1757

After-Cooking Discoloration of Potatoes. Potassium Content of Juice in Relation to Blackening Tendency of Tissue

E. G. Heisler, James Siciliano and R. H. Treadway

Eastern Regional Research Laboratory, Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture, Philadelphia 18, Pennsylvania

SUMMARY

A spectrophotometric method has been adapted for convenient use in determining the potassium content of potato juice. Forty-four samples of 1959 and 1960 crop potatoes from five states east of the Mississippi River were examined for degree of after-cooking discoloration and analyzed for potassium. Increasing discoloration proved to be a function of decreasing potassium content.

In Antigo, Red LaSoda, Early Gem, and Russet Rural, discoloration was obviously correlated with potassium. In Ontario and Katahdin samples this relation was real but not readily apparent.

INTRODUCTION

A previous publication (Hunter *et al.,* 1957) from this laboratory outlined the problem of after-cooking discoloration of potatoes and presented data on the polyphenolic constituents in normal and blackening potatoes. This type of discoloration continues to be a serious problem facing processors, particularly with raw material grown east of the Mississippi. Several processors of dehydrated and frozen potato products have gone so far as to state that after-cooking discoloration is the most troublesome problem encountered with their raw material. Only a small proportion of potatoes in any given lot may be affected by this blackening, but only a few dark pieces in cream-of-potato soup or in frozen French fries are cause for worry in a processing plant. The trade also wants dehydrated products that will reconstitute to white mashed potatoes.

Potatoes that discolor after cooking usually seem normal in the raw, peeled state. The darkening appears at the surface a half hour or so after cooking, and is generally more intense at the stem (basal) end than at the bud (apical) end.

Some processors control this type of discoloration by dipping peeled, sliced potatoes in dilute citric acid or sodium acid pyrophosphate solution before cooking. Much of the experi-

mental evidence and the practical results obtained in the processing plants support the theory that the pigment involved in after-cooking discoloration is the result of oxidation of polyphenolic compounds in the presence of iron. Pigment formation is inhibited by increasing the natural acidity of the potato juice. Thus, these two dipping agents are effective because they lower the pH of the potato, and also presumably because of their sequestering or chelating action on iron.

Processors have urged that additional fundamental chemical research be carried out on the after-cooking discoloration problem in the hope that this quality defect can eventually be eliminated by changes in cultural methods, thereby avoiding acidic dips, which are undesirable in some types of processing. A large number of potato samples were made available from the 1959 and 1960 crops for this study.

Potatoes, one of the richest sources of potassium of all crops, require a heavy annual application of potassium fertilizer in most growing areas. It was established long ago (Ashby, 1905–6) that potassium deficiency in the soil leads to low potassium content in potato tubers. Tottingham *et al.* (1947) and Smith and Nash (1938) found that application of a high level of potassium in ordinary soil culture, and in sand culture using a nutrient mixture, frequently decreased after-cooking blackening tendency in potatoes. Hence, it was considered desirable to extend this line of investigation by determining the potassium content in a wide range of potato samples exhibiting various degrees of darkening, and to search for correlation between potassium concentration and extent of discoloration.

LITERATURE REVIEW

The earlier literature on after-cooking discoloration of potatoes is contained in a review published several years ago (Yanovsky, 1955). Key references appearing in the following two years were cited by Hunter *et al.* (1957). Research on this subject has been continued in recent years in the laboratories of Ora Smith, Cornell University; Flora Hanning, University of Wisconsin; and E. C. Bate-Smith, Low Temperature Research Station, Cambridge, England.

Field tests made in England in 1956–58 showed that low potassium level in the soil leads to after-cooking discoloration in boiled and fried potatoes (Harrap, 1960). We are unaware, however, of any published research findings on correlation of potassium concentration in potato tubers with degree of after-cooking discoloration.

EXPERIMENTAL METHODS

A most advantageous way of analyzing the water-soluble substances in potato is merely to assay the juice for the desired constituents. This proceeding may not yield all of a constituent present in the tuber, but it has been found instructive particularly with respect to comparing samples from the stem and bud ends of the potato.

A spectrophotometric method developed by Bultasova *et al.* (1955) was used to determine potassium. Since this method was originally developed for use with blood serum, certain modifications had to be made for use with potato juice. An important advantage of the spectrophotometric method is that ashing or wet digestion is not required.

Apparatus and reagents. A centrifuge and spectrophotometer are required for the method employed in the potassium determinations. An international centrifuge, size 1, type SB, and a Beckman spectrophotometer, model B, were used (no endorsement implied). Solutions used in the analysis required no special precautions in preparation.

Potato sampling. Segments were removed from the stem and bud ends of the tubers by transverse slicing with a knife. Cylindrical sections 7/8 in. in diameter were then cut from the centers of the segments with a no. 15 cork borer. These cylinders were cut to approximately 1/2 in. long and then cut in half lengthwise. One half was used for the potassium determination, and the other for measurement of degree of discoloration by a reflectance test. The half cylinders used for the potassium determination were adjusted in length so that 26 pieces totaled 100.00 g. Those used for the reflectance measurement were adjusted to 65.00 g.

Determination of degree of discoloration. The reflectance obtained from a smooth surface (under glass) of cooked mashed potato was taken as a measure of discoloration. The reflectance attachment to the Beckman Model B spectrophotometer was used with $MgCO_3$ as standard. In this study, "degree of discoloration" was arbitrarily taken as $\frac{R_B - R_S}{R_S}$, where R_B is the reflectance of mash from the bud end, and R_S represents the same value for the stem end. The more discoloration in the potato, the greater the difference between R_B and R_S and the lower the value of R_S. Thus, these factors reinforce each other to amplify the value for degree of discoloration, making the system more sensitive in differentiating samples.

The 65.00 g (26 half-cylinders) of potato tissue was cooked by steaming 35 min at atmospheric pressure. The tissue was allowed to cool for 30 min, during which time the skin was carefully stripped from the top of the half-cylinders; care was taken not to remove any of the potato tissue along with the skin. After the 30 minutes' cooling period, the tissue was mashed for one minute in a Waring blender with 13 ml of water. This amount of water was necessary to obtain a mash fluid enough for the blender to handle properly. A round glass dish approximately 3/4 in. in diameter and 1/4 in. deep was filled with the mash and covered with a piece of glass, and the reflectance read.

Potassium determination. Dilute potato juice was prepared for this determination in the following way. The 100.00-g sample of potato tissue was ground 2 min in 300 ml of distilled water in a Waring blender. After homogenization, the slurry was filtered through filter paper. The filtrate was collected in an Erlenmeyer flask and heated by immersing 5 min in a boiling-water bath to coagulate the protein. Loss of vapor during heating was prevented by covering the vessel. The protein was then removed by filtering through filter paper, leaving the filtrate containing about 1% solids for the potassium determination.

The resulting samples of deproteinized potato juice, though prepared by the same procedure, varied slightly in solids content because of differences inherent in the various lots of potatoes. The exact solids content of each juice sample was determined by loss in weight after drying. Potassium was determined as the quantity present in deproteinized diluted juice, but it can be related percentagewise to the fresh potato weight or to the solids content of the juice.

The following steps were carried out in isolating the potassium. One ml of the approximately 1% solids potato juice was placed in a 15-ml centrifuge tube. One ml of freshly made 20% sodium cobaltinitrite solution was added, and 15 min was allowed for precipitation of potassium sodium cobaltinitrite. Addition of three drops of 5% solution of Aerosol AY (American Cyanamid Company) ef-

fectively prevented particles of the precipitate from floating at the surface. The mixture was then centrifuged for about 5 min, and the supernatant solution decanted. The precipitate was purified by washing with 3 ml of water containing 3 drops of the Aerosol AY solution, centrifuging, and decanting. The water wash was repeated. Then the precipitate was washed twice with 3 ml of 70% ethanol, followed by centrifugation and decantation.

Spectrophotometric determinations of the quantity of potassium present in the extracts were conducted in accordance with the following procedure. One ml of 2% solution of disodium ethylenediaminetetraacetate (dihydrate) and 5 ml of freshly made 3% hydrogen peroxide solution were added to the precipitate in the centrifuge tube. The mixture was shaken, and the tube heated in a boiling-water bath for 20 min, during which time color is developed through formation of a cobalt complex with the disodium salt of EDTA. Then the tube was removed from the bath and cooled 3 min under the tap. Six ml of water was then added to the tube, and the solution was mixed by pouring it back and forth several times from centrifuge tube to calibrated spectrophotometer tube. The light absorbance of the solution was determined at wavelength 530 mμ against a blank containing all the reagents except the potato juice.

For calibration, three standard solutions containing known amounts of potassium were run with the samples. These standard solutions were made up containing 0.5, 1.0, and 1.5 mg K per ml. The absorptivity, *a*, is obtained from the equation $a = \frac{A}{c}$, where

where *A* is the absorbance of the solution and *c* its concentration in mg/ml. The value for *a* having been determined, the concentrations of unknowns were then obtained by solving the equation for *c*.

In establishing the conditions used for concentrations of reagents and solutions, for time intervals employed in precipitating the potassium complex, and for heating the solutions to develop color for spectrophotometry, wide ranges were investigated and the optimum selected in each case.

The reproducibility of the spectrophotometric method was checked by measurements on standard solutions of potassium citrate containing 0.5, 1.0, and 1.5 mg K/ml. Fourteen replicates were run at each of these concentrations. The absorptivity had a mean value of 0.968, a standard deviation of 0.0309, and a coefficient of variation of 3.19%. This reproducibility is considered sufficiently good.

Accuracy of the method was gauged by determining the percentage of recovery of a known amount of potassium added as the citrate to potato juice. A 1:1 mixture was made of a 1% solids potato juice and a solution containing 0.1% of potassium. The potassium content was determined before and after addition of the known amount of potassium salt, and the recovery achieved by the method was 97.3%.

Since NH_4^+ forms a precipitate with sodium cobaltinitrite in a manner similar to K^+, it was considered advisable to determine the NH_4^+ content in the deproteinized potato juice used in the potassium determination. Potato juice was treated with phosphate-borate and sodium hydroxide-borate buffer reagents, and the mixture was then steam distilled to determine NH_3 liberated (Vickery and Leavenworth, 1935). No measurable quantity of NH_3 could be detected in several samples of potato juice. Thus, it was concluded that the NH_4^+ present was insufficient to have a significant effect on K^+ values obtained from freshly prepared potato juice.

RESULTS AND DISCUSSION

Potato samples representing a wide range in after-cooking discoloration were received from the following locations: 17 from Wisconsin; 21 from Michigan; 4 from Pennsylvania; and 1 each from Virginia and Maine. Table 1 shows these 44 samples in order of decreasing discoloration. It is readily observed that the stem end in every case contains considerably less potassium than the bud end. This tends to indicate that stem-end blackening is associated with low potassium content.

Table 1. Potassium content in juice of potatoes having various degrees of discolorization.

			Percent K in juice					
			Wet basis[b]				Dry basis	
Sample no.	Location grown and variety	$\frac{R_B - R_S}{R_S}$ [a]	K_B [d]	K_S [d]	$K_B - K_S$	$\frac{K_B - K_S}{K_S}$	K_B	K_S
59–23	Wis. Antigo	0.697 [c]	0.144	0.065	0.079	1.22	14.0	6.4
59–24	Wis. Red LaSoda	0.695	0.138	0.066	0.062	0.94	15.2	6.7
59–19	Wis. Katahdins	0.623	0.133	0.073	0.060	0.82	13.9	7.5
59–20	Wis. Kennebec	0.572	0.137	0.072	0.065	0.90	15.4	8.3
59–25	Wis. Red LaSoda	0.522	0.152	0.085	0.067	0.79	16.0	8.9
59–15	Wis. Early Gem	0.519	0.127	0.054	0.073	1.35	12.6	5.1
59–10	Mich. Rural Russet	0.514	0.109	0.040	0.069	1.73	11.5	4.2
59–22	Wis. Antigo	0.497	0.134	0.077	0.057	0.74	14.1	8.9
59–18	Wis. Katahdins	0.475	0.133	0.073	0.060	0.82	14.3	8.1
60–1	Pa. Merrimac	0.469	0.111	0.051	0.060	1.17	10.0	4.4
60–2	Pa. Merrimac	0.449	0.109	0.046	0.063	1.39	11.0	4.4
60–3	Pa. Merrimac	0.421	0.130	0.054	0.076	1.41	13.1	5.3
60–5	Wis. Antigo	0.405	0.119	0.091	0.028	0.30	12.4	9.0
60–4	Maine Katahdins	0.332	0.147	0.090	0.057	0.63	14.7	9.2
60–7	Wis. Katahdins	0.332	0.124	0.087	0.037	0.43	11.9	8.7
59–16	Wis. Early Gem	0.322	0.131	0.067	0.064	0.96	13.2	6.8
59–13	Mich. Huron	0.306	0.149	0.115	0.034	0.30	13.7	10.5
59–17	Wis. Ontario	0.259	0.148	0.072	0.076	1.06	14.4	6.6
60–6	Wis. Red LaSoda	0.239	0.121	0.084	0.037	0.44	9.9	6.7
60–16	Mich. Huron	0.235	0.121	0.084	0.037	0.44	10.3	7.2
60–11	Mich. Ontario	0.204	0.100	0.063	0.037	0.59	10.1	6.5
60–12	Mich. Ontario	0.183	0.109	0.079	0.030	0.38	10.7	7.8
59–9	Mich. Ontario	0.176	0.119	0.076	0.043	0.57	13.8	9.7
59–5	Mich. Ontario	0.173	0.136	0.082	0.054	0.66	13.5	7.8
59–7	Mich. Russet Sebago	0.161	0.140	0.082	0.058	0.71	16.5	9.4
59–4	Mich Russet Rural	0.161	0.104	0.062	0.042	0.68	12.4	7.9
59–14	Mich. Cherokee	0.150	0.132	0.097	0.035	0.36	13.6	10.7
59–2	Pa. Katahdins	0.148	0.139	0.108	0.031	0.29	16.6	14.0
59–1	Va. Cobblers	0.145	0.121	0.078	0.043	0.55	12.1	7.8
59–8	Mich. Cherokee	0.144	0.146	0.073	0.073	1.00	14.9	7.3
60–9	Wis. Kennebec	0.134	0.133	0.078	0.057	0.73	14.6	7.9
60–10	Wis. Ontario	0.128	0.108	0.070	0.037	0.53	11.0	6.8
60–13	Mich. Ontario	0.124	0.119	0.096	0.023	0.24	11.9	9.9
59–11	Mich. Rural Russet	0.124	0.102	0.070	0.032	0.46	12.4	9.0
60–19	Mich. Ontario	0.095	0.131	0.090	0.041	0.46	13.3	9.6
59–3	Mich. Ontario	0.078	0.122	0.080	0.042	0.53	13.1	8.1
59–12	Mich. Manota	0.069	0.130	0.107	0.023	0.21	11.4	9.9
59–6	Mich. Kennebec	0.063	0.133	0.085	0.048	0.56	16.2	11.8
60–8	Wis. Early Gem	0.052	0.115	0.059	0.056	0.94	10.3	4.9
60–14	Mich. ?	0.015	0.137	0.098	0.039	0.40	12.8	6.5
60–17	Mich. Cherokee	0.010	0.133	0.103	0.030	0.30	12.8	10.7
60–18	Mich. Russet Rural	0	0.125	0.087	0.038	0.44	12.9	9.5
59–21	Wis. Kennebec	0	0.163	0.094	0.069	0.73	16.0	10.9
60–15	Mich. Russet Rural	0	0.118	0.101	0.017	0.17	12.7	10.9

[a] "Degree of discoloration," where R_B is reflectance of cooked bud tissue and R_S reflectance of stem tissue.
[b] Approximately 1% total solids.
[c] Higher value denotes greater blackening.
[d] K_B denotes potassium in bud extract, and K_S potassium in stem extract.

Table 2. Statistical study of all the data.

X = Potassium factor.
Y = Reflectance factor.

ΣX	ΣY	ΣX^2	ΣY^2	ΣXY	Σx^2	Σy^2	Σxy	Slope $b = \frac{\Sigma xy}{\Sigma x^2}$
30.33	11.41	26.56	4.69	9.80	5.63	1.73	1.93	0.342

Analysis of variance

Source	Sum of squares	Degrees of freedom	Mean squares	F
Total $= \Sigma y^2$	1.73	43		
$b\Sigma xy$	0.66	1	0.66	25.82
Error	1.07	42	0.0255	**

Correlation between discoloration, $\frac{R_B - R_S}{R_S}$, and potassium content is not obvious. On close examination, however, both low potassium in the stem end and a large difference in the potassium contents of bud and stem ends tend to be associated with blackening. Thus by combining these two factors in the ratio $\frac{K_B - K_S}{K_S}$, similarly to that done for reflectance values, one arrives at an expression for potassium content that correlates with degree of discoloration.

A good approximation of potassium content expressed as percentage of the whole potato tissue is readily obtained from the data of Table 1. After the 100.00-g potato sample (containing about 80 ml water) is ground in 300 ml of water, the potassium salts are then contained in 380 ml of dilute juice. Hence, the values for the quantity of potassium present per 100 ml of dilute juice, in the wet-basis column of Table 1, should be multiplied by 3.8 to give the total amount present in 100.00 g of potato tissue. This calculation yields values of 0.15–0.44% potassium in stem-end tissue, and 0.41–0.63% in bud-end tissue. It can be observed that the potassium content of the bud end changes little in comparison with the threefold difference in maximum and minimum values for potassium in the stem-end tissue.

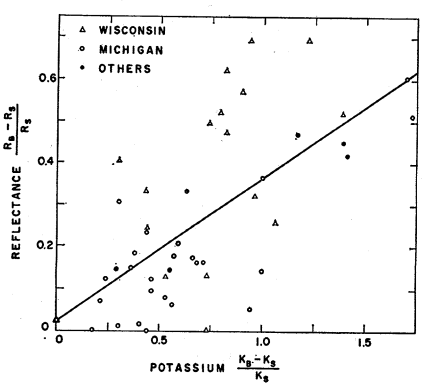

Fig. 1. Variation of degree of discoloration, $\frac{R_B - R_S}{R_S}$, with the potassium factor $\frac{K_B - K_S}{K_S}$.

In Fig. 1, values for $\frac{R_B - R_S}{R_S}$, degree of discoloration, are plotted against values for $\frac{K_B - K_S}{K_S}$. It is readily apparent that there is some correlation between these two factors. A linear regression was fitted to all the data, and an analysis-of-variance test determined that this relationship was highly significant (1% level). An example of the analysis of variance is given in Table 2. This relation, also tested on data from the 1959 and 1960 crops of potatoes separately, was again found to be highly significant. When the relation was tested for data on potato samples grouped according to the state of origin, however, it was found to be not significant. This raises a question regarding the validity of the significance found between discoloration and potassium content for the data considered as a whole. The apparent high degree of correlation found upon consideration of all data may have been due to the values for each state providing a point-type estimate; a combination of these would explain the over-all high significance.

Table 3 lists the varieties separately. It can be observed that the correlation between discoloration and potassium is obvious for some varieties: Antigo, Red LaSoda, Early Gem, and Russet Rural. The 9 samples of Ontario and 5 of Katahdin are each sufficient in number to warrant a statistical analysis. A linear regression was fitted to the data for these two varieties, and an analysis of variance test determined that the relationship was significant (5% level) for each variety. Kennebec, Cherokee, and Huron varieties did not show by simple observation a relation between blackening tendency and potassium content. There was not enough variation in blackening tendency among the Merrimac samples to warrant drawing a conclusion.

Although the relation between after-cooking blackening and potassium content has been shown to be statistically significant, this method probably could not be used to predict discoloration in an individual sample. These findings, in conjunction with data on organic acid content, phenolic acid content, pH, and mineral content, may ultimately lead to an understanding of the mechanism of blackening, and thus to its prevention.

REFERENCES

Ashby, S. F. 1905–6. A contribution to the study of factors affecting the quality and composition of potatoes. *J. Agr. Sci., (England)* **1**, 347.

Table 3. Study of varieties with respect to potassium content and blackening tendency.

Sample no.	Variety	Reflectance, bud minus stem: Stem	K content, bud minus stem: Stem
59–23	Antigo	0.697	1.22
59–22	Antigo	0.497	0.74
60–5	Antigo	0.405	0.30
59–24	Red LaSoda	0.695	0.94
59–25	Red LaSoda	0.522	0.79
60–6	Red LaSoda	0.239	0.44
59–15	Early Gem	0.519	1.35
59–16	Early Gem	0.322	0.96
60–8	Early Gem	0.052	0.94
59–10	Russet Rural	0.514	1.73
59–4	Russet Rural	0.161	0.68
59–11	Russet Rural	0.124	0.46
60–18	Russet Rural	0	0.44
60–15	Russet Rural	0	0.17
59–17	Ontario	0.259	1.06
60–11	Ontario	0.204	0.59
60–12	Ontario	0.183	0.38
59–9	Ontario	0.176	0.57
59–5	Ontario	0.173	0.66
60–10	Ontario	0.128	0.53
60–13	Ontario	0.124	0.24
60–19	Ontario	0.95	0.46
59–3	Ontario	0.078	0.53
59–19	Katahdin	0.623	0.82
59–18	Katahdin	0.475	0.82
60–7	Katahdin	0.332	0.43
60–4	Katahdin	0.332	0.63
59–2	Katahdin	0.148	0.29
59–20	Kennebec	0.572	0.90
60–9	Kennebec	0.134	0.73
59–6	Kennebec	0.063	0.56
59–21	Kennebec	0	0.73
59–14	Cherokee	0.150	0.36
59–8	Cherokee	0.144	1.00
60–17	Cherokee	0.010	0.30
59–13	Huron	0.306	0.30
60–16	Huron	0.235	0.44
60–1	Merrimac	0.469	1.17
60–2	Merrimac	0.449	1.39
60–3	Merrimac	0.421	1.41

Bultasová, H., and E. Konopásek. 1955. Indirect colorimetric determination of potassium in blood serum. *Chem. listy* **49**, 769.

Harrap, F. E. G. 1960. Some aspects of the potash nutrition of the potato. *J. Sci. Food Agr.* **11**, 293.

Ker, Ann S., E. G. Heisler, J. Siciliano, R. H. Treadway, and C. F. Woodward. 1957. After-cooking discoloration of potatoes: possible involvement of polyphenolic constituents. *Food Research* **22**, 648.

Pucher, G. W., H. B. Vickery, and C. S. Leavenworth. 1935. Determination of ammonia and of amide nitrogen in plant tissue. *Ind. Eng. Chem., Anal. Ed.* **7**, 152.

Smith, Ora, and L. B. Nash. 1938. Effect of certain minor elements on chemical composition and cooking quality of potato tubers. *Proc. Am. Soc. Hort. Sci.* **35**, 530.

Tottingham, W. E., R. Nagy, A. F. Ross, J. W. Marek, and C. O. Clagett. 1947. Blackening indices of potatoes grown under various conditions of field culture. *J. Agr. Research* **74**, 145.

Yanovsky, E. 1955. The after-cooking discoloration of potatoes—a review. Eastern Regional Research Laboratory, Phila., Pa., U. S. Dept. Agr. ARS-73-7.

The authors thank Mr. Joe N. Boyd, Biometrical Services Staff, Agricultural Research Service, U.S.D.A., for advice and suggestions in connection with the statistical treatment of data and certain conclusions drawn from those data.