Zeitschrift: Mitteilungen aus Lebensmitteluntersuchungen und Hygiene = Travaux

de chimie alimentaire et d'hygiène

Herausgeber: Bundesamt für Gesundheit

Band: 95 (2004)

Heft: 5

Artikel: Acrylamide: Swiss frying test instead of measuring reducing sugars to

evaluate potatoes for frying and roasting?

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DOI: https://doi.org/10.5169/seals-981833

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Acrylamide: Swiss frying test instead of measuring reducing sugars to evaluate potatoes for frying and roasting?

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Received 20 April 2004, accepted 1 September 2004

Introduction

Acrylamide, a probable carcinogen (1, 2), may be formed at high concentrations in roasted and fried potato products, whereby the concentration strongly depends on the properties of the potato. This paper deals with how the suitability of potatoes for frying and roasting should be evaluated.

When potatoes are fried, roasted or baked, reducing sugars are key components for the browning behavior and the development of roasting flavor (3, 4) – but also for the formation of acrylamide. Together with the free amino acids, the reducing sugars are the most relevant components of the Maillard reaction. Also the formation of acrylamide is linked with the Maillard reaction: asparagine is degraded with the support of the reducing sugars and ammonium (5–10). Asparagine and ammonium are of limited practical interest, as their concentrations in potatoes are fairly constant (11, 12), while the content of the reducing sugars varies between some 0.05 and 20 g/kg fresh weight.

The producers of potato chips (British crisps) and French fries or their prefabricates carefully selected potatoes low in reducing sugars for a long time in order to avoid strong browning. This means use of suitable cultivars and avoidance of storage at temperatures below some 8–10 °C. Now minimization of acrylamide formation adds another argument for the use of such potatoes (13–15).

To minimize acrylamide formation in roasted and fried potato products prepared in private homes and the gastronomy, but also to obtain optimum product quality, a reliable supply of suitable potatoes must be established. The Swiss distributors sell fresh potatoes in bags labeled as "suitable for...", including the fried and roasted products. So far these categories related to the structure of the cooked

potato (firm, floury), disregarding the content of reducing sugars – potatoes were sold as "suitable for French fries" even when the concentration of fructose and glucose exceeded 10 g/kg. In Switzerland, this should change for the harvest 2004: it is intended to sell a separate line of potatoes suitable for frying and roasting with a content of reducing sugar envisioned to be below about 1 g/kg fresh weight (14).

This raised the question of how to evaluate the potatoes. It is an issue of practical importance, since the number of samples to be analyzed is high and the present methods for determining reducing sugars presuppose a laboratory. The system used by the Swiss potato industry largely does without sugar analysis: the suitability of potatoes is determined through the browning resulting from a standardized frying test introduced almost 20 years ago (16). Since browning depends on the content of reducing sugars as does acrylamide formation, the browning observed by the frying test, the content of reducing sugars and the potential of acrylamide formation are interrelated.

For the standardized frying test, 10 tubers are selected from a lot of potatoes. Using a specially designed cutter, a slice of 1.2 mm thickness is excised from the center of the tuber from the basal to the apical end and fried in oil at 175 °C, using at least 3 l of oil in order to avoid a substantial temperature drop by the addition of the 10 potato slices. Frying is stopped when the formation of larger vapor bubbles comes to an end. The color of the resulting chips is classified by a scale which usually ranges between 4 and 7 (the full scale is from 1 to 10), using an official table with 20 pictures of examples for each of these classes. The potato chips belonging to class 7 show minimal browning or small zones of significant browning, whereas class 4 characterizes tubers with a rather high sugar content, and the corresponding chips show strong browning on most of the surface. The results of the 10 chips from a lot are expressed as number of chips belonging to each class starting with the high classes. As an example, a lot of potatoes classified as 8 2 0 0 gave 8 chips of class 7, two of class 6 and none of classes 5 and 4.

This study deals with the question whether fresh potatoes suitable for roasting and frying should be evaluated by the frying test or by measurement of the reducing sugars. It compares the results and provides a conversion of the classification by the frying test into contents in reducing sugar. The choice of evaluating the potatoes through the reducing sugars or the frying test has implications on the criterion used for agreements within the trade and possibly legal limits.

Experimental

Experiments were performed with potatoes for the production of French fries (U. Vollmer, Frigemo Produktion Chur AG) and chips (P. Albisser, P. Realini, Zweifel AG, Spreitenbach), tubers from agricultural research (T. Hebeisen, Swiss Federal Research Station for Agroecology and Agriculture FAL, Reckenholz-Zürich), local shops and a farmer from Wittinsburg (Basle), all from February/March 2004. For some potatoes, the sugar content was increased by storage at 4°C for a few days or reduced by reconditioning at room temperature for a few weeks.

The frying test was carried out strictly following the instructions of the manual (16) and an expert (E. Schellenberg, Qualiservice GmbH, Berne). From the center of a tuber, a 1.2 mm slice was cut over the longitudinal axis, using the device from Swisspatat (Berne, Switzerland). This slice was rinsed with tap water, then fried as a single chip in 1.2 l oil (Suprema Universal-Pflanzenöl, Migros, Zürich, Switzerland) thermostatted at 175 °C using a regulated laboratory heating plate with magnetic stirrer. The chip was repeatedly submersed and removed from the oil when the formation of large vapor bubbles came to an end (the formation of some small bubbles may continue for while). The color was classified by comparison with the table from Swisspatat, further differentiating between the classes by a decimal system. For the final evaluation, the classification was rounded off to an integer note, adding the x.5 to the lower note.

Reducing sugars were enzymatically determined from the rest of the potato using the test kit from Scil Diagnostics (Martinsried, Germany) (17). The potato pieces were grated and homogenized. 50 g of this homogenate was blended with 200 ml distilled water using a Polytron (Kinematica, Lucerne, Switzerland). If the sample was too small, the analysis was adjusted to 25 g. 5 ml of solutions Carrez I (150 g/l of potassium hexacyanoferrate(II) trihydrate; Merck, Darmstadt, Germany) and Carrez II (300 g/l of zinc sulfate heptahydrate; Fluka, Buchs, Switzerland) were admixed. Foam was broken by addition of 100 µl of 1-octanol (Fluka) and the volume adjusted to 500 or 250 ml with distilled water. Filtered samples (Schleicher & Schuell) were subjected to enzymatic analysis as described by the producer.

Results

Figure 1 shows typical samples of chips classified between 7 to 4 by the frying test. Class 7 (upper left) shows at most slight browning or stronger browning restricted to a small area. Classes 8–10, with even weaker or absent browning, are

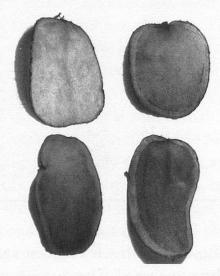


Figure 1 Results from the frying test: classes 7 to 4 (upper left to lower right)

sometimes distinguished, but there is no official color code; they are usually included into class 7. Class 6 (upper right) is characterized by well noticeable browning, possibly some darker spots. The chip of note 4 (lower right) shows strong browning over most of the surface. Normally chips with even stronger browning (classes 1–3) are included into class 4. Dark regions from damage resulting from impacts during harvest or transport are disregarded.

Table 1 lists the results in terms of classification by the frying test and content of reducing sugars (glucose plus fructose) per fresh weight for all individual tubers analyzed. The tubers were from 8 cultivars, mostly belonging to several lots. They were selected to have a sugar content covering the range between 0.2 and 4 g/kg. Gray fields group 10 tubers from the same lot, i.e. samples as in reality evaluated to classify a lot of potatoes by the frying test. The other tubers were single pieces from different lots.

Table 1 Classification by the frying test ("Test") and sums of glucose and fructose ("Glu+fru", g/kg fresh weight) for the individual tubers analyzed. The gray fields highlight groups of 10 tubers from the same lot

Test	Glu+fru (g/kg)	Test	Glu+fru (g/kg)	Test	Glu+fru (g/kg)	Test	Glu+fru (g/kg)
Agria	ESLET LES DE 1	Bintje		Victoria	a	Desiré	е
7	0.33	7	0.27	7	0.14	7	0.24
7	0.35	6.5	0.66	7	0.08	6.8	0.17
6.8	0.24	6.5	0.26	7	0.17	6	0.29
6.5	0.2	6	0.71	6.9	0.5	4.5	3.2
6	1.66	5	1.91	6.7	0.33	Urgen	
6	0.67	5	1.84	6.7	0.34	7	0.31
6	1.35	5	1.65	6.7	0.28	6.8	0.29
5.8	1.04	5	1.07	6.5	0.99	6	0.7
5	4.21	4.8	2.66	5	1.59	5.5	0.91
4.5	1.22	4.5	3.38	4.8	2.73	5.5	0.64
4	4.41	7	0.23	Charlo	tte	4.8	1.5
7	0.53	6.5	0.32	6	1.3	4.8	1.77
7	0.29	5	1.74	6	1.3	4.5	2.38
7 7 7	0.25	4.8	3.29	5.5	0.65	4.5	1.86
	0.24	Erntest	olz	5.4	1.27	4	2.57
7	0.22	7	0.46	5	2.25	5	1.51
7	0.16	7	0.21	5	2.62	4	3.87
7 7	0.15	7	0.33	4.5	1.4	Nature	ella
7	0.08	6.9	0.26	4.5	2.49	5.5	0.75
6.9	1.28	6.8	0.24	4	3.04	5.5	1.05
6.5	0.35	6.5	0.41	4	4.42	5	0.91
						4	2.48

Figure 1 plots the classification by the frying test against the measured content of reducing sugar for all tubers analyzed. The mean contents were calculated from groups and inserted as squares interconnected by a line.

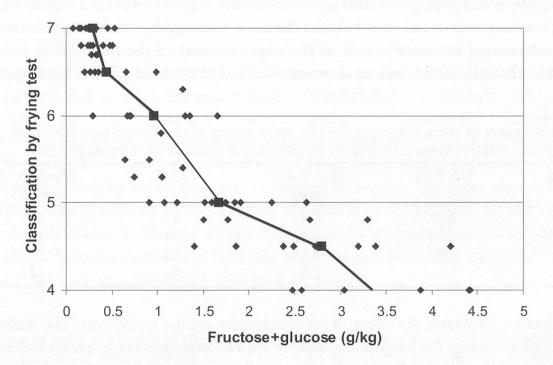


Figure 2 Classification by the frying test against the content of reducing sugars for the tubers analyzed (all cultivars), with the mean sugar contents introduced for groups as squares interrelated by a line

Table 2 lists mean values for reducing sugars and standard deviations calculated for the above results grouped to integer classes. It is concluded that, e.g., potatoes of frying class 6 on average contained 0.76 g/kg reducing sugar. Classes 7 and 4 cannot be accurately calibrated when they include the less official higher and lower classes, respectively. When class 7 includes the higher classes, a large number of samples of these top classes would have reduced the value given in table 2. However, this has little effect on the final results since the value is anyway low. The problem is more severe for class 4 if the lower classes are included, since then any tuber containing more than about 3.5 g/kg reducing sugar belongs to it. Therefore, for calibrating the reducing sugars of class 4, no tubers fitting into lower classes were included. In reality, lots of potatoes containing class 4 tubers are usually not considered suitable for frying and roasting.

The uncertainty for individual results is substantial: for class 6 tubers, the contents of reducing sugar have a standard deviation of 54%, i.e. they range within 0.35 and 1.17 g/kg with a probability of merely 65%. This variability originates, firstly, from the rather rough classification, grouping results between classes 5.5 and 6.5, which means between 0.52 and 1.22 g/kg reducing sugar when linearly extrapolated from the data of table 2. Secondly, the data in figure 2 shows that the results widely vary also when looking at a finer classification. An important part of this variability is the result of the inhomogeneous distribution of the sugars within the tuber: many chips show strong browning at one end and hardly any at the other. For the classifi-

cation, these differences are averaged within the chip. However, a region of high sugar content may or may not fall into the zone analyzed by the frying test, over- or underestimating its contribution to the sugar content of the tuber. This does not happen when the sugar content is measured, since the whole tuber is homogenized.

Table 2
Mean contents of reducing sugar for the main classes of the frying test, standard deviations, relative standard deviations (RSD) and number of samples per class

Frying test	Glu+fru (g/kg)	Stand. dev. (g/kg)	RSD (%)	Number of samples
7	0.27	0.11	41	30
6	0.76	0.41	54	16
5	1.72	0.66	38	22
4	3.3	0.9	27	14

Figure 3 illustrates the effect of inhomogeneity on the frying test. The main chip from a slice through the longitudinal axis shows a brown and a bright part (classes 4 and 6; classification of the whole chip, 5). From the halves on each side of the main slice, two more slices were taken in vertical direction, cutting the halves into 3 pieces of about equal size (see drawing). They belonged to all classes between 4 (upper left) and 7 (lower right) and show that most of the reducing sugar was concentrated in the upper left region. The lower half could have been classified as 6 or even 7. In conclusion: the frying test not necessarily provides a representative picture of the potato, while the sugar determination performed on a homogenized tuber avoids this source of uncertainty.

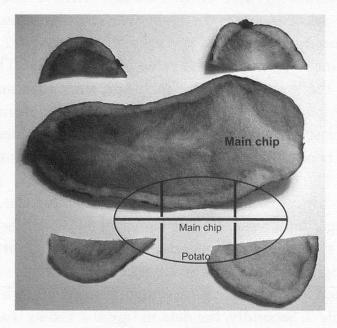


Figure 3 Frying tests of a tuber: main chip cut from the longitudinal axis and two minor chips from each of the lateral parts. The lateral chips suggest that the maximum sugar content was in the upper left region

In reality, a lot of potatoes is evaluated by the frying test being applied to 10 tubers. The reducing sugars were usually determined from 10–15 tubers, analyzed as a single, homogenized sample (14). The two criteria can be compared by looking at the results from 10 individual tubers from the same lot. In table 1, the gray background specifies the results from tubers belonging to the same lot.

Table 3 shows the calculation of the concentrations of glucose and fructose from the frying notes for the example of the Urgenta tubers (frying test 2 1 6 1) using an EXCEL table. Two tubers were classified as 7, which, according to table 2, on average contain 0.27 g/kg reducing sugar. To obtain the average, the mean sugar content for a class was multiplied by the number of samples of the given class. The sum of these contributions divided by 10 resulted in a mean content of reducing sugar of 1.49 g/kg. From the contents of reducing sugar measured for the individual tubers (table 1), an average content of 1.29 g/kg is derived.

Table 3
Content of reducing sugar of the Urgenta potatoes (10 tubers, table 1) calculated from the classification of the frying test (2161) and the mean contents of glucose and fructose of the classes in table 2

Frying test classes	7	6	5	4
Mean glu+fru (g/kg)	0.27	0.76	1.72	3.3
Urgenta	Assessment a service			
Samples/class	2	1	6	1
Samples x sugar	0.54	0.76	10.32	3.3
Sum/10			1.49 g/kg red. sı	igar

Table 4 summarizes such results for the 6 lots of 5 different cultivars listed in table 1 with sugar contents ranging from 0.35 to 2.07 g/kg. The contents of reducing sugars derived from the frying test deviated from those directly measured by 1–22% (mean value, 11%). These deviations are substantially lower than those in table 2, indicating that much of the uncertainty of evaluating a single tuber can be eliminated through the use of 10 tubers.

Table 4
Frying tests and sugar contents of 10 tubers of the same lot: reducing sugars as derived from the frying test and calculated as average of the results measured for the individual tubers

Sample	Frying test	Red. sug	Deviation	
		Derived	Measured	(%)
Agria 1	9100	0.32	0.35	9
Victoria	7120	0.61	0.72	15
Agria 2	3511	0.96	1.23	22
Bintje	1351	1.45	1.44	1
Urgenta	2161	1.49	1.29	16
Charlotte	0244	2.16	2.07	4

Discussion

The frying test was introduced to predict browning of potato chips and French fries. Now it is considered for predicting acrylamide formation during frying or roasting. The criterion used so far for predicting the potential of acrylamide formation of a potato was the sum of glucose and fructose. As shown here, the results are rather well correlated.

It is not obvious whether the frying test or the reducing sugars provide the more relevant criterion to evaluate potatoes regarding their potential of acrylamide formation. Resulting from the Maillard reaction, browning is determined by the concentrations of reducing sugars and free amino acids (in potato principally asparagine and glutamine). Owing to the fairly constant concentrations of asparagine and glutamine (12), the influence of these on browning is modest, explaining why browning is well correlated with the content of the reducing sugars.

Acrylamide also originates from the Maillard reaction, but specifically from the branch involving asparagine. Since asparagine is the predominant free amino acid in potato and the asparagine/glutamine ratio is fairly constant, its influence is of modest importance and acrylamide formation should also be well correlated with the browning. However, as browning in the frying test also reflects changes in asparagine and possibly other compounds influencing acrylamide formation (e.g. ammonium), its results should better reflect the potential of acrylamide formation than the measurement of the sugars. In fact, the frying test applies conditions close to those applied for food preparation.

In addition, there are some important practical aspects in favor of the frying test:

- 1. The test is well established in the trade and the industry without many conflicts about disagreeing results. Extension of this system to the fresh potatoes would be easy.
- 2. The Swiss trade used restrictions for frying test classes for a long time (18), i.e. there is a large data base on the harvests of many years. People involved can make use of their experience.
- 3. The test can be performed without a laboratory.
- 4. The results are available in a few minutes, which is a prerequisite when a truck can be discharged only after the quality of the potatoes is verified.
- 5. The frying test not only shows the sugar content, but also its distribution within and between the tubers. Furthermore, infections and other deficiencies are highlighted.

The argument in favor of measuring sugars:

- 1. The method is more precise: after homogenizing the whole potatoes, effects by inhomogeneous distribution of sugars are eliminated (the uncertainty from picking 10 tubers from a truck load is the same for both types of analyses).
- 2. Sugar concentrations can be measured in a wider range: below some 0.3 g/kg, the frying test is no longer selective, which limits its usefulness, e.g., for the chips industry; above some 4 g/kg, samples are classified at or below class 4.

- 3. Scientific thinking prefers concentrations to a visual evaluation of a frying test.
- 4. Potato products or prefabricates can only by analyzed through the sugars.

If the frying test is accepted as the routine method for evaluating fresh potatoes intended for frying or roasting, there must be a conversion of frying classification to the contents of reducing sugars. As shown above, this conversion seems to be reasonably precise.

Table 5 shows the conversions for some critical points. If a limit of 1 g/kg reducing sugar per fresh weight is envisioned, the above formula suggests that this would be close to the frying classes 0820, 0730 or 2440. It also says that the present minimum quality for the chips industry of 8200 (18) is equivalent to 0.37 g/kg reducing sugar. For the production of French fries, the present minimum requirement for potatoes of the cultivars Agria, Markies and Fontane is 01000 (0.76 g/kg), while for Eba, Satana and Innovator the usual limit is 0640 (1.14 g/kg). In spring 2004, also the class 0550 (1.24 g/kg reducing sugar) had to be accepted because of shortage on the market.

Table 5
Frying classifications and derived contents of reducing sugar for points of special interest

	Frying test	Red. sugar (g/kg)
Near limit of 1 g/kg	0820	0.95
	0730	1.05
	2530	0.95
	2440	1.05
	2611	1.01
Trade limit for chips	8200	0.37
Trade limits for French fries	01000	0.76
	0640	1.14
	0550	1.24

Conclusions

The decision on whether to evaluate fresh potatoes intended for roasting or frying by their content of reducing sugars or the frying classification might be reached on the grounds of the following arguments:

- 1. The frying test is well established, easy to perform, fast and inexpensive. Easy testing tends to translate into more frequent control, and testing on the spot to a simplification of decision making.
- 2. The measurement of sugars is somewhat more precise, but the browning of the frying test slightly more closely reflects the potential of acrylamide formation, also taking into account components other than the sugars. The predominant uncertainty for both approaches is the sampling from large lots.

- 3. The range of selectivity of the frying test is limited, but falls into the range of 0.3 to 4 g/kg (classification between 7 and 4) of interest for fresh potatoes sold as suitable for frying or roasting.
- 4. Existing applications of the frying test cannot be replaced by the measurement of sugars and, therefore, an obligation to determine reducing sugars means an additional analysis. Introduction of a new criterion needs to be justified by important advantages.

These arguments probably turn the balance towards the frying test: it should be given a chance to stand the test in practice. The correlation with the reducing sugars is sufficient to establish a relationship, i.e. classifications can be converted to sugar contents where the frying test is not applicable.

Acknowledgement

We thank D. Schneider, Swisspatat, and E. Schellenberg, Qualiservice GmbH, Berne, for instructions and advise.

Summary

Almost 20 years ago, the frying test was standardized to evaluate potatoes for industrial use regarding their browning during frying (chips, French fries). It is fast, cheap and well established in the Swiss trade. Since browning and acrylamide formation are related to the reducing sugars through the Maillard reaction, the frying test offers itself for the evaluation of fresh potato intended for frying and baking. The classification by the frying test was correlated with the content of reducing sugar through the parallel analysis of 82 individual tubers. The mean difference between the sugar concentrations derived from the frying test and those really measured for 10 tubers was 11%. Owing to practical advantages, the frying test is given preference over the measurement of reducing sugars. A limit of 1 g/kg fresh weight would be approximately equivalent to the classifications of 0820, 0730 or 2440.

Zusammenfassung

Der Backtest wurde in der Schweiz vor annähernd 20 Jahren zur Bewertung von Industriekartoffeln bezüglich ihres Bräunungsverhaltens beim Frittieren (Chips, Pommes frites) standardisiert. Er ist schnell, kostengünstig und im Schweizer Handel gut eingeführt. Da Bräunung und die Acrylamidbildung über die Maillard Reaktion mit den reduzierenden Zuckern verknüpft sind, bietet sich dieser Backtest auch für die Beurteilung von Frischkartoffeln für geröstete, gebackene oder frittierte Produkte an. Backnoten wurden über parallele Analysen an 82 Knollen mit den Gehalten an reduzierenden Zuckern korreliert. Die mittlere Differenz zwischen aus Backnoten berechneten und aus den gleichen Knollen gemessenen Zuckergehalten aus 10 Knollen betrug 11 %. Wegen praktischer Vorteile wird die Verwendung von Backtests für die Beurteilung frischer Speisekartoffeln bevorzugt. Die Grenze von 1 g/kg Frischgewicht entspricht ungefähr den Backnoten 0820, 0730 oder 2440.

Résumé

Le test de friture a été normalisé en Suisse il y a presque 20 ans pour l'évaluation des pommes de terre destinées à la transformation technologique concernant le brunissement pendant la friture (chips, pommes frites). Il est rapide, bon marché et bien introduit dans le commerce suisse. Comme le brunissement et la formation d'acrylamide sont liés avec les sucres réducteurs par la réaction de Maillard, ce test de friture convient aussi pour l'évaluation des pommes de terre de consommation pour rôtir, ou frir. La classification par le test de friture est corrélée avec la teneur de sucres réducteurs suite à une analyse parallèle pour 82 pommes de terre. La différence moyenne entre les teneurs de sucre calculées de la classification par le test de friture et les teneurs mesurées directement était de 11 %. En raison des avantages pratiques du test de friture, la préférence lui est donné par rapport à la mesure des sucres réducteurs. La limite de 1 g/kg de pois frais correspond environ aux notes de coloration de la friture 0820,0730 ou 2440.

Key words

Frying test, browning of potato chips, calibration on reducing sugar, reducing sugars, acrylamide in potato products

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