The Detection of Artificial Coatings on Rice

by Ernest E. Lyder

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Submitted to the School of Engineering of the University of Kansas in partial fulfillment of the requirements for the Degree of Bachelor of Science

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THESIS.

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CONTENTS

BIBLIOGRAPHY.

In writing this thesis I consulted the following works:

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THE DETECTION OF ARTIFICIAL COATINGS ON RICE.

General Discussion.

Under the regulations (1) of the national pure food law it is unlawful to place on the market a coated rice without labeling it as such, and the inadequacy of the present methods for determining whether or not a rice is coated has given an opportunity for work on this subject.

The coating on rice consists in most cases of talc (2) ($H_2 Mg_3 Si_4O_4$) or some similar substance, and glucose. In some instances, however, it has been known to be coated with parafin (3) instead of glucose and rice starch instead of talc. Most of the work here will deal with talc and glucose coatings.

Rice is prepared for market as follows: (4) the rough rice is passed through a set of stones or shellers which remove the hull. The product is then subjected to a series of scouring machines by which the bran and cuticle are removed. The rice is then passed through a machine known as the bresh which removes a portion of the flour. After this stage it is known as polished rice. The polished rice is then passed into a warm revolving drum or cylinder, holding as much as 4000 pounds. The glucose and talc are then added. Usually the glucose and the talc are added while the rice is being run into the drum. The proportions are, one one-thousandth parts of glucose and one three-thousandth parts of talc, to one part of rice.

(5). It is claimed that the coating makes the rice less susceptible to dust and other foreign substances, while being shipped or stored and that the coating in a measure protects the rice from weevil.

(6). It has been shown by experts: ~~(1) twenty-Second Annual Report of N. D. Agri. Exp. Station P. 208. (2). Ibid Second Annual Report of N. D. Agric. Exp. Station P. 208.)~~ that the real reason rice is coated is to cover up inferior quality and to make a low grade rice appear as a high grade one.

(1). F. I. D. (Food Inspection and Decission) No. 67
(2). Ibid.
(3). Ibid.
(4). Ibid.
(5). Ibid.
(6). Ibid.

The amount of coating on the rice is perhaps not very injurious to the average person, but since the coating is an undigestible substance and rice is a diet prescribed for people with weak digestion, it is best to have it pure. In fact a rice that is not polished is recognized by scientists to be more healthful than polished rice. Polished rice may cause the disease beri-beri.

METHODS.

The difficulty which arises in connection with the problem is that the artificial coating is so extremely small that it is hard to distinguish it from the natural mineral coating of the rice. In this connection it might be said that even the natural mineral content of the rice might vary, depending upon the kind of soil in which it was grown, and upon the amount of polishing it has had. Therefore rice cannot be said to have a definite amount of mineral matter in it.

As has been noted talc is a magnesium silicate and in the pure state is insoluable in acids, and does not lose weight on ignition. Glucose is a carbohydrate which is soluble in water, and is the agent used to bind the talc to the rice. These facts have suggested several methods of attack. The general analysis of the rice should show a higher ash content when coated as compared with the same sample if it were uncoated. Since however, the coating on the rice is so very small, this increase in weight due to the coating would be exceedingly small. One of the very few methods published is, however, based on this principle. This method is the one devised by F. W. Richardson, and is carried out as follows,

(1). Five grains of rice are treated in a weighed platinum dish with five grains of NH_4F, two cc of water and two cc of concentrated hydroflenoric acid. It is stirred occasionally for ten minutes with a stout platinum wire. The washings are drained off and the rice washed several times. It is then incenterated over a low flame, ashed and weighed. The difference between the ash obtained in this way and that obtained from five grains of rice which has not been treated, is the coating.

(1) Analyst Vol 35. P 293.

Another method of attack is to ash the solids which could in some way or other be dissolved off the rice and it should be found that the coated sample should yield a very high ash as compared with the uncoated (1) Analyst Vol. 35, P. 293, (1910). This method would involve finding processes and devices for separating the mineral coating from the rice without taking off very much of the starch. It would also involve separating the mineral coating from wha. starch was dissolved off. A third method might be based on the fact that since the natural ash is probably composed of potassum, sodium and magnesium salts, which the grain takes from the soil, this natural ash would be soluble in water of acids. Then since the talc is insoluble, the ratio of insoluble ash to soluble, (Insoluble ash / Soluble ash) would be expected to increase in a coated rice over the same ratio in an uncoated sample.

Fehlings solution might be used to detect the presence of glucose.

EXPERIMENTAL.

The work was started by analyzing an unknown sample by the Richardson methods, and by experimenting with the solucility of the ash.

The following is a table showing some results obtained by Richardson.

Table I.

Analysis by Richardson.

Kind of Rice	Mar. %Ash	Ave. %Ash	Min. %Ash.
Rice in Hull Foreign.	4.66	3.62	4.12
Unpolished Foreign	1.22	1.02	1.15
Polished. Foreign	.65	.28	.46
Rice Bran		.10	
Rice Hull		13.20	
Polish		6.46	

Table gives some idea of the amount of ash in an uncoated rice.

The carbon resulting from charred rice is rather difficult to burn completely and requires either a light temperature or a quite prolonged ignition, and it was thought that loss of ash by volitilization might result, Therefore, the following experiments were carried out to test this point.

~~Temperatures it was thought best to make a preliminary determination to ascertain the loss due to very high temperature.~~ Five grams of rice was incenterated over a low flame in a weighed platinum dish. The black residue was then leached by adding twenty cc of hot water. It was boiled for two minutes and the water decanted through a filter. This was repeated twice and the residue washed with ten cc of water. The residue and filter paper was then burned in a muffle at red heat. The dish was weighed and the solution, containing the soluble ash was added, and evaporated to dryness, ignited and weighed again. Another sample of the same rice was run without leaching. It was run as nearly as possible at the same temperature as the first one. The per cent of ash from the leached sample was, .464, while that from the unleached one was .458. This gave a difference of .006%, which is too small to make any appreciable dirrerence. From this it can be concluded that the teaching before ignition is unnecessary.

A determination (#1) was run on sample No. 1 by the Richardson method to test this method. Another sample No. III which is probably an uncoated rice was run at the same time by this method. The object in running a known sample and a supposedly coated sample (No.1) was to observe the manner in which the two would respond to the above method. From evidence, which will appear later, No I was a coated sample, and No III was an uncoated sample, The results were as follows:

Sample	% ash before treatment	% ash after treatment.
I	.45	.14
III	.38	.19

The results show that the coated rice lost more than the uncoated, but the uncoated one lost a great deal also. Richardson states that the difference in ash before and after treatment is the coating. The difference in the uncoated sample is .31 gms while in the uncoated, it is .19 gms From this we might conclude that one was coated over half as much as the other, when in reality it is an uncoated rice. Although this does not condemn the method, it does indicate that there is a large chance for error, and that the method does not work well in the hands of one who is not experienced in handling its details.

Several tests were made by the Richardson method to determine the relation between the soluble and

and insoluble ash. One ash, sample I obtained by the Richardson method, shows the rates of insoluble to soluble ash to be .0145/008=1.75 before treatment and 008/0029=1.73 after treatment. A rough rice II showed 1.9 before treatment, and 4.5 after. Sample I at another time, by the same method, gave .5 before treatment and 3. after treatment. The difficulty seems to be that there is not enough ash to make accurate determinate.

From the fact that the coating is an insoluble substance and is held on the rice by means of a soluble agent, it was reasoned that the coating could be dissolved off by simply treating the sample with water, which will dissolve off the glucose and the talc would fall off.

Two sample were run as follow. (Determination #2) About twenty-five grains of sample I was placed in a graduated cylinder, and the cylinder filled to the 50cc mark with warm water. The cylinder was let stand for one minute and then shaken for one minute, and the water contained in the cylinder poured quickly into a beaker. This was repeated three times and the solution evaporated to dryness in a platinum dish, heated to constant weight, ashed weighed. It was thought that the rubbing together of the grains in shaking would rub off an unnecessary amount of starch and natural mineral coating, so along with one of these determinations I ran another in which I obtained the solids in a little different way. (Determination #3). Ten grains of sample No. I were placed on a Buchner funnel which was fitted with a stop cock at the bottom so as to let the water pass through the funnel very slowly. The solution and suspension obtained in this way was evaporated to dryness in a weighed platinum dish, dried to constant weight, and ashed.

By method #3 I obtained 8.05% ash from solids, and by #2 I obtained 7.4% ash from solids. Method #3 evidently dissolved off more talc and less starch than #2, but since sample I is a heavily coated rice 8.05% would be nearly as much ash as could be obtained, in any rice. In a sample which had less coating, the per cent of ash would be very small.

In order to increase the per cent of ash I tried running the sample with cold water instead of warm. (determination #4). Twenty-five grains of sample I were placed in the graduated cylinder and cold distilled water added up to the 60cc mark. It was let stand for one

minute and then shook for one minute and then the contents of the cylinder were poured on to a sieve placed in a funnel and the liquid caught in a beaker. This was repeated twice and the rice washed with 50cc of cold water. The washings were then centrifuged, for five minutes, and the supernatant liquid poured off. The solids were evaporated to dryness on a water bath, dried, ashed and weighed. Both samples I and III were run in this way under identical conditions. The per cent of ash from I was 12. from III, was 6.73.

The per cent of ash in sample I has been raised, but not enough.

In order to further increase the amount of ash in the solids, or to effect a more complete separation of talc and starch, a determination was run like #4, but instead of catching the washings in a beaker, they were caught in a tall cylinder. The cylinder was let stand for over half an hour. Then a syphon which was made with a very small inlet and the end bent upward so as to feed from the top, was placed in the cylinder and let set for five minutes. (It was left set for five minutes so that the solution would be settled again after being disturbed). The cloudy liquid was syphoned off and 100ccd distilled water added and let stand again. This was repeated three times and the solids placed in a platinum dish, dried to constant weight and weighed. Sample III was run at the same time under identical conditions. The per cent of ash in sample I was 11.389, and in III it was 5.31%.

I ran another set to see if I could duplicate the above results. In II I got 13.3% ash and in III 2.4% which shows quite a variation.

Since the settling method is quite efficient in separating the starch and talc and the Buchner funnel method does not dissolve off mush of the starch, the question arose. Why not combine the two methods and thus get more complete separation of the talc and starch. This method was tried, duplicates being run to see if under the same conditions the results would check (determination#5). Twenty-five grams of sample #70106 was placed on the Buchner funnel, fitted with a rubber tip and pinch cock at the bottom, and about 50cc of water placed in the funnel. It was allowed to drop out slowly and the water kept over the rice in the funnel all the time. When about 200cc of water had flowed through the funnel, the pinch-cock was opened and all

the water allowed to flow out. Then the rice washed with enough water to fill the cylinder which held 300cc, and was placed to receive the washings.

The cylinder was let stand for one hour and the cloudy liquid syphoned off as in determination #4.

The results showed 36.9% ash and 35.4% ash. This may be considered fairly good checks considering that there was only .0258 and .0265 grains of solids.

Starch forms an emulsion when boiled in water. This would cause starch to remain in suspension and not settle out. It might also hold the talc in suspension with it. But I ran a determination (determination #6) to see if adding hot water would not keep the starch from precipitating. It was run on sample #70106, and the same as after syphoning off the first turn, I added hot water, I obtained 35.1% ash and from a duplicate run in cold water I obtained 36.9%., ash. This shows that the treatment did not effect the results, It may have been that the solution should have been boiled, or it may show that most of the starch had been removed by cold water. The former is probably the case.

In the above four runs made on the same sample, the results were 36.9%, 35.4%, 35.1%, and 36.9% showing great uniformity.

Ordinary salts such as are found in the natural ash of rice are soluble in acids, and I tried sample No. I by the method used in determination #3, but added a little acid (5cc HNO_3) to the solution each time before syphoning off. It did not work because it coagulated the starch which came down and increased the amount of solids, therefore decreasing the per cent of ash to 6.2 when it should have been 36.%.

The next step was to try to substitute a percolator for the Buchner funnel, thinking it would cause more water to flow over any given rice grain. I started (determination #7) by placing 100cc of water in each of three percolators fitted with wire gauze bottoms and stop cock is in case of the Buchner funnel. To each I added 50 grains of rice (a commercial sample labelled "coated with glucose and talc"). The first one I let set 20 minutes, the next 40 minutes, and the next 60 minutes. The three different times was to see how long it would take to dissolve off the coating. At the end of the designated time the stop-cock was opened and the solution

and suspension allowed to run quickly into a tall cylinder. The rice was then washed with 50cc of water and the washings let stand a half hour and syphoned off as in determination #5. From the twenty minute run I obtained .0079 grams of solids, which all burned away in the muffle. From the forty minute run I obtained .0087 grams of solids and .0003 grams of ash. From the sixty minute run I obtained .0112 grams of solids and .0002 grams of ash. The amount of ash is too small for any definite conclusions. This may be due to the fact that the sample was coated very lightly. I ran sample No. 7084 by this same method, letting it stand 20 minutes and obtained .0192 grams of solids of which 53% was ash. I then ran the same sample by the Buchner funnel method letting it stand twenty minutes, and obtained 53.8% ash from .0735 grams of solids. I tried the percolator method, using 100 grams of rice. The results were about the same as before. I got .0075 grams of solids and it all burned but .0002 grams.

It will be noticed that the same amount of ash was obtained from the Buchner funnel method as from the percolator, but the amount of solids obtained is greater. Therefore, there is less chance of error. But the Buchner funnel takes quite a bit more water than the percolator because thespace under the perforated plate must be filled up and the water that is in there is of no use. So in order that the rice be washed sufficiently several hundred CC were necessary. This makes it more inconvenient than the percolator. With the percolator a cylinder holding 300cc is all that is necessary to hold the washings. For this reason I decided to work out the method in detail, using the percolator instead of the Buchner funnel.

The first thing done in working out the details was to determine the time to let the rice stand in the percolator. Two samples No. 70086, were run, one allowed to stand twenty minutes and one forty. One hundred grams of rice was used each time. In the one which stood twenty I obtained .0171 grams of solids of which 54.2% was ash. In the one which stood forty minutes I obtained .0265 grams of solids of which 51.5% was ash. Twenty minutes was decided upon as the proper time. Then the number of times that the solution should be syphoned was determined. I tried letting it stand twenty minutes and syphoning off for three successive times and obtained 22.%. Then I let another stand for t wenty minutes for two times, and obtained 38.8%. These determinations were run on a commercial sample which gave a very decided test for glucose with Fehlings solution. Twenty minutes was thought

to be long enough because the solution did not seem to change much after that.

METHOD.

From all of the foregoing data I devise the following method.

Place a piece of rather coarse wire gauze in the bottom of a small percolator which will hold from 250 to 300cc of water. Fit the bottom of the percolator with a rubber tubing and pinch cock. Set the percolator on a filler stand and place under it a 300cc cylinder which is not more than one and one-half inches in diameter. Pour into the percolator about 25cc of distilled water, then pour carefully into this 100 grams of the sample of rice to be tested. If there is not enough water to cover the rice, put in water until it is covered. Let stand for twenty minutes, then open the stop cock and let the water run into the cylinder. Remove thepinch cock and wash the rice with small portions of water till the cylinder is filled with the water and washings. Place the cylinder in a quiet place and let stand for twenty minutes. Meanwhile bend a glass tube so as to make a syphon that will reach the bottom of the cylinder. The end of the syphon which is in the cylinder should be bent up and drawn to a rather fine point. The bend should be long enough to allow one inch of the solution to remain in the cylinder. This syphon should be placed into the solution about five minutes before the syphoning is done. At the end of twenty minutes syphon off the cloudy liquid, add 100cc of distilled water and allow to stand another twenty minutes and syphon off again. Place the remaining contents of the cylinder in a weighed porcelain or platinum dish, and evaporate to dryness, on a water bath. Then heat to constant weight in a 100° or 110° oven. Weigh the dish then ignite to constant weight.

Any polished rice, the percent of ash, in which runs above 10. is coated. An unpolished rice may run much higher than this. In fact all that were analyzed by me did run over this.

In some cases the polished rice may be over 10%, but the amount of solids is so small that the weight of ash is below the experimental error. In that case the rice is uncoated.

The following is a table showing results obtained by this method.

Table II

Kind of Rice	Samp.No.	Wt Solid	Wt Ash	% Ash	Glu. Test
Bran No. 2	XI	.0096	.002	20.8	
Siam Garden					
Native Milling					
Bran Nol Siam					
Garden					
Native Milling	XII	.0086	.0011	14.	---
	70093	.0184	.0055	30	X
	70084	.0171	.0083	55.2	X
Commercial Sam.	----	.0230	.009	38.8	X
Commercial Sample	-----				
Labled "Coated					
with Glucose					
and Talc"	---				
"Sunburst"	-- XVI	.0074	.0001	---	---
Sze Mui. China					
Rice					
Milled in U. S.	XIII	.0068	.0007	9.7	---
Unbleached &					
Uncoated Rice	XIV	.001	.0000	---	---
Pak Ning China					
No. 2	XV	.008	.0001	---	---
After Polishes					
Removed	III	.0104	.0003	---	---
After Brand is					
Removed	IV	.0130	.004	3.39	---

Table II (Cont.)

~~Kind of Rice~~					
Sze Mui Brown Rice	VI	.0381	.0019	18	---
~~Rice~~. Husk or Paddy					
Removed	VIII	.0175	.0062	34	---
Pak Ning Brown					
Rice Paddy					
Removed	X	.0073	.0015	20	---
Husk or Paddy					
Removed	IX	.0100	.0029	29	---
Rice in Brown					
Slage	II	.0283	.0068	21	----
Husk or Paddy					
Removed	VII	.0164	.0055	21	---

In particular I wish to call attention to sample number XVI which is labeled "Coated with glucose and talc". According to my method it is not coated with glucose and talc.

In conclusion I wish to say that perhaps better limits might be established by a large number of determinations but I feel quite confident that the method as worked out is applicable to any but extraordinary cases. The method might also be worked out to include those rices.which are coated with parafin and talc.

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