


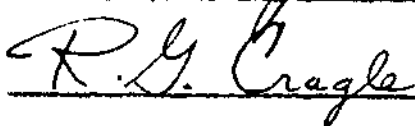
May 26, 1959

To the Graduate Council:

I am submitting herewith a thesis written by David Gene Easterly entitled "Removal of Strontium-89 and Calcium-45 from Milk by Use of Ion Exchange Resins." I recommend that it be accepted for nine quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Dairying.


Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:


Dean of the Graduate School

REMOVAL OF STRONTIUM-89 AND CALCIUM-45 FROM MILK BY
USE OF ION EXCHANGE RESINS

A THESIS

Submitted to
The Graduate Council
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the degree of
Master of Science

by

David Gene Easterly

June 1959

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Dr. B. J. Demott for his assistance in planning and conducting this study, and to Dr. R. G. Cragle for his guidance and assistance in helping to conduct this study. Great appreciation is due the UT-AEC Agricultural Research Laboratory, Oak Ridge, Tennessee, for facilities used in this study and especially to Dr. N. S. Hall, the Director, for encouragement and suggestions. Appreciation is also due R. C. McIlhenny for his advice and suggestions. The author is also exceedingly grateful to one and all of the laboratory staff for the help and advice so freely given.

TABLE OF CONTENTS

	PAGE
INTRODUCTION	1
REVIEW OF LITERATURE	2
Ion exchange	2
Radioactive strontium	7
Radiostrontium movement from atmosphere to milk	9
EXPERIMENTAL PROCEDURE	13
Removal of strontium-89 and calcium-45 from milk of dosed cows	13
Removal of Strontium-89 and calcium-45 from dosed milk	17
Post-milk and lactone-milk equilibrium studies	17
Removal of calcium-45 and strontium-89 from milk by use of a series of four columns	18
Removal of strontium-89 and calcium-45 from dosed milk by the batch method	19
RESULTS AND DISCUSSION	20
SUMMARY	22
BIBLIOGRAPHY.	50

LIST OF TABLES

TABLE	PAGE
I. Per Cent Removal of Sr ⁹⁰ and Ca ⁴⁵ from Milk of Dosed Cows by Exchange Resin Columns	21
II. Per Cent Removal of Sr ⁹⁰ and Ca ⁴⁵ From Dosed Milk by Exchange Resin Columns	23
III. Analyses of Variances From Eight Trials on Removal of Ca ⁴⁵ and Sr ⁹⁰ From Milk of Dosed Cows and Eight Trials on Removal of Ca ⁴⁵ and Sr ⁹⁰ From Dosed Milk	26
IV. Coagulation Time, Curd Tension, pH and Titratable Acidity of Milk Passed Through an Ion Exchange Column Containing Dowex 50W-X12 Calcium Form.	29
V. Effect of Resin-Milk Contact Time on Per Cent Removal of Sr ⁹⁰ and Ca ⁴⁵ From Dosed Milk	35
VI. Effect of Isotope-Milk Contact Time on Per Cent Removal of Sr ⁹⁰ and Ca ⁴⁵ From Dosed Milk.	37
VII. Per Cent Removal of Sr ⁹⁰ and Ca ⁴⁵ From Milk by Use of a Series of Four Exchange Resin Columns	39
VIII. Radioactivity Retained by Resin After Passage of Milk Containing Ca ⁴⁵ and Sr ⁹⁰	40

LIST OF TABLES (Continued)

TABLE	PAGE
IX. Effect of Milk-Resin Ratio on Per Cent Removal of Sr ⁹⁰ and Ca ⁴⁵ From Milk	41
X. Per Cent of Resin Capacity Exchange by Calcium and Strontium using the Batch and Column System	46

LIST OF FIGURES

FIGURE	PAGE
1. Modified Ion Exchange Column	14
2. Effect of Resin-Milk Contact Time on Per Cent Removal of Sr ⁸⁹ and Ca ⁴⁵ From Dosed Milk	36
3. Effect of Milk-Resin Ratio on Per Cent Removal of Sr ⁸⁹ and Ca ⁴⁵ From Milk	42
4. Relationship of Milk-Resin Ratio and the Percentage Exchange of Calcium-45 and Strontium-89	44

INTRODUCTION

The increased usage of nuclear power and the testing of atomic weapons have brought the problem of damaging effects of radiation to public attention. In recent months much publicity has been given the passage of strontium from the atmosphere into food and its accumulation in bone.

Due to its long half-life and its biological similarity to calcium, strontium is generally regarded to be one of the principal fission products which are of concern to the health of humans. The strontium level in milk has been steadily rising since 1954, the year adequate routine measures were first made. Since milk is the principal source of calcium of most Western Countries (people in the United States receive 85 per cent of their dietary calcium from milk products) (17) it has received attention as a source of strontium.

If the strontium content of milk could be reduced the overall strontium in the diet would be reduced.

The object of this investigation was to determine the feasibility of the use of ion exchange resins to remove strontium from milk.

REVIEW OF THE LITERATURE

Ion Exchange

Although the treatment of water by solid adsorbents such as sand is probably as ancient as civilization itself, the phenomenon of ion exchange was first recognized as such in soil experiments. In 1850, two Agricultural Chemists, Thompson (28) and Way (29) reported on exchange properties of certain soils. Their experiments showed that upon treating certain types of soils with either ammonium sulfate or ammonium carbonate most of the ammonia was adsorbed and lime was released. After further study they decided that such action was due to the complex silicates present in the soils, and concluded that ion exchange was taking place.

The first industrial use of ion exchange was attempted by Harms (13) in 1896. His effort to purify sugar juice by use of base exchange silicates was only partly successful. Gans (9), in 1906 also attempted to utilize ion exchange for industrial purposes. This experimenter employed both natural and synthetic aluminum silicates for the purpose of softening waters and for treating sugar solutions. A significant step in ion exchange history was the observation by Adams and Holmes (1) in 1935, that certain synthetic resins were capable of exchanging ions.

The explanation for the phenomenon of ion exchange may be grouped into three theories; the crystal-lattice exchange theory, the double-layer theory, and the Donnan membrane theory.

The crystal-lattice theory explains ion exchange by assuming that in an ionic solid the constituents of the crystal lattice are present as ions instead of molecules. Complete dissociation of the ionic solid is assumed. Each ion in the crystal is surrounded by a fixed number of ions of opposite charge, and since the coulomb attractive force between these ions is dependent upon the charge on the ions and the distance between them, the ions on the surface are bound less closely than those beneath the crystal surface. When placed in a medium such as water, these surface ions may be easily replaced by ions in solution.

The ease with which the surface ions may be replaced by another ion depends on (a) the nature of the forces binding the ion to the crystal, (b) the concentration of the exchanging ion, (c) the charge of the exchanging ion, (d) size of the two ions, (e) the accessibility of lattice ions, and (f) solubility effects (16).

The double-layer theory, as an explanation of the electrokinetic properties of colloids, has been considered by many to explain ion exchange. The exchange material is believed to be a fixed inner layer of charges surrounded by a diffuse and mobile outer layer of charges which extend into the external liquid media. There is no sharp boundary between the ions in the diffuse outer layer and those in the equilibrium external medium. It may be considered that the concentration of the ions constituting the diffuse layer as varying continuously and depending upon the concentration and pH of the external solution. Therefore, any change in the concentration of the ions in the external solution

upsets the equilibrium and a new equilibrium is obtained. Some of the ions held in the diffuse outer layer will be replaced by some of the new ions.

The Donnan membrane theory pertains to the unequal distribution of ions on two sides of a membrane, when one side contains ions too large to diffuse through the membrane. An unequal distribution will occur because of the undiffusible ions and the necessity of maintaining electroneutrality.

In applying the latter theory to ion exchange, the exchange material is assumed to be the ion too large to diffuse, and although in ion exchange no membrane is used, the interface between the solid and liquid phases is assumed to represent a membrane (16).

Otting (25) discusses the problems involved in the changing of equipment used for water treatment to a design which would be satisfactory from the sanitary viewpoint for ion exchange work in milk. The gravel in the bottom of the water softening device was replaced by a wire screen and a perforated plate to reduce the milkstone. Before a commercially feasible process resulted many changes in design of equipment and revival methods were necessary.

Milk can be modified by treatment with various types of organic ion exchange materials to produce certain desired characteristics. Haller and Morin (12) found that the type and extent of modification can be controlled at will by using the proper exchangers or combination of exchangers and by the proper regeneration of these exchangers. In one treatment these workers produced a soft curd milk of normal pH.

In another, approximately 20 per cent of the citrates, phosphates, and chlorides in addition to calcium and other cations were removed. Still another treatment removed citrates and chlorides and small amounts of calcium and other cations, but no phosphates.

In order to make cow's milk more suitable for the feeding of infants, modifications of the milk is necessary, particularly in the matter of curd tension. In 1930 Lyman (21) revealed that calcium could be removed from cow's milk by placing it in contact with greensand, a highly siliceous sand containing a little magnesia and alumina, and that the resulting milk exhibited soft-curd properties. This application of base-exchange silicates to the commercial treatment of dairy products was probably the first successful use of this principle in connection with a food product.

Murthy and Whitney (23) investigated the effect of mixed cation and anion resins upon the salt content of milk. The batch process was used to treat fresh raw skim milk with cationic and anionic resin mixtures at four different levels each. The pH and the calcium, sodium, and potassium content decreased with increases in cation resin concentration. Citrate, chloride, and sulfate content decreased with increases in anion resin concentration. The nitrogen content was not affected except when coagulation occurred.

Sasaki, et al. (26) studied the effects of treatment with ion exchange resin on heat coagulation of milk. Calcium was adsorbed on a cation exchanger of sulfonic acid structure but no clear relationship was observed between the removal of calcium and the temperature of heat coagulation of milk.

Gehrke and Almy (10) investigated the adsorption affinity to synthetic ion exchange resins of the cations and anions normal to milk. The relative order of adsorption of the cations from the synthetic whey solution was found to be Ca^{++} Mg^{++} K^+ Na^+ .

Baker and Gehrke (4) developed an ion exchange resin contact time method to study the equilibria of calcium in milk and to measure directly the ion-exchangeable calcium. They also reported (5) that heating skim milk to 40°, 60°, and 80° C. for 30 minutes had no noticeable effect on the exchangeability of calcium. However, the exchangeable calcium was significantly decreased as the temperature of heating increased from 100° to 120° C. for holding times of 30 minutes. Similar results were reported by Gehrke and Smith (11) who also observed that as the pH is increased the per cent of instantaneously exchangeable calcium decreases.

Two methods of recovering lactose from cheddar cheese whey were studied by McGlasson and Boyd (22). One method involved passing the original whey through ion exchange resins, removing the whey protein by heat treatment and further purifying the removed lactose solution with ion exchange resins. The second method differed from this only in that the original whey was not treated with ion exchange resins prior to the recovery of the protein fraction. Lactose with a higher degree of purity was recovered by the second method.

Josephson and Reeves (14) found that when mineral ion exchange treated milk was added to evaporated milk it was capable of stabilizing the evaporated product against coagulation during steriliza-

tion at 240° F. for 15 minutes. Mineral ion exchange milk was found to be effective in stabilizing milks exhibiting a wide range of instability to heat.

Nervik, et al. (24), by both a column and a bulk technique, removed nearly 90 per cent of the tracer isotopes of calcium and strontium from milk to which they had added isotopes, using Dowex-50W resin in the sodium form.

Radioactive Strontium

The strontium isotopes (mass numbers 84 through 94 and 97) may be formed as fission products and from the bombardment of other isotopes by nuclear particles. In the fission of Uranium-235 the strontium isotopes have a relatively large yield (about 5.8 per cent strontium-90). No radiation problem is presented by the stable isotopes of strontium 84, 86, 87 and 88. An isomeric form of strontium-87 and the isotopes 91, 92, 93, 94 and 97 have relatively short half-lives (range from ten hours to less than two minutes) and consequently, would decay rapidly compared to an isomeric form of strontium-85 and the isotopes 89 and 90, which have half-lives of 65 days, 55 days, and 25 years, respectively.

Strontium is one of the alkaline earths metals, belonging to Group II of the Periodic Table along with calcium, barium, and radium. Strontium-90 is generally regarded as the principal health hazard among the fission products since it is taken up by the human skeleton where it remains deposited for many years. The metabolism of stron-

tium has been found similar to that of calcium (2, 17, 15). Schulert and Peets (27) found that intravenously administered strontium-85 and calcium-45 in man were somewhat equally divided between bone and soft tissue for the first few days after administration but that after four months, about 99.5 per cent of the isotopes which were retained in the body were found in bone. The retention among the bones was greatest in vertebrae and least in long bone shaft and skull. Initially, the bone exhibited no marked preference for one isotope over the other, however, as strontium-85 was preferentially excreted by the kidney, the relative ratio of calcium-45 to strontium-85 remaining in bone gradually increased. The net retention of the isotopes appeared to level off at about 60 per cent for calcium-45 and 25 per cent for strontium-85. Although strontium retention in the body is less than calcium, the distribution throughout the body seems very similar.

Factors influencing the health hazards of strontium have been estimated by health physicists according to (1) quantities available, (2) initial body retention, (3) fraction going from blood to critical body tissue, (4) radiosensitivity of the tissue, (5) size of the critical organ, (6) biological half-life, (7) radioactive half-life, (8) energy of radiation produced by the radioisotope, and (9) specific ionization and attenuation of energy in tissue.

With the present knowledge, it is hardly possible to do more than broadly indicate the biological damage caused by strontium-90. However, the likely biological damage from ingestion of strontium-90 may be described under four headings: leukemia, bone tumor, life-shortening and genetic damage (6, 18).

According to Lewis (19) leukemia in man can be induced by ionizing radiations and can also occur spontaneously. He estimated that a 5 to 10 per cent increase in the current spontaneous incidence of leukemia would occur if the population were to reach and maintain a body level of strontium-90 amounting to one-tenth of the "maximum permissible concentration". The maximum permissible levels are recommended by the National Committee on Radiation Protection and Measurement and represent concentrations which are currently considered safe over a lifetime and which may occasionally be exceeded for short periods of time.

It has been demonstrated in laboratory animals that acute doses of radiostrontium cause bone tumors. As yet, nothing definite is known regarding the quantitative relationship between the magnitude of the dose and the incidence probability of bone tumors.

Radiostrontium Movement from Atmosphere to Milk

Radioactive fallout is the settling to earth of particles which are radioactive as a result of a nuclear explosion. Radiostrontium comes down mainly in raindrops. Part of the radiostrontium descending will lodge in plants, and part will enter the soil and then enter plants through their roots. The fraction which falls on leaves of growing plants is partially absorbed directly into the plant (7, 20).

Soil, like ion exchange resins, readily absorbs and retains most metal ions, including strontium. Approximately 80 per cent of the strontium-90 deposition is held in the top 2 inches of soil (7, 20).

About 50 per cent of the total is contained in the top one inch layer and the remaining portion in the soil to a depth of about 6 inches. The period for which radiostrontium stays in top-soil without becoming buried relatively deep, due to plowing, dispersion, or transformation into insoluble compounds, is not easily estimated, but probably extends over several years. Many factors, however, such as the nature of the soil, the extent of leaching by rain, the action of worms, and the cracking of the soil in dry weather, will affect the depth of penetration (7).

Very little is known about the actual mechanism of absorption and uptake of metal ions by plants but as strontium is chemically similar to calcium, it is reasonable to assume that calcium and strontium are absorbed in the same manner. The growing plant discriminates against strontium in favor of calcium at the ratio of about 2 to 1 (20). The absorption of strontium-90 by plants in a season is of the order of one per cent of the amount present in soil, the highest values in plants being in leaf tissue (7).

Animals markedly discriminate against strontium relative to calcium in their absorption of these elements from feed. The strontium activity in milk expressed as per gram of calcium present, is much below its value in the animal's ration. The experiments of Comar, et al. (7) and those of Cragle and Demott (8), have shown that the ratio of the strontium concentration in the animal's ration to that in the milk to be about 7-10 to 1. The cow acts as a barrier resisting the flow of strontium along the food-chain from soil to man. This

means that the strontium concentration (per gram of calcium) in milk is only about one-seventh to one-tenth of what it is in the feed the cow eats.

Since strontium and calcium metabolism are very closely associated, concentrations of strontium are generally expressed in terms of calcium. The most common and convenient unit for this purpose is the sunshine unit or sometimes called the Strontium Unit (S.U.), which is equal to the number of micromicrocuries of strontium-90 per gram of calcium. In itself it is not an absolute amount of strontium-90 but applies only to calcium contamination with strontium-90; and it provides a direct measure of this specific contamination. The maximum permissible body burden of strontium-90 for the general public is 0.1 microcurie, corresponding to 100 S. U. (as of April 22, 1959, unofficially 200 S. U.). On the basis of extensive experience of radiologists and technicians in work with X-rays and radium therapy, limited animal experimentations, experience with man and comparison with background concentrations of naturally occurring radioisotopes in our bodies, in the air we breathe and in the water and food we consume, the U. S. National Committee on Radiation Protection has recommended maximum permissible amounts and concentrations of radiation exposure.

The yearly average for the period ending July 1958 for strontium-90 in milk ranged from 4.2 to 10.2 micromicrocuries per liter, as compared to the permissible limit of 80 (unofficially 100 as of

April 22, 1959) micromicrocuries per liter (3). However, the strontium-90 level in milk has been steadily rising since the first adequate measurements were taken in 1954, roughly, in proportion to the rise in the level of strontium-90 deposition in soil. There has been approximately a fourfold increase in the average world strontium-90 content of milk from 1954 to the level of 5-6 S. U. in 1958 (17).

EXPERIMENTAL PROCEDURE

Removal of Strontium-89 and Calcium-45 from Milk of Dosed Cow

Eight daily milk samples from four Jersey cows dosed orally with one dose of calcium-45 and strontium-89 was separated mechanically by use of a DeLaval Junior Model 3300 separator and the skim milk passed through an ion exchange column at room temperature. The columns were 18 mm in diameter and 2½ inches long and contained 50 grams of either Dowex 50-W, 50-100 mesh cross linkage of 4 per cent; Duolite C-20; or Dowex 50-W, 50-100 mesh with a cross linkage of 12 per cent. These resins are strongly acidic, cross-linked polystyrene cation exchangers. Preliminary results indicated that the conventional downflow system could not be used due to packing of the resin, making it impossible to put the desired quantity of effluent through the column. Therefore, the upflow system was used (see Fig. 1) in which solutions were passed in at the bottom and out at the top of the container. Due to the turbulent action caused by the milk entering the bottom this system can not be called a true column action since the "layering" effect associated with column action is not present. Flow rate was adjusted to approximately 7 milliliters per minute to avoid channeling and control contact time.

Both the calcium and sodium form of each of these resins were tested for its effectiveness in the removal of strontium-89 and calcium-45 from skim milk. After initial conditioning of the resin, one liter of milk was passed through each column before the resin was

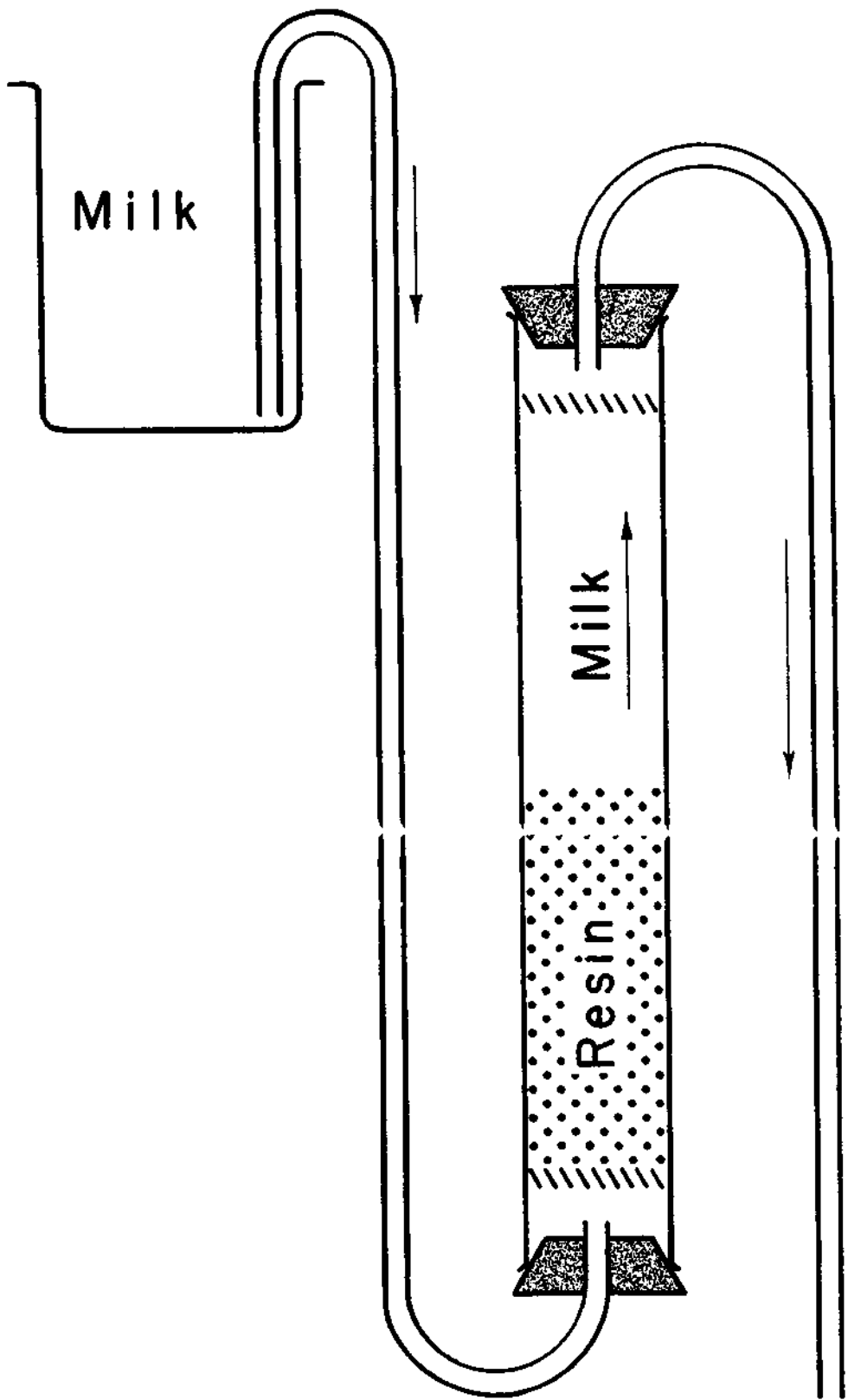


Figure 1. Modified Ion Exchange Column.

again regenerated. After each operation the cations bound by the resin were eluted by treatment with approximately 1500 milliliters of approximately 3 N hydrochloric acid. The columns were then washed with sufficient quantities of calcium chloride or sodium chloride to convert the exchangers into the desired form, followed with 100 to 200 milliliters of distilled water to wash the excess calcium or sodium chloride from the resin. The 2nd, 6th and 10th 100 milliliter portions coming through the column were sampled for analysis. Two twenty-five milliliter samples of milk were taken from each of the 100 milliliter portions. The samples were transferred to porcelain crucibles and dried in an oven at 90-100° C. for a minimum of 16 hours. They were then transferred to a muffle furnace and ashed at 600° C. for approximately 16 hours. Approximately 2 ml of hydrochloric acid was added to the ashed samples to bring the calcium and strontium into solution. The samples were then transferred quantitatively to a 40 milliliter centrifuge tube. One drop of methyl red was added as an indicator. The calcium and strontium were precipitated by adding 3 milliliters of saturated ammonium oxalate, then, by neutralizing the sample with ammonium hydroxide until the solution was faintly alkaline, and by adjusting the solution to a final pH of approximately 5.0 using acetic acid. After the solution was allowed to stand overnight for complete precipitation of the calcium and strontium oxalate, it was centrifuged and the precipitate washed twice with distilled water and transferred quantitatively into a tared cup-and-tube assembly. This assembly consisted of a tapered-end polyethylene cylinder with a

stainless-steel Tracerlab cup forming the bottom. The 4-inch plastic tube was pressed securely into the cup until the assembly was water-tight.

Following centrifugation at 1800 revolutions per minute (920 times gravity) for 10 minutes in a 20 inch diameter International centrifuge, the supernatant was drawn off and the cup removed and dried to a constant weight in an oven at approximately 60° C. The samples were then measured for radioactivity by conventional methods using a thin mica window Geiger-Müller tube connected to a scaler unit.

The activity measurements of calcium-45 are greatly dependent upon the mass of the sample measured primarily because of self-absorption of its relatively low beta energy (0.26 Mev.). The total calcium and the correction for self-absorption were calculated from the mass weight of the oxalate in the dry cup.

All samples were counted with an aluminum absorber of 54.5 or 66.6 mg/cm² and again with no absorber. Both of these absorbers will stop essentially all the calcium-45 beta rays from the sample and will reduce the strontium-89 counts by factors of 1.39 and 1.50 respectively. Therefore, when no absorber was used the activity was due to both isotopes but when the same sample was measured again with an absorber the activity represented a portion of the strontium-89 only. The calcium-45 contribution was calculated by difference. The observed count with the aluminum absorber present, times the appropriate factor represents the corrected strontium-89 count. The total observed count

with no absorber present, minus the corrected strontium-89 count, times the mass correction factor for calcium oxalate self-absorption represents the corrected calcium count.

The same procedure as described above was used for duplicate samples of standards, having no resin contact.

Removal of Strontium-89 and Calcium-45 from Dosed Milk

In this experiment "dosed milk" was used instead of milk from "dosed cows". Here the calcium-45 and strontium-89 were put directly into the milk instead of being administered to the cow. Calcium-45 and strontium-89 were put into fresh raw whole milk at approximately 4 P. M., mixed thoroughly and left undisturbed for 16 hours at 40° F. The following morning the milk was thoroughly mixed again, heated in a water bath to 30° C., and mechanically separated. After bringing the skim milk to room temperature the procedure described previously was followed.

Resin-milk and Isotope-milk Equilibrium Studies

In order to determine how long an ion exchange resin must be in contact with milk containing calcium-45 and strontium-89 to reach equilibrium, a liter of raw skim milk was dosed with calcium-45 and strontium-89, mixed thoroughly and left undisturbed for approximately 16 hours at 40° F. After heating the milk to room temperature, four-100 milliliter samples were put into 250 milliliter beakers and 5 grams of Dowex 50-W, X-12, 50-100 mesh, in the calcium form were added to each beaker. After one minute of mixing, sample one was filtered and two

25 milliliter milk samples ashed, precipitated with ammonium oxalate and counted. The same procedure was followed for samples two, three and four after 10, 60, and 120 minutes of agitation respectively. All samples were mixed by hand for the first minute and by use of a mechanical agitator thereafter. Two 25 milliliter samples of milk having no resin contact were used as standards. The percentage removal of calcium-45 and strontium-89 was calculated for each contact time.

In order to determine how long a sample of milk must be in contact with calcium-45 and strontium-89 for the sample to reach equilibrium, four - 100 milliliter samples of raw skim milk at room temperature were dosed with calcium-45 and strontium-89. After mixing for 1, 10, 30 and 60 minutes the samples were treated by exposure to 5 grams of Dowex 50-W, X-12, 50-100 mesh, in the calcium form for 60 minutes after which the samples were filtered by use of a suction funnel. Two 25 milliliter samples from each exposure time were ashed, precipitated with ammonium oxalate and counted. The percentage removal of calcium-45 and strontium-89 was calculated for each exposure time.

Removal of Calcium-45 and Strontium-89 from Milk by Use of a Series of Four Columns

One liter of milk was passed through a series of four columns, each containing 12.5 grams of Dowex 50-W, X-12, 50-100 mesh in the calcium form. The 2nd, 6th and 10th 100 milliliter portions passing through the last column were sampled for analysis in the same manner as described previously. This experiment was repeated four times. Following the last run the four columns were disconnected and the

resin was washed with 1 liter of 3 N hydrochloric acid. Samples of the eluate from each of the four columns were assayed for radioactivity.

Removal of Strontium-89 and Calcium-45 from Dosed Milk by the Batch Method

Raw skim milk was dosed with calcium-45 and strontium-89, agitated thoroughly by hand and left undisturbed for approximately 16 hours at 40° F. After heating the milk to room temperature six - 200 milliliter samples were put into 400 milliliter beakers and 1, 5, 10, 20, 40, and 100 grams of Dowex 50-W, X-12, 50-100 mesh, in the calcium form, were added. After mechanical agitation for four hours the samples were filtered by use of a suction funnel. Two - 25 milliliter milk samples from each beaker were dried, ashed, precipitated with ammonium oxalate, dried and counted. Two 25 milliliter samples of milk having no resin contact were used as standards. The percentage removal of calcium-45 and strontium-89 was calculated for each quantity of resin.

RESULTS AND DISCUSSION

Values for the percentage of removal of strontium and calcium, from milk of dosed cows, by use of ion exchange resins are summarized in Table I. Significant differences were noted between resins, between ionic form of the resin as well as between portions passed through the column. Results indicate that Dowex 50-W, with a cross linkage of 12 per cent, in the calcium form is the most effective resin tested for removal of strontium-89 and calcium-45 from milk. From these data it is suggested that exchange of like (Ca-Ca) or similar (Ca-Sr) ions is more easily accomplished than the exchange of unlike (Na-Ca or Na-Sr) ions from milk. All three resins in the calcium form showed a slightly higher percentage of removal of strontium than calcium for all samples tested, although the degree varied with resins and the portion of milk passed through the column. A higher removal of strontium and calcium was attained in the first portion of milk passed through the columns as compared to other portions. The percentage removal decreased as the amount of milk passed through the column increased.

The same general conclusions may be drawn from the data presented on removing strontium and calcium from dosed milk (Table II). However, between resins, between ionic form of the resin and between the portion of milk passed through the column, no significant differences for removal of calcium were shown. There was no significant difference between resins for removal of strontium from dosed milk, whereas in the case of milk from dosed cows, between resins, between

TABLE I

PER CENT REMOVAL OF Sr⁹⁰ AND Ca⁴⁵ FROM MILK OF DISED COWS BY EXCHANGE RESIN COLUMNS

Trial	100 ml. Portion of Klutriated Milk Sample	Ca form of resin						Sr form of resin					
		Dowex 50W-4X			Duolite C-20			Dowex 50W-12X			Duolite C-20		
		Sr	Ca		Sr	Ca		Sr	Ca		Sr	Ca	
1	2nd	67	80	73	79	66	62	14	48	44	68	1	47
	6th	55	53	60	59	38	52	5	39	16	52	1	51
	10th	52	40	38	51	44	52	0	31	0	34	0	48
2	2nd	75	80	78	78	64	56	31	48	69	71	12	35
	6th	50	50	68	61	54	45	13	30	42	51	3	28
	10th	55	38	55	48	48	39	0	16	17	30	0	26
3	2nd	60	61	61	52	63	58	29	36	65	70	0	22
	6th	67	58	53	53	48	41	7	19	34	35	0	10
	10th	35	34	44	41	46	39	0	2	18	21	0	10
4	2nd	84	72	82	77	68	59	49	60	79	80	19	50
	6th	59	58	54	56	54	53	9	36	46	56	5	39
	10th	48	46	46	50	50	44	0	22	12	36	9	29
5	2nd	76	74	76	74	65	69	40	57	54	78	0	43
	6th	60	57	60	53	65	54	10	33	38	55	0	34
	10th	36	41	52	48	45	43	0	17	35	31	0	26

TABLE I (continued)

PER CENT REMOVAL OF Sr⁸⁹ AND Ca⁴⁵ FROM MILK OF DISED COWS BY EXCHANGE RESIN COLUMNS

Trial	100 ml. Portion of Klutriated Milk Sample	Ca form of resin						Na form of resin					
		Dowex		Dow x		Duolite		Dowex		Dowex		Duolite	
		50M-4X Sr	Ca	50M-2X Sr	Ca	C-20 Sr	Ca	50M-4X Sr	Ca	50M-12X Sr	Ca	C-20 Sr	Ca
6	2nd	86	74	67	70	70	58	33	42	67	69	4	40
	6th	56	56	60	64	66	44	0	38	40	54	0	28
	10th	58	37	48	45	41	36	3	18	7	39	3	11
7	2nd	81	81	85	89	73	71	37	46	67	64	0	44
	6th	69	53	58	55	65	46	13	26	31	66	4	34
	10th	48	38	50	48	50	35	0	21	2	30	0	19
8	2nd	82	81	86	74	89	77	23	51	64	43	0	30
	6th	59	18	50	46	48	49	7	26	25	40	0	43
	10th	23	39	48	36	43	43	0	20	0	25	0	40
Average	2nd	76	75	76	74	70	64	32	49	64	68	4	39
	6th	59	50	58	56	55	48	8	31	34	51	2	33
	10th	44	39	48	46	46	41	0	18	11	31	2	26

TABLE II

PER CENT REMOVAL OF Sr⁹⁰ AND Ca⁴⁵ FROM DODED MILK BY EXCHANGE RESIN COLUMNS

Trial	100 ml. Portion of Elutriated Milk Sample	Ca form of resin						Sr form of resin					
		Dowex 50W-4X			Dowex 50W-2X			Dowex 50W-4X			Dowex 50W-12X		
		Sr	Ca	Ca	Sr	Ca	Ca	Sr	Ca	Sr	Ca	Sr	Ca
1	2nd	83	83	89	79	78	71	61	70	87	88	20	38
	6th	71	64	68	70	55	54	33	30	59	66	0	24
	10th	61	53	65	62	43	44	12	36	34	39	0	16
2	2nd	75	79	75	78	68	65	33	50	57	69	6	40
	6th	64	61	62	65	56	62	14	32	40	49	0	20
	10th	54	45	59	59	50	57	0	39	12	36	0	22
3	2nd	76	81	78	80	62	60	31	49	60	74	8	45
	6th	56	57	62	64	49	47	9	40	38	56	0	30
	10th	50	54	58	49	41	55	0	22	9	41	0	18
4	2nd	84	72	80	76	64	56	30	54	68	74	16	34
	6th	73	15	67	62	55	49	21	35	36	55	6	19
	10th	63	41	58	38	35	41	0	22	22	28	0	20
5	2nd	81	77	72	72	72	69	60	61	62	60	28	35
	6th	61	61	61	47	55	47	28	32	48	42	15	28
	10th	55	35	53	34	47	35	6	22	30	33	0	11

TABLE II (continued)

PER CENT REMOVAL OF Sr⁹⁰ AND Ca⁴⁵ FROM DOSED MILK BY EXCHANGE RESIN COLUMNS

Trial	100 ml. Portion of Elutriated Milk Sample	Ca form of resin						Sr form of resin					
		Dowex 50W-4X			Dowex 50W-12X			Dowex 50W-4X			Dowex 50W-12X		
		Sr	Ca	Ca	Sr	Ca	Ca	Sr	Ca	Ca	Sr	Ca	Ca
6	2nd	81	74	81	82	78	88	47	55	69	71	34	50
	6th	64	53	67	61	60	56	28	38	54	56	17	34
	10th	54	44	62	57	54	49	30	26	34	33	11	28
7	2nd	76	59	75	63	63	41	48	38	71	68	18	9
	6th	55	30	66	40	55	29	27	3	50	36	9	0
	10th	52	21	54	26	41	3	7	0	30	0	22	0
8	2nd	73	78	76	82	66	69	38	46	59	70	6	42
	6th	56	57	63	63	53	57	20	36	38	50	0	26
	10th	52	45	52	50	41	41	5	19	20	28	0	17
Average	2nd	79	75	77	76	69	64	44	53	67	72	17	37
	6th	63	50	65	59	55	50	23	31	45	51	6	23
	10th	55	42	58	47	44	41	8	22	24	30	4	17

ionic forms of the resin and between portions of milk passed through the column were all significantly different. Using Dowex 50W-XL2 in the calcium form, the percentage removal of strontium decreased at a faster rate, as measured by the amount of milk passed through the column, when metabolized milk was used, as compared to milk which was dosed 16 hours before the exchange treatment. The average of eight trials showed 76, 59 and 45 per cent removal of the strontium from metabolized milk on samples from the 2nd, 6th and 10th 100 milliliter portions of milk respectively and 79, 63 and 55 for the equivalent samples when dosed milk was used. The removal of strontium from dosed milk is significantly different ($P < .01$) from the removal of strontium from milk of dosed cows while no significantly different removal of Ca^{45} was noted under the same circumstances. This may be due to the incorporation of strontium into the protein molecule in metabolic milk, whereas in dosed milk this would not likely be the case.

Data from eight trials on removal of calcium and strontium from milk of dosed cows and data from a similar experiment using dosed milk were subjected to analyses of variances. The F values for the main effects, and first and second order interactions in these experiments are presented in Table III. Significant differences were noted between resins for the removal of both calcium-45 and strontium-89 milk of dosed cows but not for the removal of either from dosed milk. Significant differences were noted between days following dosing of the cow for the removal of calcium-45 from milk and also

TABLE III

ANALYSES OF VARIANCES FROM EIGHT TRIALS ON REMOVAL OF Ca⁴⁵ AND Sr⁹⁰ FROM MILK OF
Dosed Cows AND EIGHT TRIALS ON REVAL OF Ca⁴⁵ AND Sr⁹⁰ FROM Dosed MILK

Total	Dosed Cows - Sr ⁹⁰		Dosed Milk - Sr ⁹⁰		Dosed Cows - Ca ⁴⁵		Dosed Milk - Ca ⁴⁵	
	F Value	Tested by	F value	Tested by	F Value	Tested by	F Value	Tested by
Resins	8.12*	RFS	3.02 NS	RF	23.15**	RD	4.35	RF
Days	2.55 NS	DF	2.50 NS	DF	4.88**	RD	29.62**	Error
Form	657.45**	DF	21.76*	RF	77.81*	FS	15.33 NS	RF
Samples	16.85**	RFS	25.37**	RFS	75.10*	FS	40.38**	BS
RD	NS	Error	2.2*	Error	3.28**	Error	1.60 NS	Error
RF	NS	RFS	6.43**	RFS	6.08 NS	RFS	16.54**	Error
BS	NS	RFS	NS	RFS	3.44 NS	RFS	5.33**	Error
DF	2.56*	Error	8.70**	Error	2.21 NS	Error	1.19 NS	Error
DS	2.00 NS	Error	1.05	Error	1.57 NS	Error	0.98 NS	Error
FS	NS	Error	NS	RFS	4.38*	Error	0.43 NS	Error

TABLE III (continued)

ANALYSES OF VARIANCES FROM EIGHT TRIALS ON REMOVAL OF Ca⁴⁵ AND Sr⁹⁰ FROM MILK OF
 Dosed Cows AND EIGHT TRIALS ON RE MOVAL OF Ca⁴⁵ AND Sr⁹⁰ FROM Dosed MILK

Total	Dosed Cows - Sr ⁹⁰		Dosed Milk - Sr ⁹⁰		Dosed Cows - Ca ⁴⁵		Dosed Milk - Ca ⁴⁵	
	F Value	Tested by	F Value	Tested by	F Value	Tested by	F Value	Tested by
RDF	NS	Error	2.05 NS	Error	1.64 NS	Error	0.62 NS	Error
RDS	NS	Error	1.05 NS	Error	1.28 NS	Error	0.68 NS	Error
RFS	14.00**	Error	16.95**	Error	3.46*	Error	1.68 NS	Error
DFS	1.59 NS	Error	0.7 NS	Error	3.75**	Error	0.68 NS	Error
CV	15.7%		10.3%		11.4%		15.3%	

*P < .05

**P < .01

between trials conducted on different days on dosed milk. Strontium-89 removal was not significantly different for either. Significant differences on the removal of calcium-45 and strontium-89 between portions passed through the column (samples) were noted on both dosed milk and milk from dosed cows.

Raw skim milk, without the addition of isotopes, was passed through an exchange column identical to the ones used for milk containing the isotopes. Data on the titratable acidity, curd tension, pH, and rennet coagulation time are shown in Table IV. Before the milk was passed through the exchange column the average pH was approximately 6.71, titratable acidity 0.162 per cent, coagulation time 490.6 seconds, curd tension 61 grams, and the taste was that of normal raw skim milk. The first 100 milliliters of milk passed through the column had a slightly lower pH, a higher titratable acidity, higher curd tension and a lower rennet coagulation time compared to the standard. Under conditions which removed the highest percentage of strontium and calcium from milk, these effects were more pronounced. Therefore, as more milk was passed through the column the closer these properties approached normal milk with the exception of curd tension which continued to increase. The shorter rennet coagulation time is partially indicative of a higher calcium content in treated milk. As calcium concentration increases it tends to form calcium hydrogen phosphate, releasing hydrogen ions from calcium dihydrogen phosphate consequently lowering the pH. Milk so treated (without added radioactivity) was

TABLE IV

COAGULATION TIME, CURD TENSION, pH AND TITRABLE ACIDITY OF MILK PASSED THROUGH AN ION EXCHANGE COLUMN CONTAINING DOWEX 50M-X12 CALCIUM FORM

Trial	Control	100 ml. Portion of Kilterated Milk Sample													
		1	2	3	4	5	6	7	8	9	10	11			
1	Coagulation Time (Sec)	480	40	52	98	85	113	121							
	Curd Tension (grams)	60	110	108	85	140	160	120							
	pH	6.75	6.1	6.07	6.11	6.18	6.21	6.28	6.29	6.31	6.38	6.41	6.41		
	Per Cent Acidity	.164	.18	.20	.195	.19	.195	.195							
2	Coagulation Time (Sec)	485	26	36	43	61	81	108							
	Curd Tension (grams)	60	80	130	115	132	130	127							
	pH	6.7	6.1	6.00	6.05	6.1	6.15	6.2	6.22	6.28	6.3	6.35	6.38		
	Per Cent Acidity	.16	.195	.20	.195	.19	.195	.19							

CABLE IV (continued)

COAGULATION TIME, CURD TENSION, pH AND TITRATABLE ACIDITY OF MILK PASSED THROUGH AN ION EXCHANGE COLUMN CONTAINING DOWEX 50W-X12 CALCIUM FORM

Trial	100 ml. Portion of Enriched Milk Sample											
	Control	1	2	3	4	5	6	7	8	9	10	11
3	Coagulation Time (Sec)	525	26		36	54	75	90	90	110		
	Curd Tension (grams)	58	70	120	135	150	150	190	190	140		
	pH	6.7	5.98	6.05	6.1	6.1	6.21	6.25	6.32	6.38	6.38	6.39
	Per Cent Acidity	.165		.195	.20	.195	.195	.19	.19	.185		
4	Coagulation Time (Sec)	522	26	35	54	82	90	90	114			
	Curd Tension (grams)	60	80	130	135	140	150	150	135			
	pH	6.7	6.2	6.05	6.1	6.18	6.24	6.25	6.32	6.38	6.44	6.45
	Per Cent Acidity	.16		.19	.195	.19	.195	.19	.195	.19		

TABLE IV (continued)

COAGULATION TIME, CURD TENSION, pH AND TITRATABLE ACIDITY OF MILK PASSED THROUGH AN ION EXCHANGE COLUMN CONTAINING DOWEX 50W-XL2 CALCIUM FORM

Trial	Control	100 ml. Portion of Elutriated Milk Sample										
		1	2	3	4	5	6	7	8	9	10	11
5	Coagulation Time (Sec)	455	24	34	34	53	69	89	89	108		
	Curd Tension (grams)	58	76	120	140	140	150	160	160	140		
	pH	6.7	6.2	6.1	6.2	6.23	6.29	6.32	6.33	6.38	6.4	6.45
	Per Cent Acidity	.165	.195	.205	.200	.195	.195	.19	.195	.19		
6	Coagulation Time (Sec)	485	23	34	54	67	91	111				
	Curd Tension (grams)	70	80	140	144	142	152	140				
	pH	6.68	6.12	6.18	6.19	6.23	6.28	6.3	6.33	6.35	6.4	6.4
	Per Cent Acidity	.165	.195	.20	.20	.20	.195	.19	.195	.19		

TABLE IV (continued)

COAGULATION TIME, CURD TENSION, pH AND TITRATABLE ACIDITY OF MILK PASSED THROUGH AN ION EXCHANGE COLUMN CONTAINING DOWEX 504-X12 CALCIUM FORM

Trial	Control	100 ml. Portion of Elutriated Milk Sample																		
		1	2	3	4	5	6	7	8	9	10	11								
7	488	26	43	64	72	93	114													
	Coagulation Time (Sec)																			
	60	70	110	128	140	130	125													
	Curd Tension (grams)																			
	6.72	6.12	6.18	6.22	6.29	6.38	6.39	6.4	6.48	6.48	6.49									
	pH																			
	.16	.195	.195	.195	.195	.195	.185													
	Per Cent Acidity																			
8	485	22	36	54	71	92	116													
	Coagulation Time (Sec)																			
	63	90	120	138	145	135	119													
	Curd Tension (grams)																			
	6.7	6.08	6.1	6.2	6.28	6.3	6.33	6.39	6.4	6.46	6.48									
	pH																			
	.16	.195	.20	.195	.19	.19	.19													
	Per Cent Acidity																			

TABLE IV (continued)

COAGULATION TIME, CURD TENSION, pH AND TITRATABLE ACIDITY OF MILK PASSED THROUGH AN ION EXCHANGE COLUMN CONTAINING DOWED 50W-X12 CALCIUM FORM

Trial	Control	100 ml. Portion of Elutriated Milk Sample											
		1	2	3	4	5	6	7	8	9	10	11	
Avg. Coagulation Time (Sec)	490.6	26.6	38.2	59.1	71.5	92.3	112.7						
Curd Tension (grams)	61	82	121.9	127.5	142.4	158.7	130.8						
pH	6.71	6.12	6.05	6.17	6.23	6.27	6.29	6.34	6.38	6.41	6.43		
Per Cent Acidity	.162	.192	.199	.196	.192	.189							

tasted and found to have a slightly bitter flavor in those samples which exhibited the largest pH drop.

Data on the removal of strontium and calcium from milk as influenced by the resin-milk contact time are presented in Table V. All contact times were made on a milk-resin ratio basis of 20 to 1 using the batch techniques. Times of 1, 10, 30 and 60 minutes were used. The average of three trials showed 62 per cent strontium-89 and 52 per cent calcium-45 were removed after a contact time of one minute, while 76 per cent strontium-89 and 67 per cent calcium-45 were removed after 120 minutes, the greatest difference being from one to ten minutes ($P < 0.05$). This is illustrated more clearly in Fig. 2 which indicates that the solution had approached equilibrium after 10 minutes but not at the end of one minute.

The data for the removal of strontium and calcium as influenced by the isotope-milk contact time are presented in Table VI. Each sample was intermittently hand agitated for either 1, 10, 30 or 60 minutes, then treated by exposure to Dowex 50W-X12 in the calcium form for 60 minutes under constant agitation. The milk to resin ratio was 20 to 1. Results show approximately 30 per cent removal of strontium-89 and approximately 75 per cent removal of calcium-45 with very little difference between milk agitated for one minute and that agitated for 60 minutes before exchange treatment. The isotopes are fully incorporated into the milk within one minute or the rate of incorporation at this stage is so slow that 60 minutes is not suffi-

TABLE V

EFFECT OF RESIN-MILK CONTACT TIME ON PER CENT REMOVAL OF
 Sr^{90} AND Ca^{45} FROM DOSED MILK

Trial	Resin-milk Contact Time (minutes)	Per Cent Sr^{90} Removal	Per Cent Ca^{45} Removal
1	1	66	56
	10	69	54
	60	77	70
	120	76	69
2	1	57	44
	10	71	64
	60	68	55
	120	78	70
3	1	64	55
	10	75	62
	60	77	72
	120	75	60
Average	1	62	52
	10	72	60
	60	74	66
	120	76	67

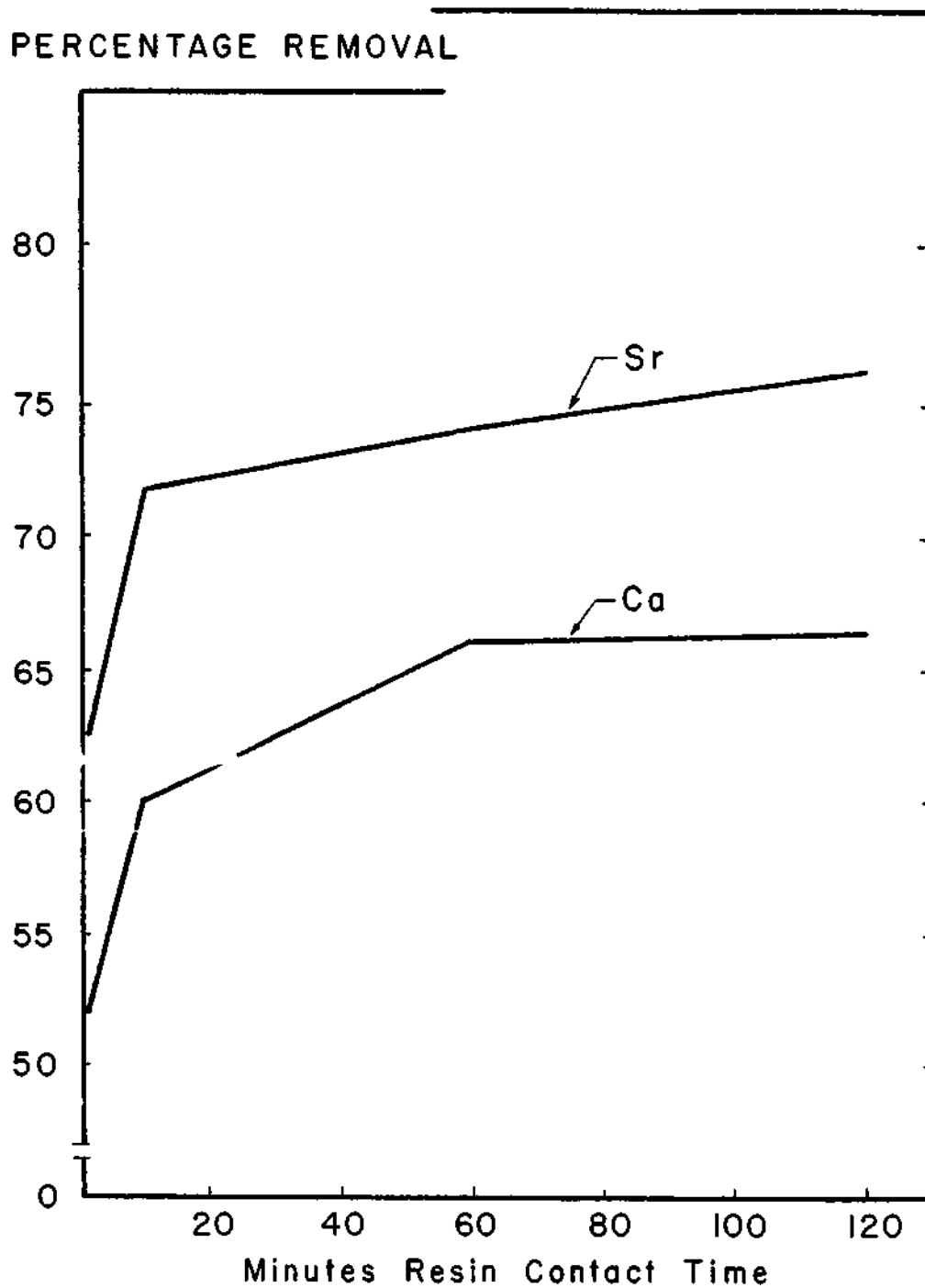


Figure 2. Effect of Resin-Milk Contact Time on Percent Removal of Sr⁸⁹ and Ca⁴⁵ from Dosed Milk.

TABLE VI

EFFECT OF ISOTOPE-MILK CONTACT TIME ON PER CENT REMOVAL OF Sr^{90}
AND Ca^{45} FROM DOSED MILK

Trial	Isotope-milk Contact time (minutes)	Per Cent Sr^{90} Removal	Per Cent Ca^{45} Removal
1	1	78	71
	10	79	70
	30	76	72
	60	72	61
2	1	83	78
	10	84	77
	30	73	71
	60	80	70
3	1	83	81
	10	73	73
	30	82	87
	60	81	78
4	1	80	73
	10	77	71
	30	83	74
	60	73	61
Average	1	81	76
	10	79	72
	30	79	76
	60	77	68

cient time to show a definite trend, the latter probably being the case since less of the isotopes were removed after contact with the milk 16 hours than 60 minutes.

The data on removal of strontium and calcium from milk by use of a series of four ion exchange columns are shown in Table VII. This experiment was conducted to compare the action of four columns in a series, each containing 12.5 grams of resin, to one column containing 50 grams of resin (Table 2). No differences were noted in the percentage removal of strontium and calcium between the two methods.

Following the last trial each of the four columns of resin was washed with 1 liter of 3 N hydrochloric acid. Forty milliliter samples of the eluate from each of the four columns were assayed and the radioactivity of both calcium and strontium was found to decrease in the resin from the first column to the last (Table VIII).

The data in Table IX and Fig. 3 indicate a direct relationship between the percentage of strontium and calcium removed from milk and the amount of resin used. Because Dowex 50W-X12 in the calcium form had appeared to be more effective in the removal of strontium and calcium from milk than either Dowex 50W-X4 or Duolite C-20 (Tables I and II), it was used in this batch experiment. The percentage removal of strontium-89 ranged from a high of 94, where one part resin was used per two parts of milk, to a low of 21, where one part resin per 200 parts of milk was used. Similarly the percentage calcium-45 removal ranged from a high of 93 to a low of 16

TABLE VII

PER CENT REMOVAL OF Sr^{90} AND Ca^{45} FROM MILK BY USE OF
A SERIES OF FOUR EXCHANGE RESIN COLUMNS

Trial	100 ml. Portion of Elutriated Milk Sample	Per Cent Sr^{90} Removal	Per Cent Ca^{45} Removal
1	2nd	74	75
	6th	67	63
	10th	62	51
	14th	45	38
2	2nd	77	72
	6th	52	59
	10th	57	50
	14th	55	42
3	2nd	71	73
	6th	67	52
	10th	46	30
	14th	40	31
4	2nd	82	74
	6th	73	51
	10th	51	36
	14th	36	31
Average	2nd	76	73
	6th	65	56
	10th	54	42
	14th	44	36

TABLE VIII

RADIOACTIVITY RETAINED BY RESIN AFTER PASSAGE OF
MILK CONTAINING Ca^{45} AND Sr^{90}

Column	Sr^{90} Counts/Min/ 40 ml. Eluate	Ca^{45} Counts/Min/ 40 ml. Eluate	$\text{Sr}^{90}/\text{Ca}^{45}$
1	82	451	0.1818
2	66	427	0.15456
3	39	308	0.12662
4	18	180	0.100

TABLE IX

EFFECT OF MILK-RESIN RATIO ON PER CENT REMOVAL
OF Sr⁸⁹ AND Ca⁴⁵ FROM MILK

Trial	Ratio of Milk to Resin (wt. basis)	Per Cent Sr ⁸⁹ Removal	Per Cent Ca ⁴⁵ Removal	Increase of Ca Compared to Non- treated milk (%)
1	2	94	93	56.7
	5	89	85	20.2
	10	85	76	21.5
	20	67	56	23.7
	40	50	28	20.4
	200	17	8	6.9
2	2	94	94	54.4
	5	88	83	23.6
	10	83	78	22.5
	20	69	57	20.3
	40	56	42	- 3.8
	200	18	17	0.1
3	2	93	92	60.7
	5	87	83	22.6
	10	82	74	21.8
	20	73	60	22.0
	40	56	34	- 0.5
	200	28	23	- 6.5
Average	2	94	93	57.3
	5	88	84	22.1
	10	83	76	21.9
	20	70	57	22.0
	40	54	34	5.4
	200	21	16	3.3

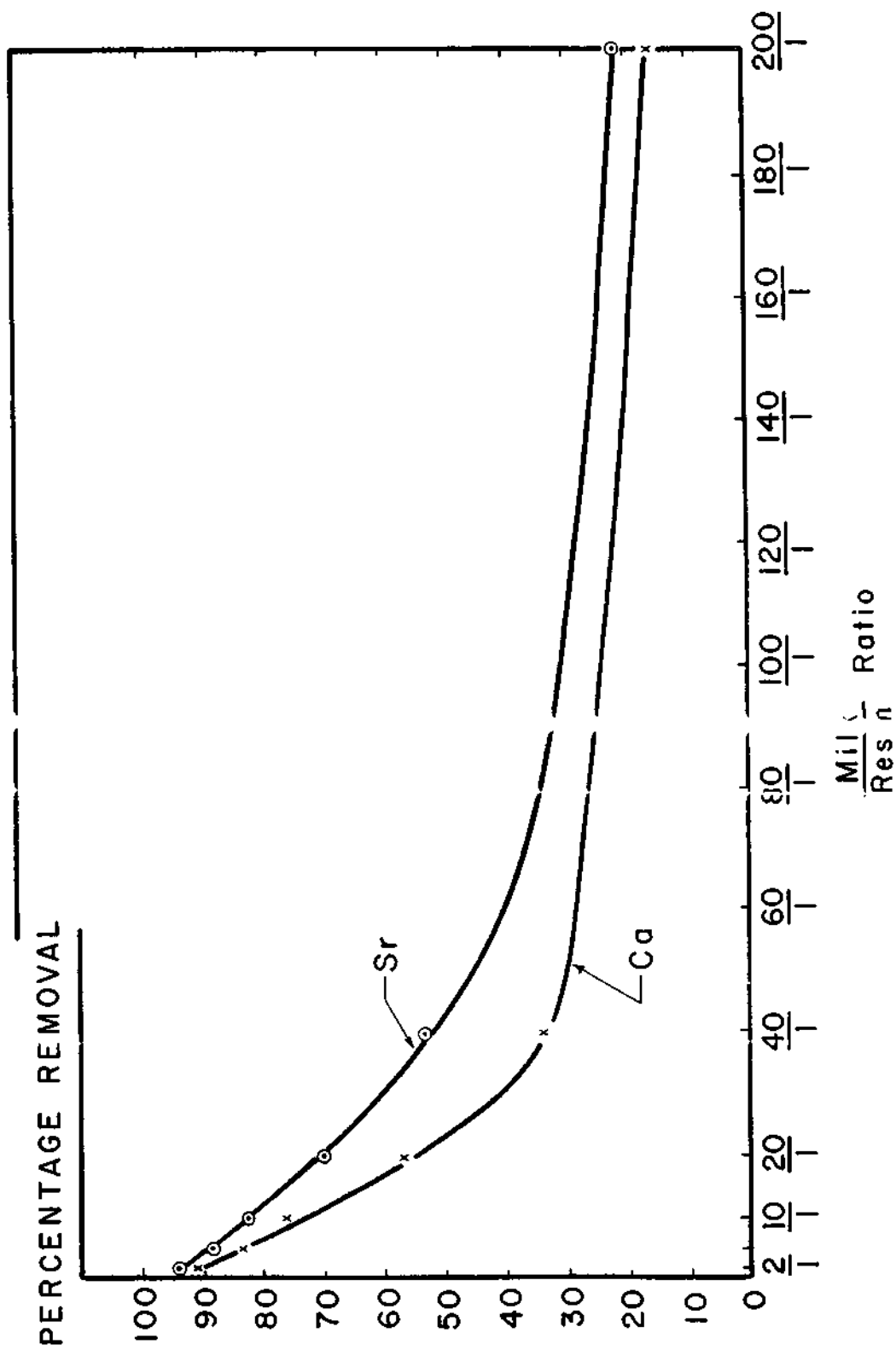


Figure 3. Effect of Milk-Resin Ratio on Percent Removal of Sr⁸⁹ and Ca⁴⁵ from Milk.

per cent. The total resin exchange capacity (Meq./gm.) was approximately twice the amount required for complete removal of the calcium from the milk at a milk-resin ratio of 20 to 1. At the 20 to 1 ratio the average percentage removal of strontium was approximately 70 and calcium 57.

Relationships between resin weight and exchange of calcium-45 and strontium-90 from milk are useful for predictions for different ratios. Since calcium in milk is in a very high concentration (6.23 meq./100 ml.) in relation to strontium (.00093 meq./100 ml.) a linear equation was derived for calcium-45 exchange on the assumption of isotope dilution.¹ This equation is:

$$w = a \frac{1 - f_M^e}{\dots}$$

where: w = weight of moist resin

$$a = \text{slope} \frac{\text{quantity of resin}}{\frac{\% \text{ removed}}{\% \text{ not removed}}}$$

$$f_M^e = \text{Ca}^{45} \text{ percentage found in milk.}$$

This is plotted in Fig. 4 with w on the y axis and $\frac{\text{per cent of isotope removed from milk}}{\text{per cent of isotope not removed from milk}}$ on the x axis.

This equation was tested for strontium also and a non-linear relationship was observed which may have been due to ion selectivity of the resin.

¹Preliminary calculations on these relationships were made by R. C. McIlhenny, Radiochemist, UT-AEC Agricultural Research Laboratory.

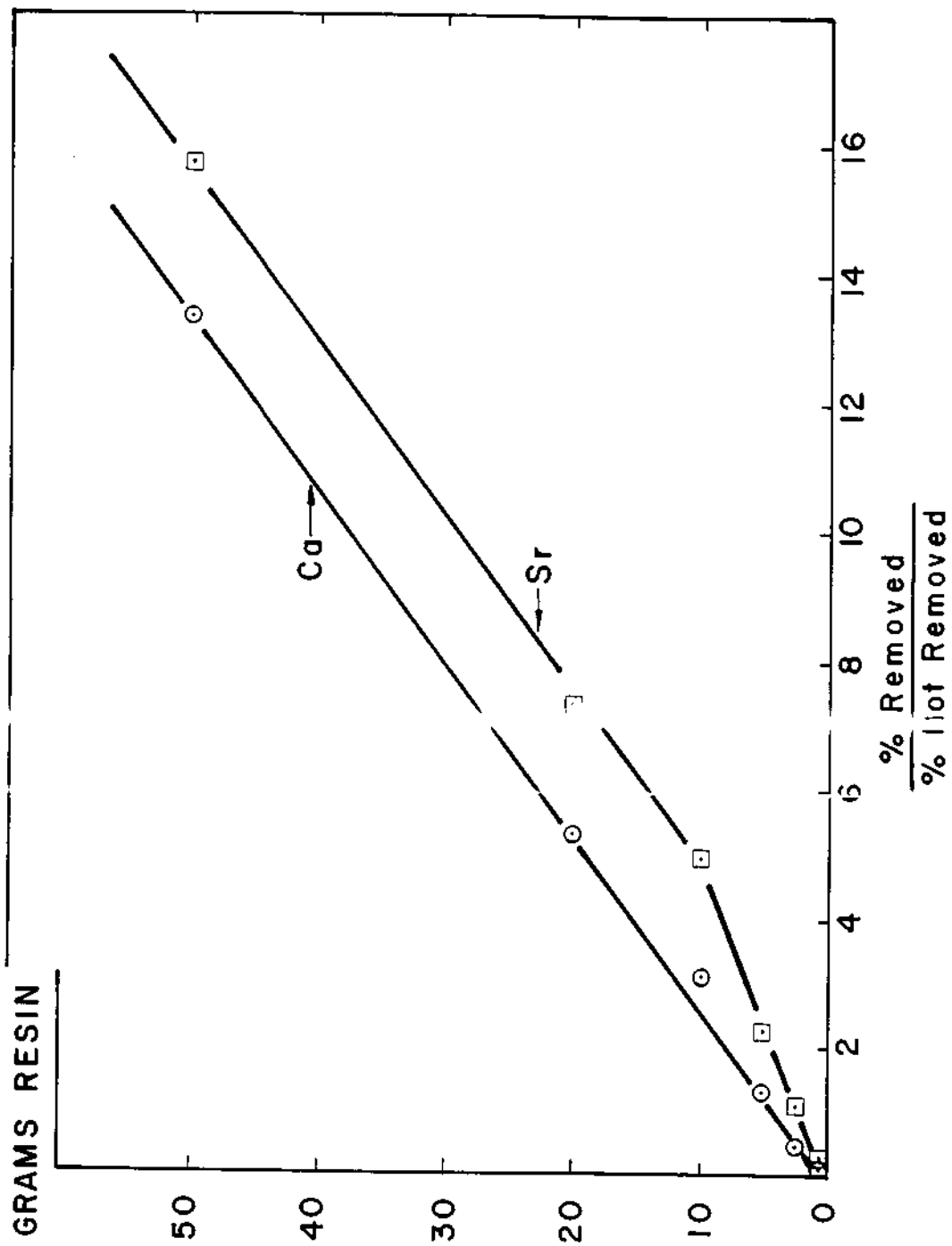


Figure 4. Relationship of Milk-Resin Ratio and the Percentage Exchange of Ca45 and Sr89.

On the basis of calcium oxalate weights, milk treated with the resin contained more calcium than the non-treated milk (Table VIII). This may be due to the excess calcium chloride not being washed from the recharged resin when the batch system was used. Some additional calcium may also come from the exchange of calcium on the resin for strontium and other ions in milk. In general the percentage of calcium removal from milk was less than strontium based on the total calcium and strontium in the untreated milk.

An estimation of the efficiency of the column system versus the batch system was made. The following four equations were derived by the method of least squares from the data presented in Tables 1 and 2.

Ca^{45} dosed milk:

$$y = -33.26 + 1.48736x + \frac{117.8174}{1.063x}$$

Milk from Ca^{45} dosed cows

$$y = -154.0086 + 6.75665x + \frac{238.6207}{1.061x}$$

Sr^{90} dosed milk

$$y = -187.0063 + 5.58810x + \frac{269.86}{1.037x}$$

Milk from Sr^{90} dosed cows

$$y = -98.6204 + 4.20296x + \frac{183.4547}{1.059x}$$

Where y = % removal and X = 100 ml. portions passed through the column.

The integrated forms of these equations for determining the area under the curve were respectively:

$$A = -33.26x + .74368x^2 - \frac{1928.5873}{1.063x} + 1928.5873$$

$$A = -154.0086x + 3.3783x^2 - \frac{4030.0743}{1.061x} + 4030.0743$$

$$A = -187.0063x + 2.7940x^2 - \frac{7430.0660}{1.037x} + 7430.0660$$

$$A = -98.6204x + 2.10x^2 - \frac{3199.895}{1.059x} + 3199.895$$

Since the columns contained 107 milliliters of milk and 50 grams of resin when completely filled, a convenient point of comparison was the per cent of removal for some volume less than 107 ml. and a comparable volume in the batch system. Therefore the area under the curve was determined for 100 milliliters of milk. The comparisons of the systems are presented in Table X. It is estimated that the column was only 86 per cent as efficient as the batch system for removal of Sr^{88} . The corresponding value for Ca^{45} was 88 per cent. The lower efficiency for the column can be attributed to the milk-ion and resin-ion complex not being allowed to come to equilibrium. Milk was found to contain an average of 6.23 meq. of calcium per 100 milliliters and is estimated to contain 0.00096 meq. of strontium per 100 milliliters. The calculations presented in Table X are based on these values.

TABLE X

PER CENT OF RESIN CAPACITY EXCHANGE BY CALCIUM AND STRONTIUM USING THE
BATCH AND COLUMN SYSTEM

System used	Ratio Milk Resin or portion through column	Resin Capacity (meq.)	Isotope Removed	Percentage removed	Meq. Exchanged	Per Cent Resin Capacity Exchanged
Batch	2 - 1	135	Ca ⁴⁵	93	5.79	4.27
Batch	5 - 1	54.3	Ca ⁴⁵	84	5.24	9.6
Batch	10 - 1	27.1	Ca ⁴⁵	76	4.74	17.4
Batch	20 - 1	27.1	Ca ⁴⁵	56	7.10	26.2
Batch	40 - 1	13.5	Ca ⁴⁵	34	4.24	31.3
Batch	200 - 1	2.7	Ca ⁴⁵	16	1.99	73.6
Batch	2 - 1	135	Sr ⁹⁰	94	--	--**
Column	1st 100 ml.	135	Ca ⁴⁵	82	5.10	3.77**
Column	1st 100 ml.	135	Sr ⁹⁰	81	--	--**
*Column	1st 100 ml.	135	Sr ⁹⁰	81	--	--**
*Column	1st 100 ml.	135	Ca ⁴⁵	74	4.62	34.1

*Milk from Dosed cows. All other samples were dosed milk.

**Stable strontium in milk is negligible compared to calcium.

SUMMARY

Much publicity has been given the passage of strontium from the atmosphere into food and its accumulation in bone in recent months. The strontium level in milk has been accumulating at a rate which is causing some alarm due to the damaging effect it may have on the health of humans.

Modified ion exchange resin columns and the batch system have been used to remove strontium-89 as well as calcium-45 from both dosed milk and milk from dosed cows. Dowex 50W-X12, Dowex 50W-X4 and Duolite C-20 were used, the first found to be most effective, by removing 76 per cent of the strontium and 74 per cent of the calcium from milk of dosed cows and 77 and 76 per cent respectively from dosed milk. These data represent only the second 100 milliliter portion of one liter passed through the column.

Using this modified column technique the per cent resin capacity exchanged was only 86 per cent as effective for removal of strontium-89 and 88 per cent for the removal of calcium-45.

Dowex 50W-X12 resin was left in contact with milk for periods of 1, 10, 60 and 120 minutes to study the exchange rate. Differences existed between the 1 and 10 minute periods only.

Using the batch system and dosed milk, the percentage of removal of strontium-89 and calcium-45 decreased as the ratio of milk to resin increased. The percentage of removal ranged from a high of 94 and 93

for strontium and calcium respectively at a milk-resin ratio of 2 to 1 to a low of 21 per cent strontium and 16 per cent calcium at a milk-resin ratio of 200 to 1.

An approximately linear relationship was found between the ratio of calcium-45 removed over that not removed and the quantity of resin used.

BIBLIOGRAPHY

BIBLIOGRAPHY

- (1) Adams, B. A., and Holmes, E. L. Adsorptive Properties of Synthetic Resins. J. Soc. Chem. Ind. 54: 1:6T. 1935.
- (2) Alexander, G. V., Nusbaum, R. E., and MacDonald, N. S. The Relative Retention of Strontium and Calcium in Bone Tissue. J. Biol. Chem. 218: 911. 1956.
- (3) Anonymous. Radioactivity in Milk. Science 128: 762. 1958
- (4) Baker, J. M., and Gehrke, C. W. An Ion Exchange Resin-Contact-Time-Method for the Study of Inorganic Equilibria in Milk. J. Dairy Sci. 37:1409. 1954.
- (5) Baker, J. M., and Gehrke, C. W. The Exchangeable Calcium in Raw and Heated Milk as Determined by the "Resin-Contact-Time-Method". J. Dairy Sci. 39: 1221. 1956.
- (6) Brown, W. M. C. Some Reflections on the Possible Hazards to Man of Low Doses of Radiation. Proceedings of the Nutrition Society 18: 38. 1959.
- (7) Comar, C. L., Russell, R. S. and Wasserman, R. H. Strontium-Calcium Movement from Soil to Man. Science 126: 485. 1957.
- (8) Cragle, R. G. and Demott, B. J. Strontium and Calcium Uptake and Excretion in Lactating Dairy Cows. J. Dairy Sci. 42: In Press.
- (9) Gans, R., Jahrb. preuss. geol. Landesanstalt (Berlin) 26, 179 (1905); 27, 63 (1906); Centr. Mineral Geol. 22, 728 (1913); German Patent 197, 111 (1906); U. S. Patents 914, 405 (March 9, 1909), 943, 535 (December 14, 1909), 1, 131, 503 (March 9, 1915). Quoted by Nachod, F. C. and Schubert, J., editors. Ion Exchange Technology, p3. Academic Press, Inc. New York N. Y. 1956.
- (10) Gehrke, C. W., and Almy, E. F. Action of Mineral Ion Exchange Resins on Milk Constituents. Ind. Eng. Chem. 42: 2344. 1950.
- (11) Gehrke, C. W., and Smith, R. B. The Effect of Heat and pH on the Ion-Exchangeable Calcium and Magnesium in Skim Milk as Determined by the Resin-Contact-Time-Method. J. Dairy Sci. 40: 600. 1957.
- (12) Haller, H. S., and Morin, A. G. Ion Exchange as a Means of Varying the Salt Constituents of Milk. J. Dairy Sci. 33: 305. 1950.

- (13) Harm, F., German Patent 95, 447 (June 2, 1896). Quoted by Nachod, F. C. and Schubert, J., editors. Ion Exchange Technology, p5. Academic Press, Inc. New York, N. Y. 1956.
- (14) Josephson, D. V., and Reeves, C. B. The Utilization of the Mineral-Ion Exchange Principle in Stabilizing Evaporated Milk. J. Dairy Sci. 30: 539. 1947.
- (15) Kulp, J. L., Eckelmann, W. R., and Schulert, A. R. Strontium-90 in Man. Science 125: 219. 1957.
- (16) Kunin, R. Ion Exchange Resins. 2nd Ed. John Wiley and Sons, Inc. New York, N. Y. 1958.
- (17) Larson, B. L., and Ebner, K. E. Significance of Strontium-90 in Milk. A Review. J. Dairy Sci. 41: 1647. 1958.
- (18) Lenihan, J. M. A. Nutritional Hazards Caused by Radioactive Contamination of Foods. Proceedings of the Nutrition Society 18: 34. 1959.
- (19) Lewis, E. B. Leukemia and Ionizing Radiation. Science 125: 965. 1957.
- (20) Libby, W. F. Radioactive Fallout and Radioactive Strontium. Science 123: 657. 1956.
- (21) Lyman, J. F. U. S. Patent 1, 954, 109 (April 10, 1934) as quoted by Otting, H. E. Ind. Eng. Chem. 41:457. 1949.
- (22) McGlasson, E. D. and Boyd, J. C. Improved Methods in the Recovery of Lactose Using Ion Exchange Resins. J. Dairy Sci. 34: 119. 1951.
- (23) Murthy, G. K., and Whitney, R. McL. The Effects of Cationic and Anionic Resins on the Salt Content of Raw Skimmilk. J. Dairy Sci. 36: 559. 1953.
- (24) Nervik, W. E., Kalkstein, M. I., and Libby, W. F. Purification of Milk for Calcium and Strontium with Dowex 50W Resin. UCRL-2674 1954.
- (25) Otting, H. E. Ion Exchange Application in Milk Products. Ind. Eng. Chem. 41: 457. 1949.
- (26) Sasaki, R., Tsugo, T., and Yajima, A. Effects of Treatments with Ion-Exchange Resin on Heat Coagulation of Milk. Chem. Abstr. 52: 9465. 1958.

- (27) Schulert, A. R., Peets, E. A., Laszlo, D., Spencer, H., Charles, M., and Semachson, J. Comparative Metabolism of Strontium and Calcium in Man. J. of Applied Rad. and Isotopes 4: 144. 1959.
- (28) Thompson, H. S. On The Absorbent Power of Soils. J. Roy. Agr. Soc. Engl. 11: 68. 1850.
- (29) Way, J. T. On the Power of Soils to Absorb Manure. J. Roy. Agr. Soc. Engl. 11: 313. 1850.