

**DETERMINATION OF ^{134}Cs AND ^{137}Cs IN MILK BY SORPTION
ON FRESHLY PREPARED PRECIPITATE OF Cu(II)
HEXACYANOFERRATE IN COMBINATION WITH
GAMMA SPECTROMETRY**

Zoltán HÖLGYE and Dana DRÁBOVÁ

Institute of Hygiene and Epidemiology, 100 42 Prague 10

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A simple and rapid method for the determination of ^{134}Cs and ^{137}Cs in cow's milk has been worked out. The method is based on the separation of radiocaesium from milk by sorption on a freshly prepared precipitate of Cu(II) hexacyanoferrate, on the separation of the precipitate by centrifugation, and on the gamma-spectrometric measurement of the precipitate activity.

Due to the substantial increase of the ^{134}Cs and ^{137}Cs contents in the surface layers of soil in Czechoslovakia and in other states after the Chernobyl radiation accident, the long-term measurements of the concentration of these radionuclides in food and particularly in milk are being planned. Radiocaesium in milk can be determined¹⁻³ using radiochemical methods based on the separation of these radionuclides from milk using ion exchangers, liquid extraction, coprecipitation, etc., and the measurement of the separated final product activity. At present, the most frequently used method for the determination of the ^{134}Cs and ^{137}Cs activity concentration is the direct measurement of native samples by gamma spectrometry. However, if the activity concentration of these radionuclides in milk decreases under the value of units of Bq l^{-1} and less, it is advisable – from the point of view of the sensitivity and precision of the gamma-spectrometric determination in real time – to concentrate radiocaesium from the samples.

The sorption of ^{137}Cs on hexacyanoferrates of transition metals is often used for the separation of ^{137}Cs from aqueous solutions⁴⁻⁷. The separation can be achieved by coprecipitation⁵, by sorption on a freshly prepared precipitate⁶, or by the ion exchange chromatography on a granulated sorbent⁷. Numerous methods and technological procedures have been proposed in order to separate radiocaesium from waste waters from the nuclear power stations⁸, from sea water⁹, etc., using hexacyanoferrates of transition metals.

In this Laboratory we have set for ourselves the aim to study the conditions for the ^{137}Cs separation from milk by coprecipitation as well as by sorption on the freshly

prepared cuprum(II) hexacyanoferrate. Our aim was to work out a simple and rapid method for the determination of ^{134}Cs and ^{137}Cs in milk based on the concentration of these radionuclides from milk using the Cu(II) hexacyanoferrate and the gamma spectrometric measurement of the precipitate activity.

EXPERIMENTAL

Milk preparation. Four types of naturally or intentionally contaminated milk were used for these experiments: the consumer's 1.8% milk (with 1.8% of fat), the whole milk (with 3.5% of fat), the raw milk, and the centrifugated raw milk. The consumer's 1.8% milk and whole milk are pasteurized and homogenized milks prepared in Czechoslovakia in dairies, similarly as in most other states. The intentionally contaminated milk was prepared by adding carrier-free ^{137}Cs (in the form of chloride) to the naturally contaminated milk 30 min before the experiments.

Apparatus. In experiments concerning the determination of ^{137}Cs separation conditions from the intentionally contaminated milk the sample activity was measured using the NaI(Tl) detector in connection with the two-channel analyzer. For the determination of ^{134}Cs and ^{137}Cs in the naturally contaminated milk the sample activity was measured using the shielded HP-Ge detector in connection with the multi-channel analyzer. The centrifuge with the cuvette volume of 200 ml was used for the centrifugation of milk. The centrifugation time of 3 min at 3 000 rpm was used. All reagents used were of the analytical grade.

Coprecipitation of ^{137}Cs with $\text{Cu}_2[\text{Fe}(\text{CN})_6]$: given volumes of 0.25 mol l^{-1} solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ and of 0.5 mol l^{-1} solution of $\text{Cu}(\text{NO}_3)_2$ were added to 100 ml of milk in the polyethylene centrifugation cuvette (200 ml). The sample was mixed for 2.5 min and centrifugated after 30 min standing.

^{137}Cs sorption on freshly prepared $\text{Cu}_2[\text{Fe}(\text{CN})_6]$: the fresh precipitate of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ was added to the milk sample in the polyethylene cuvette (the 200 ml centrifugation cuvette in the case of experiments with 100 ml of milk or respectively larger bottle in experiments with larger volumes of milk). The sample was mixed (usually for 2.5 min) and centrifugated after 30 min standing. $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ for the experiments with 100 ml of milk was prepared as follows: 1 drop of 4 mol l^{-1} HNO_3 and the given volumes of 0.25 mol l^{-1} solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ and of 0.5 mol l^{-1} solution of $\text{Cu}(\text{NO}_3)_2$ were added to 10 ml of water in the polyethylene cuvette. The precipitate was carefully mixed for 1 min and after 10 min standing and another 20 s mixing the mixture was added to the milk sample. In the case of larger volumes of milk the precipitate of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ was separated from milk by centrifugation as follows: milk with the precipitate was transferred into the 200 ml polyethylene centrifugation cuvette and centrifugated. The fat from the surface of milk was removed and the milk above the precipitate was decanted. Another volume of milk with the precipitate was added to the cuvette and again centrifugated. This procedure was repeated until the whole amount of precipitate was separated from the milk.

In these experiments the ^{137}Cs separation degree from milk was calculated from the measurement of ^{137}Cs activity in milk before and after sorption or after coprecipitation. The ^{137}Cs activities in the precipitate of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ and in the fat layer after centrifugation were also measured.

Gamma-spectrometric determination of the ^{134}Cs and ^{137}Cs activities in the naturally contaminated milk: 1.2 l of milk was sampled in equal volumes into six plastic bottles. In the course of the activity measurement these bottles were placed around the HP-Ge detector with the relative efficiency of 15 per cent and with the resolution of 1.8 keV for the 1 332 keV gammas of ^{60}Co .

The detector is shielded by 10 cm of lead. For the determination of the ^{134}Cs and ^{137}Cs activity concentration in the naturally contaminated milk the activity of the dried precipitate of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ was measured in a plastic dish of the diameter of 6 cm. The dish was placed on the detector. The detection efficiency for the determination of ^{134}Cs and ^{137}Cs in native samples was evaluated from the detector efficiency curve at the given geometry. This curve was determined using a set of standard solutions with monoenergetic emitters. The detection efficiency for the ^{134}Cs and ^{137}Cs activity measurements in $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ precipitate was determined using the ^{137}Cs standard solution uniformly distributed in the dried precipitate (in a plastic dish of the diameter of 6 cm). The efficiency obtained by these measurements was checked using a set of monoenergetic standards in the geometry of a planar source of the diameter of 6 cm placed on the detector.

RESULTS

Conditions for ^{137}Cs Separation from the Intentionally Contaminated Milk

Table I summarizes the results of experiments concerning ^{137}Cs separation from 100 ml of milk, separated either by coprecipitation or by sorption on the freshly prepared precipitate of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$. It is evident that in the coprecipitation the degree of ^{137}Cs separation from milk is very low. The addition of reagents to milk

TABLE I
Separation of ^{137}Cs from 100 ml of intentionally contaminate milk

Volumes of reagents used, ml		Ratio of the ^{137}Cs activity (in per cent) in the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ precipitate ^a					
0.25 ml l ⁻¹ $\text{K}_4[\text{Fe}(\text{CN})_6]$	0.5 mol l ⁻¹ $\text{Cu}(\text{NO}_3)_2$	1.8% milk		whole milk		raw milk	
		A	B	A	B	A	B
0.2	0.1	25	<2	38	<2	39	<3
0.2	0.15	65	<2	78	<2	78	<2
0.2	0.2	>95	<2	>95	<2	>95	<2
0.2	0.22	>95	<2	>95	<2	>95	<2
0.2	0.23	>95	<2	>95	<2	>95	<2
0.2	0.24	>95	<2	>95	<2	>95	<2
0.2	0.26	>95	<2	>95	<2	>95	<2
0.5	0.4		<5		<5		<5
0.5	0.5		<5		<5		<5
0.5	0.6		<5		<5		<5

^a A Using the freshly prepared precipitate of Cu(II) hexacyanoferrate, B using coprecipitation with Cu(II) hexacyanoferrate.

yielded a colloidal precipitate that could not be separated by centrifugation. On the other hand, using the freshly prepared $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ ^{137}Cs could be removed from all kinds of milk under study. A high degree of separation was achieved using precipitates that were prepared by mixing the reagents in the stoichiometric ratio or with a moderate excess of cupric ions. In the subsequent experiments 0.2 ml of the 0.25 ml l^{-1} solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ and 0.23 ml of the 0.5 mol l^{-1} solution of $\text{Cu}(\text{NO}_3)_2$ were used for the separation of ^{137}Cs from 100 ml of milk.

During the centrifugation of milk, to which the freshly prepared $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ was added, the precipitate is collected predominantly in the sediment and the fat (present in the milk) is collected on the surface of milk. Table II gives the distribution of ^{137}Cs between the sediment and fat in all kinds of milk under study. It was found that in the case of the consumer's 1.8% milk, whole milk, and centrifugated raw milk the activity of ^{137}Cs is contained predominantly in the sediment and only a negligible part (<0.5%) is in the fat layer. However, in the case of raw milk about 8% of ^{137}Cs activity was found in the fat layer and only 91% in the sediment.

After the addition and mixing of fresh precipitate of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ to the milk the equilibrium distribution of ^{137}Cs between the sediment and milk is established very rapidly. After 1 min mixing of the precipitate in 100 ml of 1.8% milk and centrifugation 92% of ^{137}Cs activity was found in the precipitate and after 2, 3, or 5 min mixing the ^{137}Cs activity in the sediment was always higher than 95 per cent.

Moreover, it was found that the presence of non-radioactive caesium in milk up to $1.5 \text{ mg}/100 \text{ ml}$ of milk has no effect on the degree of ^{137}Cs separation from milk. Higher concentrations of caesium in milk decrease the separation degree. Also the type of the cupric salt (sulphate, chloride) used for the preparation of the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ precipitate has no effect on the degree of ^{137}Cs separation from milk.

Table III presents the results concerning the ^{137}Cs separation from various volumes of the consumer's 1.8% milk, whole milk, and centrifugated raw milk. This table shows that the ^{137}Cs separation degree (i.e., the content of ^{137}Cs activity in

TABLE II
Distribution of ^{137}Cs activity (in per cent) between the precipitate of Cu(II) hexacyanoferrate in the sediment and fat on the surface of milk after centrifugation

1.8% Milk		Whole milk		Raw milk		Centrifugated raw milk	
sediment	fat	sediment	fat	sediment	fat	sediment	fat
99.0	<0.5	98.6	<0.5	91.4	8.1	96.6	<0.5

$\text{Cu}_2[\text{Fe}(\text{CN})_6]$ after centrifugation) ranges from 94.5 to 99.1 per cent in the types of milk under study. Using the *t*-test it has been found that in no type of milk there is a statistically significant difference (with the significance level of 0.05) between the ^{137}Cs separation from 500, 1 000 and 1 500 ml of milk. Within these limit the separation degree is independent of the volume of milk taken for the experiment.

Instructions for the Determination of ^{134}Cs and ^{137}Cs in One Liter of Naturally Contaminated Milk

On the basis of the ^{137}Cs separation conditions from the intentionally contaminated milk the following instructions for the determination of the ^{134}Cs and ^{137}Cs activity concentrations in the naturally contaminated milk have been worked out.

Consumer's 1.8% milk and whole milk: 3 drops of $4 \text{ mol l}^{-1} \text{ HNO}_3$, 2 ml of 0.25 mol l^{-1} solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ and 2.3 ml of 0.5 mol l^{-1} solution of $\text{Cu}(\text{NO}_3)_2$ are added to 20 ml of water in a polyethylene bottle. The precipitate formed is carefully mixed for 1 min and after 10 min standing and another 20 s mixing it is added to 1 l of milk in a polyethylene bottle. The sample is mixed for 2.5 min and after 30 min standing the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ precipitate is separated by centrifugation. The precipitate is transferred into a vessel suitable for the activity measurement (probe, dish) by repeated mixing with a small volume of water. The precipitate is then dried in the given vessel. Another possibility is first to dry the precipitate, then to crush it and finally to transfer it into a vessel suitable for measurement. The activity concentration of ^{134}Cs or ^{137}Cs in milk (in Bq l^{-1}) is then calculated from the count rate in the peak of total absorption, from the detection efficiency, and from the chemical yield of separation. For the determination of

TABLE III
Separation of ^{137}Cs from different volumes of intentionally contaminated milk

Milk volume ml	Volume of reagents used, ml		Ratio of ^{137}Cs activity (in per cent) in the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ precipitate		
	$0.25 \text{ mol l}^{-1} \text{ K}_4[\text{Fe}(\text{CN})_6]$	$0.5 \text{ mol l}^{-1} \text{ Cu}(\text{NO}_3)_2$	1.8% milk	whole milk	centrifugated raw milk
500	1.0	1.15	99.1 ± 0.9	97.8 ± 1.1	95.7 ± 1.2
1 000	2	2.3	98.4 ± 1.8^a	96.4 ± 1.6	95.3 ± 1.1
1 500	3	3.45	96.5 ± 0.9	95.6 ± 0.9	94.5 ± 1.4

^a Results are the mean values from 4 experiments, all other results are the mean values from 3 experiments.

radiocaesium in 1 l of milk by the method described above, the single value of the chemical yield, 96.2 per cent, can be generally used.

Raw milk: Fat is separated from the milk by centrifugation. The content of ^{134}Cs or ^{137}Cs in the milk is then determined using the same procedure as described for the consumer's 1.8% milk and whole milk.

Results of Control Tests

Table IV presents the results of the ^{137}Cs determination in 1 l of different kinds of naturally contaminated milk, using both the direct gamma-spectrometric measurement of ^{137}Cs activity in milk (DM) and the gamma-spectrometric measurement after separation (MS) of the freshly prepared precipitate of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$. The values of the ^{134}Cs activity concentration, that amounted in all samples to about 30 per cent of the ^{137}Cs volume activity, were not included in Tables IV and V for the sake of simplicity. The individual samples of 1.8% milk and whole milk came from different dairies and the samples of centrifugated raw milk were from different milk cows. As shown in Table IV a good agreement has been found between the activities of ^{137}Cs as determined in all samples by the two methods. The value of MS/DM for the given sample represents the chemical yield of ^{137}Cs separation by sorption on $\text{Cu}_2[\text{Fe}(\text{CN})_6]$. The *t*-test proved that there is no statistically significant difference between the values of MS/DM for different kinds of milk on the significance level of 0.05.

The results of the parallel determinations of ^{137}Cs in the consumer's 1.8% milk, whole milk and centrifugated raw milk are given in Table V. The given kind of milk was transferred into a polyethylene bottle (10 l) and after a thorough stirring 4 samples of the volume of 1 l were taken for the individual parallel analyses. This table shows a good agreement between the values of ^{137}Cs activities in all samples of all kinds of milk.

DISCUSSION

These results prove that the content of ^{134}Cs and ^{137}Cs in milk can be quickly determined with good reproducibility using the sorption on freshly prepared precipitate of Cu(II) hexacyanoferrate and the subsequent gamma-spectrometric measurement of the precipitate. The advantage of this method (in comparison with other radiochemical methods of caesium determination in milk) is given by the fact that neither total nor partial removal of organic substances from milk by mineralization which is a time consuming operation, is required. In comparison with the direct gamma spectrometry of ^{134}Cs and ^{137}Cs in milk this method allows to decrease the lower limit of the detectable activity concentration, to use shorter times of measure-

TABLE IV

Determination of ^{137}Cs activity concentration in different kinds of naturally contaminated milk, determined either by the direct semiconductor gamma spectrometry (DM) or by the gamma-spectrometric measurement after sorption on Cu(II) hexacyanoferrate (MS). In all cases the standard deviation is given by the precision of the activity determination using the semiconductor gamma spectrometry

MS (Bq l^{-1})	1.8% Milk				Whole milk				Centrifugated raw milk					
	DM (Bq l^{-1})	MS/DM	MS Bq l^{-1}	DM Bq l^{-1}	MS/DM	MS Bq l^{-1}	DM Bq l^{-1}	MS/DM	MS Bq l^{-1}	DM Bq l^{-1}	MS/DM	MS Bq l^{-1}	DM Bq l^{-1}	MS/DM
12.4 ± 0.8	13.9 ± 1.3	0.89	5.2 ± 0.6	5.0 ± 0.6	1.04	3.9 ± 0.5	3.5 ± 0.4	1.11	18.8 ± 1	22.0 ± 2	0.84	4.3 ± 0.6	4.1 ± 0.5	1.05
5.7 ± 0.6	5.3 ± 0.5	1.07	12.6 ± 1	13.2 ± 1.3	0.95	8.4 ± 1	9.6 ± 1	0.86	2.3 ± 0.4	2.2 ± 0.3	1.04	4.6 ± 0.5	5.5 ± 0.6	0.84
4.0 ± 0.6	4.1 ± 0.6	0.97	3.7 ± 0.3	4.1 ± 0.6	0.90	5.5 ± 0.5	5.8 ± 0.6	0.95	13.6 ± 0.5	15.0 ± 1.3	0.91	13.5 ± 1.5	14.9 ± 1.5	0.94
3.0 ± 0.3	2.7 ± 0.5	1.11	5.5 ± 0.5	5.8 ± 0.6	0.95	13.6 ± 0.5	15.0 ± 1.3	0.91	13.5 ± 1.5	14.9 ± 1.5	0.94	13.5 ± 1.5	14.9 ± 1.5	0.94
15.4 ± 1	16.2 ± 1.8	0.95	13.6 ± 0.5	15.0 ± 1.3	0.91	13.5 ± 1.5	14.9 ± 1.5	0.94	13.5 ± 1.5	14.9 ± 1.5	0.94	13.5 ± 1.5	14.9 ± 1.5	0.94
Average		0.99												0.96

ments, etc. These advantages result from the better geometry for the activity measurements as radiocaesium is concentrated in a small volume (~ 1 ml) of the sorbent.

In comparison to other inorganic ion exchangers, e.g., to ammonium phosphomolybdate¹⁰, the advantage of using hexacyanoferrates of transition metals for the separation of Cs from the milk is given – according to our opinion – by the fact that the separation process proceeds also in the region of neutral values of pH. As the acidity of cow's milk¹¹ is in the range of $\text{pH} = 6.3-6.8$, no adjustment of the milk pH is required before sorption. This fact is very important with respect to the sensitivity of the milk colloidal system¹¹ to the changes of pH (e.g., the coagulation of milk casein proceeds already at $\text{pH} = 4.6$).

The differences between the distribution of ^{137}Cs between fat on the milk's surface and the precipitate of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ after the centrifugation of the consumer's 1.8% milk and whole milk on one side and the raw milk on the other side (cf. Table II) can be explained by the different size of fat spherules in these kinds of milk and by the relation of these fat spherules to the finer fractions of the precipitate. The consumer's 1.8% milk and whole milk are homogenized milks, i.e., the diameter of fat spherules¹¹ is lower than $2\ \mu\text{m}$. On the other hand, the diameter of these spherules in raw cow's milk¹¹ is in the range $0.1-22\ \mu\text{m}$. We assume that during the centrifugation of raw milk, with added precipitate of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$, the finer fractions of the precipitate are carried away by the fat spherules to the surface of the liquid. This process is not possible in the case of the consumer's 1.8% milk or whole milk with spherules of fat less than $2\ \mu\text{m}$. Centrifugation of fat from the raw milk before adding the precipitate prevents the losses of radiocaesium due to this process.

The average chemical yields of ^{137}Cs separation (cf. Tables III and IV) from the naturally and intentionally contaminated milk under study using the fresh precipitate

TABLE V
Parallel determinations of ^{137}Cs in individual kinds of naturally contaminated milk

Parallel sample No.	Activity concentration of ^{137}Cs in milk, Bq l^{-1}		
	1.8% milk	whole milk	centrifugated raw milk
1	15.3	13.9	4.9
2	14.5	13.3	4.4
3	16.3	13.0	4.9
4	15.4	13.6	4.3
average	15.4 ± 0.8	13.5 ± 0.4	4.6 ± 0.3

of Cu(II) hexacyanoferrate are very close together. Comparing various pairs of these yields by the *t*-test, no statistically significant differences have been found on the significance level of 0.05. This good agreement allows us to use a single value of the chemical yield of the ^{137}Cs separation from 1 l of milk according to the instructions given above (the same situation is met in the separation and determination of ^{137}Cs or other radionuclides from various biological or environmental materials¹²⁻¹⁴). The value of this yield was found to be 96.2 per cent and it is given by the mean value from all yields of ^{137}Cs separation from 1 l of milk as obtained in our experiments.

However, the separation of ^{134}Cs and ^{137}Cs from milk using the freshly prepared precipitate of Cu(II) hexacyanoferrate has its own limits. Radiocaesium can be separated by this procedure only from milk that is completely homogeneous in all the volume. Only in such a milk the precipitate can be separated by the centrifugation. In a milk that is not homogeneous (e.g., in acidified milk) the precipitate is retained on the surface of the structures formed, decreasing thus the yield of separation. These changes are usually due to the activity of bacteria in the milk and they appear more often in the raw milk. The addition of a disinfectant (e.g., of formaldehyde in the amount of 2 ml of the 38% formaldehyde per 1 liter of milk) can postpone the formation of inhomogeneities in milk.

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