	4.5	0.29	1.4
1.00	1.0	9.0	0.32	1.6
1.50	1.5	13.5	0.28	2.1
2.00	2.0	18.0	0.31	1.7
2.50	2.5	22.5	0.29	1.8

The distribution ratio of ^{137}Cs does not depend on the amount of tissue sample when it is dissolved in the volume of concentrated HNO_3 proportional to the sample amount and diluted correspondingly, as shown in Table 6.

Experiments have shown that for a rapid analysis of samples of biological origin it seems to be sufficient at a higher content of incorporated ^{137}Cs just to make a quick pretreatment of biological samples by their dissolving in a 10-fold excess of concentrated HNO_3 on the water boiling bath, till the foam development is finished, because the distribution ratio of ^{137}Cs is high enough as it is.

Acidity of aqueous phase exerts one of the most significant influences upon the value of distribution ratio. Fig. 7 shows that changes in distribution ratio value by extraction of ^{137}Cs with the solution of 10^{-2} M dicarbolide-H^+ in nitrobenzene from

nitric acid solutions, depend on the concentration of the acid. The mentioned dependence seems to be linearly proportional to nitric acid concentration also in the region of molar concentrations. The slope of the dependence practically does not change by changing concentration of the extractant. The curve is shifted only toward the lower values at the lower concentration of extraction agent in nitrobenzene and *vice versa*.

Extracting ^{137}Cs from 0.5 M nitric acid, the value of ^{137}Cs distribution ratio was 25.7, in full agreement with the value 22.0 published by *Rais et al.* [11].

By using higher concentration of extraction agent (max. 0.3 M) proportionally higher values of distribution ratio are achieved. It seems to be advantageous to use for extraction 0.1—0.3 M dicarbolide-H^+ in nitrobenzene. Slightly lower distribution ratio values under corresponding conditions as compared with dicarbolide-H^+ were found when using chlorinated derivative of dicarbolide-H^+.

Though using dicarbolide-H^+ for the extraction of ^{137}Cs seems to be more advantageous for making extractions from weak acid solutions (0.1 M-HNO_3), the values of decontamination factors of ^{137}Cs from ^{95}Zr, ^{106}Ru, and ^{144}Ce showed that optimal conditions for isolation of caesium require approximately 0.5 M nitric acid concentration in aqueous phase.

To isolate ^{137}Cs from organic tissues, using ferrocyanide of cobalt(II), ferrocyanide of copper(II), ammonium molybdophosphate, and dicarbolide-H^+, samples have been used with *in vivo* incorporated fission and activated radionuclides (Table 2) dissolved in concentrated nitric acid on water boiling bath till the foam development was finished. The efficiency of the separation process was determined by gamma spectrometry. Tables 7—9 show the values of fractions of individual radionuclides from organ tissues being absorbed on precipitate. Table 10 shows the values of fractions extracted using dicarbolide-H^+ in nitrobenzene. In spite of the significant dispersion the results showed that on ferrocyanide precipitates a high retention of ^{60}Co and ^{65}Zn ions takes place. Though the contamination

Table 7

Fractions of the original amount of radionuclides in organ tissue absorbed on the precipitate of ferrocyanide of cobalt(II)

Tissue dissolved in concentrated nitric acid	Activity of radionuclide absorbed on ferrocyanide of cobalt(II) in %					
	^{144}Ce	^{137}Cs	^{106}Ru	^{95}Zr	^{65}Zn	^{60}Co
Lungs	<0.1	100.0	20.94	78.7	70.0	88.9
Liver	<0.1	100.0	22.2	—	84.8	100.0
Kidney	—	99.0	21.80	—	100.0	97.6
Heart	—	91.7	19.9	—	100.0	77.8

Table 8

Fractions of the original amount of radionuclides in organ tissues absorbed on the precipitate of ferrocyanide of copper(II)

Tissue dissolved in concentrated nitric acid	Activity of radionuclide absorbed on ferrocyanide of copper(II) in %					
	^{144}Ce	^{137}Cs	^{106}Ru	^{95}Zr	^{65}Zn	^{60}Co
Lungs	7.4	100.0	0.1	12.4	11.1	22.2
Liver	0.1	100.0	0.1	—	—	26.1
Kidney	—	99.0	0.1	—	—	35.7
Heart	—	99.6	0.1	—	—	31.1

Table 9

Fractions of the original amount of radionuclides in organ tissues absorbed on the precipitate of ammonium molybdophosphate

Tissue dissolved in concentrated nitric acid	Activity of radionuclides absorbed on ammonium molybdophosphate in %					
	^{144}Ce	^{137}Cs	^{106}Ru	^{95}Zr	^{65}Zn	^{60}Co
Lungs	0.1	87.5	30.4	16.9	8.8	0.1
Liver	0.1	99.1	37.0	—	8.9	—
Kidney	—	99.5	26.8	—	9.2	—
Heart	—	97.1	23.8	—	10.0	—

Table 10

Fractions of the original amount of radionuclides in organ tissues extracted by 10^{-2} M dicarbolide-H^+ in nitrobenzene from 1 M nitric acid

Tissue dissolved in concentrated nitric acid	Activity of radionuclide extracted by dicarbolide-H^+ in %					
	^{144}Ce	^{137}Cs	^{106}Ru	^{95}Zr	^{65}Zn	^{60}Co
Lungs	—	93.8	—	1.1	—	—
Liver	—	80.5	—	—	—	—
Kidney	—	72.4	—	—	—	—
Heart	—	54.4	—	—	—	—

of isolated caesium by zirconium and ruthenium is lower, there are still high percentages of the radionuclides present in analyzed sample. The retained amounts of bivalent ions on ferrocyanide of copper(II) are generally lower than those on ferrocyanide of cobalt(II).

Considerable amounts of potassium in biological material, being a nonisotopic carrier for ^{137}Cs, decrease the value of ^{137}Cs distribution ratio already in concentrations around 1 mg cm^{-3}. In mineralizates of biological material of animal origin there can be 1×10^{-4}—5×10^{-5} g of potassium in 1 cm^3 of mineralizate, which after 10-fold dilution does not yet decrease the value of ^{137}Cs distribution ratio, but simultaneously this fact eliminates the necessity of adding an isotopic carrier for ^{137}Cs.

Isotopic back-carriers of ^{144}Ce and ^{95}Zr, experimentally used in concentrations 10^{-1} M, decreased the amounts of these contaminants on all precipitates from 3 to 60 times, as seen from Table 11.

Table 11

Fraction of activity (in %) absorbed on precipitates with and without an isotopic back-carrier
Concentration of carrier 10^{-1} mol dm^{-3} in 0.5 M nitric acid

Radionuclide	Ferrocyanide of cobalt(II)		Ferrocyanide of copper(II)		Ammonium molybdophosphate	
	carrier-free	carrier	carrier-free	carrier	carrier-free	carrier
^{144}Ce	0.5	0.1	3.2	0.1	0.1	0.0
^{106}Ru	11.1	—	2.4	—	13.2	—
^{95}Zr	54.8	2.1	27.9	0.5	45.1	0.8

Ammonium molybdophosphate retains in higher amounts than 10% only ^{65}Zn, ^{95}Zr, and ^{106}Ru. The chemical yield of ^{137}Cs separation with ferrocyanide precipitates is practically quantitative, with ammonium molybdophosphate the mean value is 96% and by extraction using 10^{-2} M dicarbolide-H$^+$ it is in the range 75—99% depending on the acidity of aqueous phase and concentration of extractant. Isolation of ^{137}Cs with precipitates used, seems to be of low selectivity. In spite of a lower yield, the extraction method seems to be more suitable for isolation of ^{137}Cs from biological samples because the individual radiochemical impurities are coextracted into nitrobenzene only in amounts smaller than 1%, and not greater than 1.1% with ^{95}Zr. Extraction of ^{137}Cs by dicarbolide-H$^+$ is highly selective and it seems to be suitable for isolation of caesium after a quick mineralization of biological tissue. Finally, it may be stated that among the tested methods for isolation of Cs from the aspect of their selectivity the extraction using dicarbolide-H$^+$ seems to be the most suitable. Retention of ^{137}Cs on the precipitate of ammonium molybdophosphate appears to be more selective than that on ferrocyanides. Dissolution of the samples of biological tissues with *in vivo* incorporated radionuclides in a 10-fold excess of concentrated HNO_3 on the water

boiling bath seems to be a proper preanalytical treatment. The extraction yield of ^{137}Cs from a mineralizate by single extraction using dicarbolide-H^+ in nitrobenzene is within the range from 75% practically to 100%, depending on extractant concentration and acidity of aqueous phase. The other fission and activated products contaminate the isolated ^{137}Cs less than 5%, in the case when ^{137}Cs is the main contaminant of the biological tissues. Using extraction of ^{137}Cs and double scrubbing of impurities it is possible to isolate ^{137}Cs from biological samples with *in vivo* incorporated radionuclides where the other radionuclides are even in a 100-fold excess as compared with ^{137}Cs and to make nonspectrometric, radiometric determination of its activity with an error not exceeding several per cent.

Especially good results from the selectivity aspect were achieved for isolation of ^{137}Cs from muscle tissue in which as a result of the selective effect of the muscle fibre membrane, predominantly ^{137}Cs is retained from *in vivo* incorporated fission and activated radionuclides.

The extraction yield of isolated ^{137}Cs may be substantially increased by using higher concentration of extractant in nitrobenzene and by complete mineralization of biological tissue.

The selectivity of isolation of ^{137}Cs seems to be the highest from 0.5 M nitric acid aqueous phase.

The suggested procedure of ^{137}Cs isolation allows the radiometric determination of ^{137}Cs in organ tissue at any real internal contamination of the biological object by fission and activated radionuclides.

References

1. *Methods of Radiochemical Analysis.* World Health Organization, Geneva, 1966.
2. Middleton, G. and Stuckey, R. E., *Analyst* (London) *79,* 139 (1959).
3. Sansoni, B. and Kracke, W., *Z. Anal. Chem. 243,* 209 (1968).
4. *HASL Procedures Manual.* HASL-300, U.S. AEC, Health and Safety Laboratory, New York, 1972.
5. Blume, W. and Rehak, W., *Report SZS-68.* Staatliche Zentrale für Strahlenschutz, Berlin—Fridrichshagen, 1968.
6. Linuma, T. A., Izawa, M., and Watari, K., *Health Phys. 20,* 11 (1971).
7. Watari, K., Imai, K., and Izawa, M., *J. Nucl. Sci. Technol. 4,* 190 (1967).
8. Sutton, D. C., Calderon, G., and Rosa, W., *Health and Safety Lab. 6,* 215 (1976).
9. Nonaka, N., Sato, K., and Higuchi, H., *Radioisotopes 25,* 599 (1976).
10. Hawthorne, M. F., *Pure Appl. Chem. 29,* 547 (1972).
11. Rais, J., Selucký, P., and Kyrš, M., *J. Inorg. Nucl. Chem. 38,* 1378 (1976).
12. Ščasnár, V. and Koprda, V., *Radiochem. Radioanal. Lett. 34,* 23 (1978).
13. Ščasnár, V. and Koprda, V., *Radiochem. Radioanal. Lett. 39,* 75 (1979).
14. Koprda, V. and Ščasnár, V., *J. Radioanal. Chem. 51,* 245 (1979).

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