

B R8816156

ISSN 0101-3084

CNEN/SP

ipen Instituto de Pesquisas
Energéticas e Nucleares

A METHOD FOR DETERMINATION OF Sr-90 Y-90 BY USING EDTA
AND ION-EXCHANGERS-APPLICATION TO THE DETERMINATION
OF THOSE RADIOISOTOPES IN MILK

Célia Machado Silva e F. W. Lima

IPEN - PUB - 103

PUBLICAÇÃO IPEN 103

MAIO/1987

SÃO PAULO

**A METHOD FOR DETERMINATION OF Sr-90 Y-90 BY USING EDTA AND
ION-EXCHANGERS-APPLICATION TO THE DETERMINATION OF
THOSE RADIOISOTOPES IN MILK**

Célia Machado Silva e F. W. Lima

DIVISÃO DE RADIOQUÍMICA

**CNEN/SP
INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES
SÃO PAULO – BRASIL**

Série PUBLICAÇÃO IPEN

INIS Categories and Descriptors

B11

**EDTA
ION EXCHANGE
MILK
STRONTIUM 90
YTTRIUM 90**

A METHOD FOR DETERMINATION OF Sr-90 Y-90 BY USING EDTA AND ION-EXCHANGERS-APPLICATION TO THE DETERMINATION OF THOSE RADIOISOTOPES IN MILK

Célia Machado Silva e F. W. Lima

Este trabalho foi desenvolvido, em 1963, na Divisão de Radioquímica do então Instituto de Energia Atômica, IEA, hoje Instituto de Pesquisas Energéticas e Nucleares, com a intenção de preparar método que contornasse a precipitação prévia das proteínas ou então a evaporação de volume razoavelmente grande de leite (pelo menos um litro), seguida de calcinação do resíduo, e que pudesse ser aplicado de forma rotineira e sistemática para a determinação de Sr-90 em leite animal ou humano.

O trabalho é novamente trazido a conhecimento público, isto é, é republicado, esperando que seja de utilidade aos grupos brasileiros que estão envolvidos, presentemente, em determinação de radioatividade ambiental e de produtos de importância alimentar, tais como leite, em virtude dos acidentes nucleares que ocorreram no hemisfério norte. As atividades de Sr-90 encontradas nas amostras de leite, em 1963, poderão servir de referência para as que forem eventualmente determinadas no presente.

Trabalhos muito recentes sobre o assunto⁽¹³⁾, desenvolvidos pelo "Nordic Liaison Committee for Atomic Energy" apresentam método cuja etapa principal, isto é, complexação do Y-90 com EDTA, é a mesma do presente trabalho.

ABSTRACT

A method in which the complex of ethylenediaminetetraacetic acid (EDTA) with yttrium, used in conjunction with ion-exchangers for determination of Sr-90 is described. The method was applied to the determination of concentration of Sr-90 in milk, avoiding, in this way, protein elimination by acid precipitation or by evaporation of milk and ashing the residus.

Analysis of samples of milk from various places in the State of São Paulo, Brazil, were carried out and the results are reported. Values found are much lower than maximum permissible concentration.

UM MÉTODO PARA DETERMINAÇÃO DE Sr-90 Y-90 USANDO EDTA E RESINA TROCADAS DE ÍONS - APLICAÇÃO PARA A DETERMINAÇÃO DESSOS RADIOISÓTOPOS NO LEITE

RESUMO

Descreve-se o método desenvolvido para a determinação de Sr-90-Y-90 por meio de complexação com

ácido etilendiaminotetraacético (EDTA) e resinas trocadoras de íons. O método foi aplicado à determinação da concentração daquele radioisótopo em leite, evitando-se, dessa forma, a eliminação das proteínas por precipitação ácida ou por evaporação do leite e queima do resíduo.

Foram feitas análises de amostras de leite, procedentes de vários lugares no Estado de São Paulo, Brasil, apresentando-se resultados correspondentes. Os valores encontrados estão muito abaixo da concentração máxima permitível.

INTRODUCTION

Determination of Sr-90 in milk is usually carried out by lengthy procedures consisting of an initial protein separation, the protein being usually eliminated by acid precipitation, or by evaporation of milk and ashing of the residue. These methods are effective but are space and time consuming and search for simpler procedures is justifiable. Porter et al⁽¹⁾ developed a procedure in which yttrium citrate carrier is added to the milk sample and a volume of about one liter of milk is passed through a cationic ion-exchanger and next through an anionic exchanger. Yttrium is retained in the anion-exchanger, eluted, precipitated as oxalate, and counted. The total yield of the procedure, for recovery of yttrium, is reported as being of 55%.

The final counting of the separated Y-90, in low background counting systems, is usually of the order of 2 to 6 counts per minute for one liter sample of milk. Procedures that would give higher recovery for yttrium are always desirable in order to give samples with higher activities for the final counting determination.

The method described in this paper is based on the fact that yttrium-EDTA complex is much more stable than the yttrium-citrate complex. Citrate-ions and proteins are both major components of milk and yttrium would probably exist as the anionic complexes of those milk constituents. The retention of yttrium by the anionic ion-exchanger, on the process developed by Porter et al⁽¹⁾, is due to the existence of those complexes at the normal milk pH of 6.6 to 7.0, in accordance with the mentioned authors.

If yttrium-EDTA complex is added as carrier to the milk samples, a higher than 55% recovery will be obtained. For samples with very low content of Sr-90 - Y-90 a higher recovery of Y-90 will allow the determination of Sr-90 in milk with a higher precision.

In order to verify the method, samples of milk were purposely contaminated with Y-90 and Sr-90 at various activity levels, and the separation procedure described by Porter et al⁽¹⁾, as well as the one described in this paper, were applied. A Y-90 recovery of 55% was observed for the first method, in accordance with the value reported by Porter, and of 86% for the second.

Biological trace results are sometimes open to doubt because of possible differences in chemical form between radionuclides existing in the cow's milk and those purposely added to it afterwards. In order to decide if the tracer experiments mentioned above were valid, samples of milk were analysed by the procedure described in this paper, as well as by standard ashing procedures⁽²⁾. From Table I and II it is seen that results are in agreement, within experimental errors. Precision can be evaluated from the data presented in Table III in which duplicate and triplicate set of analysis, for various samples, are recorded.

Table I

Results of Analysis of Milk Samples to Which Known Amounts of Y-90 Were Added

Sample*	Activity Added (cpm/mL)	Activity Recovered (cpm/mL)	Recovered (%)
1	8871	7346	84.8
2	12066	10226	84.8
3	33600	28368	84.8
4	49480	25368	51.3

* Samples 1, 2 and 3 processed in accordance with method described in this work; sample 4, method described in ref. (1).

Table II

Results of Analysis of Samples of Milk for Sr-90

Sample	Type of Milk	Present Work	Ashing*
1	Powder, whole	6.1 pCi/100 g	6.1 pCi/100 g
2	Powder, skim	3.6 pCi/100 g	3.2 pCi/100 g
3	Fresh, whole	9.3 pCi/L	9.6 pCi/L

* Process described in ref. (2)

Table III

Results to Evaluate Precision of Analysis Carried out by the Method Proposed in this Paper

Sample	Sr-90 pCi/L
1	8.3 ± 0.1
	8.2 ± 0.1
2	9.3 ± 0.6
	10.1 ± 0.6
3	6.8 ± 0.9
	7.9 ± 0.9
4	10.9 ± 0.1
	10.8 ± 0.1
5*	6.1 ± 0.4
	6.3 ± 0.4
	6.6 ± 0.4

* Powder milk, pCi/100 g

MATERIALS AND REAGENTS

Glass column, with syphon, 5 cm diameter and 25 cm length (cationic exchanger).

Glass column, with syphon, 3 cm diameter and 18 cm length (anionic exchanger). Carrier solution of Y-EDTA. Dissolve 5.75 g of EDTA in concentrated ammonium-hydroxide. Add 15 mL from a solution of yttrium nitrate with concentration of 10 mg of yttrium per mL. Add ammonium hydroxide to adjust pH to 7 (universal indicator paper) and make to volume in a 50 mL volumetric flask.

Cation ion-exchanger, Amberlite IR-120, 30 to 50 meshes.

Anionic ion-exchanger, Amberlite IR-401, 30 to 50 meshes.

Prepare the 5 cm diameter column with 140 mL of cation exchanger. Put the exchanger in the sodium form by passing 1,000 mL of a 4 M sodium chloride solution at 5 mL per minute. Wash the excess of sodium chloride with deionized water. The exchanger is regenerated, after each analysis, with 500 mL of a 4 M sodium chloride solution.

Prepare the 3 cm diameter column with 30 mL of anion exchanger. Put the exchanger in the chloride form by passing 400 mL of a 2 M hydrochloric acid solution. Wash with deionized water until no more acid indication on the universal indicator paper is shown. After each analysis regenerate the exchanger with 200 mL of a 2 M hydrochloric acid solution.

METHOD

To one liter sample of milk 3 mL of formaldehyde at 40% and 2 mL of carrier solution of Y-EDTA, are added. The sample is stored under refrigeration at about 10° C, for 15 days, in order that secular equilibrium Sr-90-Y-90 may practically be attained.

The sample is transferred to a separatory funnel and passed through the cationic exchanger and next through the anionic exchanger columns at about 5 mL per minute. The flow is stopped when milk surface is at about 2 mm of the cationic exchanger. 200 mL of deionized water is next passed through the columns in order to remove the milk from the resin interstices. Next, warm water is passed until the resin is completely washed out of milk.

The anionic exchanger column is then eluted with 250 mL of 2 M hydrochloride acid solution at the rate of 1 mL per minute. The first portion of the eluate is disposed off. When the pH of the eluate reaches a value of 4 the next 100 mL of eluted fraction are collected. Thymol blue indicator is added, next concentrated ammonium hydroxide solution, up to yellow-rose colour of indicator, followed by 10 mL of a one molar solution of oxalic acid. The solution is stirred for two minutes. Ammonium hydroxide solution is again added until yellow-rose colour of the indicator and the precipitate is left to settle in a refrigerator for about one hour.

The precipitate is centrifuged, washed with 10 mL of hot water and centrifuged again. The precipitate is dissolved with 1 mL of hydrochloric-acid 6 M and 15 mL of hot water. If any insoluble material remains it is separated by centrifuging.

In order to precipitate the yttrium oxalate the solution is first treated with concentrated ammonium hydroxide up to yellow-rose colour of thymol blue indicator. 10 mL of oxalic acid one molar is added and the solution is stirred for about two minutes and a new portion of ammonium hydroxide is added until yellow-rose colour of the indicator. The precipitate is left standing for about one hour and then centrifuged. The precipitate is filtered by transferring with hot water, to a chimney type sintered glass filter, using medium porosity filter paper, and mounted for counting

The yttrium oxalate sample is counted in a low background counting system and a decay line is drawn to check purity by half-life determination. Zero time for the separation of Y-90 and Sr-90 is taken as half the time for the one liter sample to percolate through the ion exchangers columns.

RESULTS AND DISCUSSION

Table IV summarizes the results obtained for samples of milk from various places in the State of São Paulo, Brazil.

Table IV

Sr-90 In Milk Samples From Various Places in the State of São Paulo, Brazil
(August 1962 to February 1963) (picocuries/liter)

Place	August		September		October		November		December		January		February	
	Day	pCi/L	Day	pCi/L	Day	pCi/L	Day	pCi/L	Day	pCi/L	Day	pCi/L	Day	pCi/L
1	3	9.5	4	9.3	9	9.8	16	9.6						
	6	6.9	20	9.3	9	9.7								
	10	9.5	20	10.1	17	10.9								
	14	8.7	28	6.6	17	10.8								
	24	9.8	28	7.9										
	27	7.4												
	31	8.3												
	31	8.2												
2							27	9.6	17	10.0	8	10.0	5	10.9
									26	13.4	15	9.5		
											23	9.7		
											31	11.4		
3							27	2.6	17	3.4	8	2.7	1	2.1
									26	2.7	15	2.3	5	2.4
											23	1.5	6	2.4
4							27	6.6	17	5.1	8	2.8		
									26	3.4	15	3.8		
											23	4.3		
5							26	2.9	17	3.3	8	2.9	5	1.8
									26	4.0	15	2.4		
											23	1.9		
											31	1.9		

Amounts of Sr-90 for milk from places 3, 4 and 5 are lower than the ones from places 1 and 2. Milk from 3, 4 and 5 are from cows living, part of the time, in stables. Cows from places 1 and 2 are kept in open field most of the time, although they have their food supplemented by an amount of sugar beet and bean straw, when green pasture becomes scanty. Animals from places 3, 4 and 5 are fed with corn and cottonseed cakes, rice and, partly, natural green pasture⁽³⁾.

It has been shown by Tukey et al⁽⁴⁾, Russell et al⁽⁵⁾ Larson et al⁽⁶⁾, Nishita et al⁽⁷⁾ that Sr-90 will not move within the plant. The contamination is a consequence of a direct absorption of strontium deposited on the leaves and other exposed parts.

Corn and cottonseed cakes as well as rice rations are prepared from parts of the plants which are protected from direct exposure to fallout particles. This would give a lower concentration of Sr-90 in seeds and in cotton and corn cakes made up of them, such as the ones given to cows kept in stables (places 3, 4 and 5).

Cows from places 1 and 2 are fed, mainly, by green pasture, and also by sugar beet and bean straw. It is thus seen that their feeding habits are such that a prominent part of the food is composed of external or exposed parts of the plant. This might be the cause for a higher amount of Sr-90 in their milk.

Maximum permissible concentration of Sr-90 in milk has been reported as 80 picocuries per liter, Campbell⁽⁹⁾, quoted in Tentoni and Morisi⁽⁸⁾. Concentrations of that radioisotope in milk from places reported in Table IV are much lower than that value.

Milk samples listed on Table III have also been analysed for calcium content. The concentration of calcium is the same, within experimental errors, for milk from places 1, 2, 3, 4 and 5, meaning 1.3 grams per liter of milk. No correlation seems to exist for the calcium content and Sr-90 in the samples mentioned. The same lack of correlation may also be noticed in the data published by Campbell et al⁽¹⁰⁾. For those milk samples Sr-90 varied from 1.0 to 37.3 picocuries per liter and calcium from 1.01 to 1.33 grams per liter. It seems that the concentration of calcium is so much higher as compared to the very small concentration of the alkaline earth radioisotope Sr-90, that the small variation of calcium concentration found in milk will not affect the concentration of Sr-90.

Concerning the chemical processing of samples by using ion-exchangers, the method is much more simpler than the ashing procedures and can be carried out in shorter periods of time.

The higher stability constant of yttrium-EDTA, as compared to the complex yttrium-citric acid, makes the use of that complexing agent preferable to citric acid, as shown by the higher yield of 85%, as presented in this paper, compared to the yield of 55% obtained by using citric acid.

Stability of calcium and strontium ions with EDTA at the pH values at which the milk samples are percolated through the ion-exchangers, i.e., at pH values of about 6.5, is not high. However, at this pH value yttrium complexes very well with EDTA. In this way, by working with the milk samples at the pH conditions described, the formation of the anionic species Y-EDTA will be enhanced and the corresponding ones for the alkaline earths, Ca-EDTA and Sr-EDTA, will be diminished. Consequently, calcium and strontium will be retained efficiently by the cationic exchanger while the anionic Y-EDTA complex will pass through and be retained by the anionic exchanger.

From Table V it is seen that log K values for Y-citric acid is 3.6, while for Y-EDTA it is equal to 18.09; for Ca-citric acid it is equal to 3.22 and for Sr citric acid, 2.7. These figures show that the M-citric acid complex constants are lower than the M-EDTA constants and, consequently, the citric acid complexes would be more easily broken by the cationic exchanger than the EDTA complexes, specially in the range of pH at which milk is passed through the exchangers. This would result in a lower amount of yttrium absorbed, as negative complex, into the anionic exchanger as compared to the amount of

Table V
Stability Constants for Citric Acid and EDTA Complexes, Chaberek and Martell⁽¹¹⁾

	Log K
Ca Cit ⁻	3.22
Sr Cit ⁻	2.7
Y Cit	3.6
Ca EDTA ⁻⁻	10.59
Sr EDTA ⁻⁻	8.63
Y EDTA ⁻	18.09

yttrium complexed with EDTA for which the stability constant is very high. Moreover, the stability constants for Y-citric acid and Sr-citric acid are more closer to each other ($10^{3.6}$ and $10^{2.7}$, with a quotient equal to $10^{0.09}$; than the ones for Y-EDTA and Sr-EDTA ($10^{18.09}$ and $10^{8.63}$, with a quotient equal to $10^{9.46}$). This would result in a much larger possibility of yttrium being contaminated by strontium in the anionic exchanger, when using citric acid, as complexing agent, than when using EDTA.

One could not expect that in a complex solution such as milk, considerations based purely on stability constants of yttrium and strontium with citric acid or EDTA would permit to foresee theoretically the exact behaviour of the complexes and corresponding ions. However, the basic facts, as considered above, prevail as shown by the experiments.

As conclusion it can be said that the method presented in this paper avoids the cumbersome elimination of proteins by acid treatment or by concentrating and ashing the sample. The higher yield for Y-90 recovery, when using EDTA, as described, makes this complexing agent preferable to citric acid. Also, radiochemical purity of separated Y-90 is better when using EDTA. A complete chemical processing by the method presently described takes about eight hours with various samples being processed at same time by one single analyst.

Contamination of the separated Y-90 by other radioisotopes of rare earths, from fission products, was not observed. Rare earth elements are not absorbed from the gut and also are very poorly taken up by plants⁽¹²⁾. Determination of the half-life of the separated Y-90 from milk showed that contamination by other fission product radioisotopes did not occur.

ACKNOWLEDGEMENTS

The authors acknowledge with thanks the work of Mr. Silvio B. Herdade and Miss Olga Maffra, of the Nuclear Physics Division, on standardizing the counting equipment.

REFERENCES

1. PORTER, C.; CAHILL, D.; SCHNEIDER, R.; ROBBINIS, P.; PERRY, W.; KAHN, B. Determination of strontium-90 in milk by an ion exchange method. *Anal. Chem.*, **33**:1306, 1961.
2. NEWBOULD, P. *Estimation of Sr-90 in plant material and soil. Seminar, April 1962. Piracicaba, S.P., Escola Superior de Agricultura Luiz de Queiroz.*

3. LEÃO, RENATO L. Private communication.
4. TUKEY, H.B.; WITTEW, S. H.; BUKOVIC, M.J. Absorption of radionuclides by above ground plant parts and movement within the plant. *J. Agric. Food Chem.*, 9:106, 1961.
5. RUSSEL, R. S.; SQUIRE, H. M.; MARTIN, R. P. *The effects of operation hurricane on plants and soils*. Harwell, Berks, England, Atomic Energy Research Establishment, July 1955. (AERE-SPAR-3)
6. LARSON, K. H.; OLAFSON, J. H.; NEEL, J. W.; STEEN, A. J. *The uptake of radioactive fission products by radishes and ladino clover from soil contaminated by actual sub-surface detonation fallout materials*. Oak Ridge, Te., U.S. Atomic Energy Commission, 1953. (UCLA-272)
7. NISHITA, H.; ROMNEY, R. M.; LARSON, K. H. Uptake of radioactive fission products crop plants. *J. Agric. Food Chem.*, 9:101, 1961.
8. TENTONI, R. & MORISI, G. Radioattività "beta" di alcuni campioni di latte dell'Agro milanese. *Il Latte*, 33(11), 1959.
9. CAMPBELL, J. E. *The occurrence of strontium-90, iodine-131 and other radionuclides in milk*. May through April 1958 submitted to HALS by the US Public Health Service apud ref. 8, p. 19.
10. CAMPBELL, J. E.; MURTHY, C. K.; STRAUB, C. P.; LEWIS, K. H.; TERRIL, J. C. Radionuclides in milk. *J. Agric. Food Chem.*, 9:117, 1961.
11. CHABEREK, S. & MARTELL, A. E. *Organic sequestering agents*. New York, N. Y., Wiley, 1959.
12. LARSON, B. L. & EBNER, K. E. Significance of strontium-90 in milk: a review. *J. Dairy Sci.*, 41:1647, 1958.
13. TAIPALE, T. K. ed. *The sampling and analysing methods for radionuclides used in the nordic countries for environmental samples*. Stockholm, Nordic Liason Committee for Atomic Energy, 1965.