# THE LOSSES OF CALCIUM IN COOKING KALE

by

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## INTRODUCTION

Sherman has stated that the average American diet is more likely to be deficient in Calcium than in any other mineral. Calcium is one of the requirements of every individual. It is needed as a constituent of the skeletal tissues, the bones and teeth, and also is an essential factor in the construction of the soft tissues, blood cells and nerve cells. The growing child and the pregnant woman need a much larger supply in their diet than the normal adult, to allow for growth; while lactation requires an even larger amount. (21) (43).

The body's supply of calcium comes through its food, although a very small amount may be found in some water. A liberal supply of milk is the surest means of providing an adequate intake of calcium, especially for children. As a result of balance experiments a dietary standard has been set as a quart of milk per child per day and a pint of milk per day for each adult. These standards are the results of the studies of Sherman and Hawley (40) who found that storage of calcium in children was raised 70% by increasing the intake of milk from 750 to 1000 grams a day. The results of a study by Daniels (15) indicate that one pint of milk will supply sufficient calcium for the well nourished child between 3 and 5 years, provided the diet is rich in protein, phosphorus and vitamins. Stearns (42) states that as a result of a series of studies upon the retention of calcium by children fed different amounts of milk, the total daily retention of calcium by infants was as great or greater than the retention of the older children for any given quantity of milk studied, but in all cases a higher retention of calcium resulted when a quart of milk was fed than with a pint.

Many studies, including those of Lininger, (27) and of Leighton and Clark (26), have shown improved growth and physical and mental well being in school children, when additional milk was added as a supplement to their usual diet. The milk was given to the children as a mid-morning lunch at school. Large groups were used and no record was kept of the home diet.

Other foods vary a great deal in the amount of calcium found in them; also, the calcium content of different samples of one food may vary considerably; (11) likewise, the availability of the calcium of different foods may not always be the same.

Many balance experiments have tested the availability and efficiency of vegetables as sources of calcium in the diet. Rose, (38) in a study on four young women eating a diet in which 35% of the calcium was furnished by carrots, found a positive calcium balance in three cases. In the fourth case, the loss of calcium was small and was accompanied by a digestive upset. Blatherwick and Long (4) found that the calcium from mixed vegetables, including cabbage, squash, celery, asparagus, etc., was well utilized, and their data indicate that the calcium derived from vegetables is capable of meeting the maintenance needs of man. Rose and MacLeod (37) in an experiment with adult women on a diet in which 73% of the calcium was derived from almonds, found that calcium equilibrium could be secured about as efficiently as when milk or carrots furnished the same amount. When 85% of calcium was furnished by almonds the utlization was not quite as good. McLaughlin (29) found that on a diet in which 70% of the calcium came from spinach, six out of seven adult women maintained positive calcium balances, while calcium equilibrium was maintained in the seventh. However, although the calcium content of the diet containing spinach was greater than that of the milk diet with which it was compared, the retentions in all cases were lower on the spinach diet. Mallon, Johnson, and Darby (31) concluded that the calcium of lettuce, which furnished 93% of the total calcium of the diet, was perhaps even better utilized than that of pasteurized whole milk. Fincke and Sherman (16) working with rats found that when half the calcium of the diet was supplied by kale, the calcium was nearly as well utilized as when it all came from milk. When spinach was substituted for kale to provide the same amount of calcium, the calcium of spinach was utilized poorly, evidently due at least in part, to the presence of oxalic acid.

Kramer, Potter, and Gillam (25) in a study on ten adult women found that calcium from ice cream was at least as well utilized as that from milk. Kramer, Latzke, and Shaw (24) reported that fresh and evaporated milk and quickly boiled milk are superior to pasteurized or dried milk as sources of calcium for both children and adults.

A very good source of calcium is found in American Cheddar cheese. Mallon, Johnson, and Darby (30) in a metabolism study on two women determined that the calcium of cheese was as well utilized as the calcium from pasteurized whole milk.

Very few fruits may be ranked as good sources of calcium. Chaney and Blunt (10), however, found that calcium assimilation was decidedly benefited when orange juice was added to the diet of two children. This may have been due to some other factor than an increase in calcium.

Soy beans which are used to a great extent in China were shown by Adolph and Chen (1) to be equally as effective a source of calcium as cow's milk. Pittman (35) studied the utilization of the calcium of the navy bean. When 80 to 85% of the calcium of the diet was supplied by beans, negative balances were obtained in all cases. She suggests that this may be due to association of calcium with indigestible material. However, the total amount of calcium in the diet was low.

Burton (6) reported that the calcium of oats was not as well utilized as that of wheat. The oat diet contained a smaller amount of calcium than the wheat diet, but Burton states that the decrease in retention of calcium on the oat diet was even greater than the decrease in intake of calcium between the two diets. She found this true for both adults and children.

Many factors have been found to affect calcium absorption. Since calcium compounds are soluble in acid, anything which would lower the pH of the digestive tract would increase absorption of calcium. Roe and Kahn (36) state that the serum calcium of human subjects is definitely elevated by administration of calcium lactate in aqueous solution. Kline and Keenan (23), feeding lactose to chicks on a rachitic ration, found it had a favorable effect upon calcium absorption; and Gross (17), feeding lactose to dogs, believed lactose produced better absorption of calcium from the intestinal tract. Both lactic acid and lactose would increase the acidity of the intestinal tract. An alkaline condition in the digestive tract, on the other hand, tends to decrease the absorption. As the pH of material leaving the stomach approaches neutrality, the phosphate and carbonate ions tend to combine with calcium. When the pH is above 7, the calcium is precipitated in the form of tertiary phosphate and also carbonate; also, the fatty acids react with calcium to form insoluble soaps. These products are quite insoluble and very poorly absorbed, according to Cantarow (8).

Coons, Coons and Schiefelbusch state that the best retention of calcium in human pregnancy is found when the diet is base forming (13). Morgan and others, (33) found the greatest storage of calcium occurred on neutral or base forming diets. Their work was with dogs. Thus a diet which is acidic in the digestive tract and neutral or basic in the tissues seems to favor calcium retention.

There are different opinions in respect to the effect of fiber upon the absorption of calcium. Bloom (5) in an experiment with rats reported that fiber had no effect upon the retention of calcium even when the total amount of fiber was increased many times. Ascham (2) states that increased fiber in the diet seems to increase the calcium in the feces of dogs, but her results were not conclusive. The good utilization of calcium in diets in which the calcium came largely from carrots, almonds and other vegetables would seem to indicate that the presence of fiber does not hinder assimilation.

Mallon, Jordan and Johnson state that fat cannot be said to have a definite influence on calcium retention (32), while Holt and Fales (20) found that calcium absorption was markedly reduced on a low fat diet in seven cases and gave a negative balance in three.

Vitamin D in the diet seems to increase the absorption of calcium from the digestive tract, and abnormal conditions of high or low calcium and phosphorus in the serum resulting in rickets, tetany etc., are alleviated and the blood calcium tends to return to normal when vitamin D is given (8). However, Hart and Steenbock (18) state that feeding half a pound daily of cod liver oil showed no favorable influence upon the calcium assimilation of cows producing large quantities of milk.

Bethke, Kick and Wilder (3) believe that the ratio of calcium to phosphorus in the diet is of importance, but the work of Shohl (41) indicates that not only the ratio but also the levels of calcium and phosphorus are important. Rickets may be produced in rats in which the ratio might be within the normal range but the actual amounts of calcium and phosphorus low.

Cantarow (8) states that when the calcium and phosphorus in the diet is in good proportion, the presence of other minerals does not seem to exert an unfavorable influence, which was confirmed in the case of magnesium by the work of Carswell and Winter (9).

The secretions of the parathyroid gland also affect calcium metabolism, but the way in which this is accomplished is still in doubt. Increased secretion of parathormone results in increased elimination of calcium and phosphorus from the body; while decreased activity of the gland causes the blood calcium to fall until a state of tetany results. The exact mechanism of how this is accomplished, however, is not certain (8).

Courtney, Fales and Bartlett (14) found that a large proportion of the mineral content of most vegetables is lost in the water used in boiling. This loss varies a great deal in different vegetables from a very small amount of calcium in spinach to a loss of 28% of the calcium of carrots. This loss seemed to be decreased only slightly by reducing the time of cooking. Calcium apparently was the least affected of all minerals. A very great saving in mineral content is effected by using the method of steaming. Peterson and Hoppert (34) state that the calcium loss in cabbage and spinach was 10% when they are steamed or pressure cooked and 20 to 30% when they are boiled. The greatest loss occurred in iron and the least in calcium. Certain vegetables showed notably large losses of calcium, particularly cabbage.

Although steaming does conserve the minerals, King (22) does not recommend cooking leafy green vegetables in such a way because of the unpalatable product obtained. The smaller loss of minerals in cooking would be more than counterbalanced by their loss in palatability.

Since the calcium of kale had been shown to be nearly as well utilized as that of milk, this investigation was undertaken to determine how much calcium was lost in cooking kale by two common methods: boiling in a large amount and in a small amount of water. Preliminary experiments were first carried out to determine the ways of cooking kale to insure a palatable product.

Halliday and Noble (19) and also Lowe (28) recommend that the following different standards should be met in green vegetable cookery: it is desirable to retain the minerals and vitamins, and also have a product pleasing in texture, color and flavor.

The green coloring of the leaves is due to the presence of chlorophyll which is decomposed by heat and this decomposition gives the leaf an olive green color. The extent of the decomposition depends upon the time of cooking; therefore, we want as short a cooking time as possible. The effect of heat upon chlorophyll is modified if the reaction is alkaline.

Green vegetables are cooked with the cover off because part of the volatile acids will pass off with the steam and the development of the olive green color is less intense. The highest percent of these acids pass off during the first few minutes of cooking.

Vegetables which start to cook in boiling water show less loss of minerals than those started in cold water. Therefore a strong flavored vegetable is usually cooked in a large amount of boiling water with the cover off, for as short a time as possible.

In these preliminary experiments several methods of cooking kale were tried and the products checked on a score card for color, flavor and tenderness. At first 100 gram samples were used, but as this seemed too large for an average serving, the amount was later decreased to 57 grams (2 oz.) per sample. This was the amount used in the final analysis of calcium.

Kale was prepared by steaming, by cooking in a casserole, by boiling in small and large amounts of water for different lengths of time. Each product was judged by several persons and as a result of this scoring two methods were selected. In one, the 57 gram sample of kale was cooked for 15 minutes in one cup of water, while in the other, the same amount of kale was cooked for twenty minutes in two cups of water. Boiling is perhaps the most commonly used method of cooking and both these chosen methods gave palatable products. The flavor was so much the same that they could not be distinguished. Therefore, these two methods were selected for the experimental work.

Plan of experiment. Since kale has been found to contain a good supply of calcium in a form which is easily assimilated by the human body, it was thought interesting to determine the amount of calcium which is lost during the cooking process. Weighed samples from one lot of kale were analyzed for the calcium content while raw and after cooking by the two methods outlined above.

Preparation of materials. The variety of kale used for analysis was Brassica oleracea, var. acephal. It was grown on one of the Oregon State College farms and was furnished through the courtesy of the Horticultural Department, being cut as needed throughout the months of October and November. The kale was gathered and brought to the laboratory the day before cooking and weighed. The leaves were stripped from the petiole and tougher part of the midrib, and the edible portion weighed. About 50% of the kale as obtained was found to be edible portion. The leaves were then thoroughly washed. The kale was unusually clean so that washing three times was always sufficient. It was spread on the table to dry over night, at the end of which time it was free from visible moisture but not withered. It was then weighed into 57 gram (2oz.) samples.

All cooking was done in small aluminum kettles. The kale was placed in these kettles and a measured amount of boiling water poured over it. Tap water was used throughout for cooking purposes, as this would be comparable to conditions in the home. The kale was cooked uncovered for the required length of time, when it was drained in a wire strainer for thirty seconds, the cooking water, if any, being saved for analysis. From each lot of kale, raw samples were taken for analysis, and samples for cooking in each of the two ways. When the kale was cooked in one cup of water, the liquid had all evaporated by the end of the fifteen-minute cooking period; in the case of the samples cooked for twenty minutes in two cups of water there was about a half a cup of liquid left in the cooking kettle.

The samples were dried in evaporating dishes in an electric oven for six or more hours at 100° C. They were then covered and stored until analyzed. The cooking liquid was evaporated slowly over a flame and finally dried in an electric oven.

The samples were ashed in an electric muffle furnace until white. This ashing took four or more hours at a dull red heat. The ash was dissolved in 5 cc. of concentrated hydrochloric acid, filtered, and the solution made up to 250 cc. in a volumetric flask.

Method of analysis. Aliquots of 100 cc. were withdrawn from the solution by pipette and placed in 250 cc. beakers; a small piece of litmus paper was dropped in and ammonium hydroxide added drop by drop until the solution became alkaline. One drop of methyl red was then added and acetic acid added drop-wise until the solution became pink. The beaker was covered and heated to 85 to 95 C. when 25 cc. of saturated ammonium oxalate solution was poured in slowly with constant stirring. The beaker was then covered and allowed to stand over night.

The solution was filtered and the beaker and cover-glass washed with a 0.5 percent solution of ammonium oxalate, then three times with distilled water, filling the filter three-fourths full each time. A hole was made in the filter paper and the precipitate washed into a beaker with 100 cc. of distilled water, and 10 cc. of 9 M sulfuric acid added. The solution was heated to 75° to 80° C. and titrated while hot with standard potassium permanganate solution. The first permanent pink color was taken as the end point. The reaction involved is:

$$2KMnO_4 + 5CaC_2O_4 + 8H_2SO_4 \rightarrow$$

$$2MnSO_4 + K_2SO_4 + 5CaSO_4 + 8H_2O + 5CO_2$$

<u>Preparation of Reagents.</u> Reagents were prepared whenever possible in sufficient amounts to last throughout the entire period. Two potassium permanganate solutions were made up which were approximately 0.02 M. In the first, 1 cc. oxidized an amount of calcium oxalate equivalent to 0.00231 gm. calcium; 1 cc. of the second solution oxidized oxalate equivalent to 0.00281 gm. calcium. The solution was standardized with C. P. Baker's Special Sodium Oxalate for standardization.

The calcium content of the raw kale varied from a weight of 0.1607 gm. to 0.2295 gm. per sample and averaged 0.1826 gm. As shown in Table I, this corresponds to a percentage of calcium in the sample of 0.28% to 0.40%. The average for the raw kale was 0.31%. Samples from the same lot of kale checked closely.

Analysis of samples from one lot of Kale A, when cooked 15 minutes in one cup of water, gave a weight of calcium varying from 0.1347 gm. to 0.1512 gm., with an average of 0.1398 gm. As shown in Table II, the percentage of calcium in this lot varied from 0.22% to 0.26% averaging 0.24%. This represented the percentage calcium loss during the cooking period of from 15 to 24%. Kale from Lot D, with the highest content of calcium in the raw sample, showed a small percentage loss in cooking, 5% and 10% loss as compared with 23% and 24% losses in the other samples.

When samples from Lot A were cooked twenty minutes in two cups of water the analysis showed 0.0830 gm. and 0.1087 gm. of calcium or 0.14% to 0.19%, or a loss in cooking of 39% and 54% (Table III). This is double the loss incurred with kale cooked in a small quantity of water. Samples from Lot D cooked twenty minutes showed an analysis of 0.1385 gm. and 0.1390 gm. of calcium, a percentage calcium content of 0.24% and a 39% loss in cooking. Sample G gave a weight of 0.1470 gm. of calcium or 0.26%, and showed a

8% loss in cooking. The average of the different lots cooked in this way was 0.1232 gm. or 0.21% calcium and the average loss was 36%. The cooking liquid showed an average weight of calcium of 0.0642 gm. or a percentage of 0.11%. Variations in this analysis is due probably to one of two things; the cooking utensils were not rinsed out and some of the calcium would be precipitated upon the sides of the kettle, also, tap water was used in cooking the samples of kale and this would have a varying content of calcium.

Table IV, giving the summary of results of the analyses on all samples, shows that Lot D gave the highest calcium content in the raw state and showed only a small loss in the short period of cooking, 10% and 5%; but a 39% loss in the longer cooking period. Lot A with a content of calcium of 0.31% in the raw vegetable, showed after 15 minutes of cooking in one cup of water an average of 0.25% calcium or a 21% loss. After cooking 20 minutes in two cups of water the same lot showed an average of 0.17% calcium or an average loss of 46%. Samples in Lot G showed an 8% loss of calcium in the longer cooking period.

Therefore the average loss of calcium for the 15 minute period of cooking in one cup of water was 16%, while the average loss for the 20 minute period in two cups of water was 36%. Cooking in a large amount of water, then, at least doubled the loss of calcium in these experiments. The results might not be the same in cases where the kale was not grown under similar conditions and cut at the same time of the year.

Comparing these results with those of other investigators, Courtney, Fales, and Bartlett (14) reported that carrots when boiled for 30 minutes showed a calcium loss of 28.4%. In the same condition asparagus lost 26.6%, onions, 26.1% and New Zealand spinach 3.6%.

Peterson and Hoppert (34) analyzed raw beet greens and found that they contained 0.0944 gm. of calcium per 100 grams of raw vegetable; raw cabbage and spinach gave 0.0338 gm. and 0.0763 gm. respectively. They reported a loss of 15.9% of the calcium when beet greens are boiled in a large amount of water and a loss of 8.6% when boiled in a small amount of water. In the case of cabbage they found a loss of 72.2% when cooked in a large amount of water and a loss of 61.6% when cooked in a small amount. The salts of cabbage seem to be particularly soluble in water and those of spinach insoluble, as only a trace of calcium seems to be lost when spinach is boiled for either a short or long time.

Peterson and Hoppert report the average loss of calcium for all the vegetables to be 20 to 30% when they are boiled for thirty minutes. The results of this investigation indicate that the losses of calcium in cooking kale by these methods are within the range reported by Peterson and Hoppert.

The calcium content of the raw kale was found to be at least four times greater than that of any of the vegetables reported by Peterson and Hoppert, or by Courtney, Fales and Bartlett. In view of the fact that its calcium is well utilized, kale therefore, becomes an excellent source of calcium in the dietary.

The calcium content of kale was determined when raw and when cooked in two ways: boiled for 15 minutes in one cup of water, and for 20 minutes in two cups of water.

An average of 16% of the calcium of the kale was lost when it was cooked for 15 minutes in one cup of water, while an average of 36% of the calcium was lost when it was cooked for 20 minutes in two cups of water.

Therefore, in this variety of kale, grown under these conditions of soil and season, at least twice as much calcium was lost when the kale was cooked in a large amount of water for a longer time than when cooked in a smaller amount of water for a shorter time.

## TABLE I

### Calcium Analyses of Raw Kale

| Lot No. | Sample No. | Wt. of Kale Gms. | Wt. of Ca in Sample Gms. | Percent Calcium |
|---|---|---|---|---|
| A | I | 57 | .1795 | 0.31 |
| D | I | 57 | .2295 | 0.40 |
| G | I | 57 | .1607 | 0.28 |
| | II | 57 | .1607 | 0.28 |
| Ave. | | | .1826 | 0.31 |

TABLE II

Calcium Analysis of Kale cooked 15 Minutes

In a Small Amount of Water

| Lot No. | Sample No. | Wt. of Kale Gms. | Amount of Water | Wt. of Ca in Sample Gms. | Percent Ca In Sample | Percent Ca Loss |
|---|---|---|---|---|---|---|
| A | II | 57 | 1 cup | .1367 | 0.24 | 23 |
| A | III | 57 | 1 cup | .1367 | 0.24 | 23 |
| A | IV | 57 | 1 cup | .1512 | 0.26 | 15 |
| A | V | 57 | 1 cup | .1347 | 0.22 | 24 |
| D | II | 57 | 1 cup | .2142 | 0.36 | 10 |
| D | III | 57 | 1 cup | .2195 | 0.38 | 5 |
| Ave. | | | | .1655 | 0.28 | 16 |

# TABLE III

## Calcium Content of Kale Cooked 20 Minutes In a Large Amount of Water

| Lot No. | Sample No. | Wt. of Kale Gm. | Amount of Water | Wt. of Ca In Sample Gms. | Percent Ca | Percent Loss | Wt. of Ca in Cooking Liquid Gms. | Percent Ca In cooking Liquid |
|---|---|---|---|---|---|---|---|---|
| A | VI | 57 | 2 cups | .0830 | 0.14 | 54 | .0417 | 0.07 |
| A | VII | 57 | 2 cups | .1087 | 0.19 | 39 | .0765 | 0.13 |
| D | IV | 57 | 2 cups | .1385 | 0.24 | 39 | .0665 | 0.12 |
| D | V | 57 | 2 cups | .1390 | 0.24 | 39 | .0540 | 0.08 |
| G | III | 57 | 2 cups | .1470 | 0.26 | 8 | .0825 | 0.14 |
| Ave. | | | | .1232 | 0.21 | 36 | .0642 | 0.11 |

## TABLE IV

### Summary of Calcium Analyses of Raw and Cooked Kale

| Lot No. | Wt. Sample Gms. | Raw Kale | | Kale cooked 15Min In 1 cup water | | | Kale cooked 20 min. in 2 cups water | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Kale | | | Cooking Liquid | |
| | | Wt. Ca. Gms. | Percent Ca | Wt. Ca Gms. | % Ca | % Loss | Wt. Ca Gms | Percent Ca | Percent Loss | Wt. Ca Gms | Percent Ca |
| A | 57 | .1795 | 0.31 | .1367 | 0.24 | 23 | .0830 | 0.14 | 54 | .0417 | 0.07 |
| | 57 | | | .1367 | 0.24 | 23 | .1087 | 0.19 | 39 | .0765 | 0.13 |
| | 57 | | | .1512 | 0.26 | 15 | | | | | |
| | 57 | | | .1347 | 0.22 | 24 | | | | | |
| G | 57 | .1607 | 0.28 | | | | .1470 | 0.26 | 8 | .0825 | 0.14 |
| | 57 | .1607 | 0.28 | | | | | | | | |
| D | 57 | .2295 | 0.40 | .2142 | 0.36 | 10 | .1390 | 0.24 | 39 | .0665 | 0.12 |
| | 57 | | | .2195 | 0.38 | 5 | .1385 | 0.24 | 39 | .0540 | 0.08 |
| Average | | .1826 | 0.31 | .1655 | 0.28 | 16 | .1232 | 0.21 | 36 | .0642 | 0.11 |

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