

STUDY OF SOLIDS LEACHED DURING RICE COOKING USING THE TRANSMITTANCE AT 650 NM

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ABSTRACT

The objective of this research was to develop a method to predict the amount of total solids leached during rice cooking using light transmittance at 650 nm with an ultraviolet-visible spectrometer. Rice was cooked in excess water for different durations, the transmittance was measured, and the solids were determined gravimetrically after evaporation of the water. Results of leached solids obtained gravimetrically showed a good correlation with the logarithm of the transmittance ($R^2 = 0.9731$), thus indicating the feasibility of the method. As a result, calibration curves were developed using rice starch and rice flour as standards. Calibration curves generated with rice starch has shown to overpredict the amount of solids leached. When rice flour was used, the method predicted that the solids leached with an average error of 2.3%, with a minor tendency towards underprediction.

PRACTICAL APPLICATIONS

During the industrial production of instant rice, important amounts of solids leach out from the rice, producing yield loss and high biochemical oxygen demand (BOD) waste streams. A quick method to estimate the leaching potential of different rice varieties would be important to adjust processing parameters and minimize leaching. The results presented in this study show that the transmittance at 650 nm can be used to estimate the solids leached during rice cooking. Still, the successful implementation of this method depends on the finding of suitable standards.

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INTRODUCTION

During the process of rice cooking in water, several mechanisms take place simultaneously. Kernels are heated, water is absorbed, starch is gelatinized and, at the same time, solids are leached from the kernel to the surrounding water. The composition of the leached solids is mainly a mixture of starch, lipids, proteins and other minor components. Starch represents approximately 90% of the mass of the dried kernel, and it is the main component that leaches out during the cooking process.

Starch molecules when mixed with water do not form true solutions. Instead, they form suspensions, and the turbidity of these suspensions increases with the concentration of solids. Considering this, we hypothesized that measurements of the transmittance of the cooking water would be a good predictor of the solids leached during rice cooking. Transmittance has been used previously by other researchers to measure pasting properties of starch. The use of transmittance at 650 nm to determine starch paste clarity was proposed by Craig *et al.* (1989), and then used successfully by a number of researchers (Cho and Lim 1998; Bello-Perez *et al.* 2000; Yin *et al.* 2005; Achille *et al.* 2007).

The research work presented in this paper is part of a more comprehensive project to find quick methods to estimate water uptake, volumetric expansion and solids leached during the course of rice cooking. The objective of this particular study was to find a simple method to measure the solids leached during cooking. Preliminary data showed that the transmittance at 650 nm correlates with cooking time. This created the opportunity to explore this technique that eventually would be simple to be incorporated in an automated machine that would measure water uptake, volumetric expansion and solids leached simultaneously.

MATERIALS AND METHODS

Materials

Preliminary studies were conducted with long-grain commercial rice of an unidentified variety purchased at a local market. Rice was cooked in excess water using two ratios of rice/water: 10 g in 200 mL and 10 g in 400 mL. Samples were cooked for 20 min, and the transmittance was measured every 5 min.

At exception of preliminary studies, the starting material for this research was rough rice (paddy) of the varieties Wells and the hybrid XP723. The rough rice was equilibrated to 12% moisture content before dehushing in a laboratory

rice huller, Satake Rice Machine (Satake Engineering Co., Ltd., Tokyo, Japan). Milling was conducted in a McGill #2 mill (Rapsco, Brookshire, TX) for different durations. The broken rice was separated from the intact rice using a double-tray shaker table (Grainman, Grain Machinery MFG, Miami, FL), then placed in Ziploc bags and stored at 4C until used. Rice starch was purchased from Sigma (St. Louis, MO) and generic rice flour was purchased from a local market. The rice starch was used without further purification and the flour was sieved through a 100-mesh screen. Deionized water was used for all the cooking experiments and the preparation of calibration curves.

Cooking Device

Rice was cooked, in excess water, in a 1-L three-neck round bottom flask electrically heated with a heating mantle controlled by a rheostat. The level of water was kept constant through the experiment by condensing the water vapor with a vertically placed condenser connected to one of the necks. The other two necks were plugged, except when loading the rice and taking samples.

With the exception of preliminary trials, experiments started by taking 400 mL of water to a boil and then adding 10 g of rice. Samples of 1 mL of the boiling water containing the leached solid were taken every 5 min for a total of 20 min and transferred to a 2-mm path length cuvette. Immediately, the transmittance at 650 nm was read with a Varian Cary 50 ultraviolet-visible spectrophotometer (Varian Analytical Instruments, Walnut Creek, CA), and the sample was returned to the boiling flask.

Correlation Between Transmittance and Solids Leached

Ten grams of Wells rice, milled for 30 s, was cooked in 400 mL of water at different times (5, 10, 15 and 20 min). After each time was reached, the cooking water was drained into aluminum pans, the transmittance was measured on an aliquot and the water was made to evaporate by keeping the pans for 24 h in a drying oven set at 100C. Total solids were calculated gravimetrically and used to establish a linear correlation between the logarithm of the transmittance (absorbance) and solids content for each duration.

Validation Study

Validation of the method was conducted by generating calibration curves with rice starch and rice flour dispersed in water at similar concentrations that were found when rice was cooked. Then, Wells rice was cooked for 5, 10, 15 and 20 min, the transmittance was measured, and the water was collected and transferred to aluminum pans. Total solids loss was determined gravimetrically after evaporating the water overnight. The transmittance was used to predict

the concentration of solids using the calibration curves and then compared with the actual values obtained gravimetrically in a measured versus predicted plot. The accuracy of the method was estimated by calculating the deviation of the predicted values relative to the actual values with the following equation:

$$\text{Error (\%)} = 100 \times \frac{\text{actual} - \text{predicted}}{\text{actual}} \quad (1)$$

Effect of Degree of Milling and Lipids on the Transmittance

Rice flours were prepared by grinding Wells rice that was previously milled for 0 (brown rice), 20 and 60 s. Rice was transformed into rice flour using a Thomas Wiley Model 4 Laboratory Mill (Thomas Scientific, Swedesboro, NJ) with a 0.5-mm sieve. The rice flour was subsequently sieved through a 100-mesh screen.

Each of the three flours was split in half, and one of the halves was treated with petroleum ether to remove the lipids. Then, suspensions of regular and deoiled rice flours were prepared at concentrations ranging from 0.5 to 2.5 g in 400 mL. Immediately, the transmittance was read at 650 nm. Before plotting the results of transmittance versus concentration of the suspension, the concentrations were corrected by moisture content.

Lipid Removal

Lipids from rice flour were removed using the lipid extraction system, Soxtec Avanti 2055 (Foss North America, Eden Prairie, MN), following the procedure of Matsler and Siebenmorgen (2005). Five grams of rice flour was weighed into cellulose thimbles of 33 mm i.d. by 80 mm external length (Foss North America). The thimbles containing the samples were predried for 1 h in an oven maintained at 100C. Lipids were extracted from the sample using 70 mL of petroleum ether heated at 135C. The extraction cycle consisted of immersing the thimbles in the extraction cups and boiling for 20 min. Then, the thimbles were raised above the solvent to rinse the samples with petroleum ether condensate for 30 min. The thimbles were then removed from the Soxtec unit and placed in an oven maintained at 100C for 30 min, then cooled in a desiccator to room temperature (22C) for 30 min.

Statistical Analysis and Data Plotting

Experiments were conducted in triplicate according to full factorial experimental designs. When needed, data were fit to linear or quadratic equations using the method of least squares.

For the purpose of plotting and correlations, transmittances were transformed as logarithm of the transmittance that is equivalent to absorbance. Therefore, absorbance and logarithm of the transmittance have been used interchangeably in the paper.

RESULTS AND DISCUSSION

Correlation Between Absorbance and Solid Leached

Preliminary experiments showed a linear correlation between the absorbance, measured on the cooking water, and time (Fig. 1). They also showed that the absorbance of the cooking water was dependent on the rice to water ratio. These results suggested a possible correlation between the absorbance and solids leached. To prove this hypothesis, a plot was developed using the absorbance of the cooking water and solids leached after cooking the rice for different times. Results illustrate (Fig. 2) a linear response of the solid content determined gravimetrically with the absorbance ($R^2 = 0.9731$), which confirms the hypothesis. These results suggested the prospect of using this concept as a quick method for determining solids leached during rice cooking.

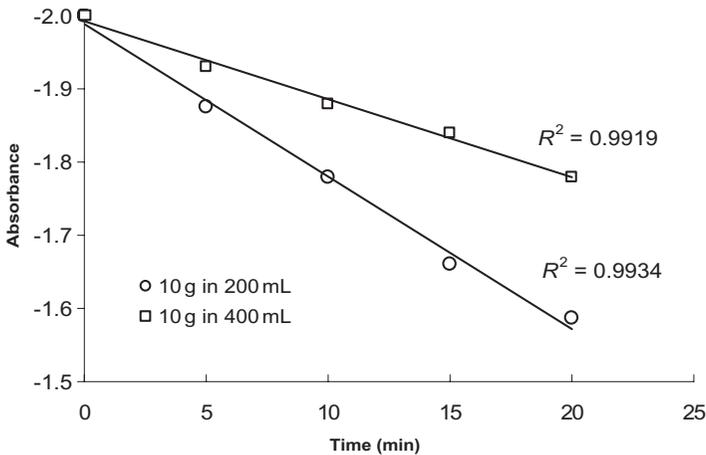


FIG. 1. LINEAR RELATIONSHIP BETWEEN THE ABSORBANCE AT 650 nm OF THE COOKING MEDIUM AND TIME FOR COMMERCIAL RICE

Rice was cooked in excess water in two different rice/water ratios. Points are the average of three experiments.

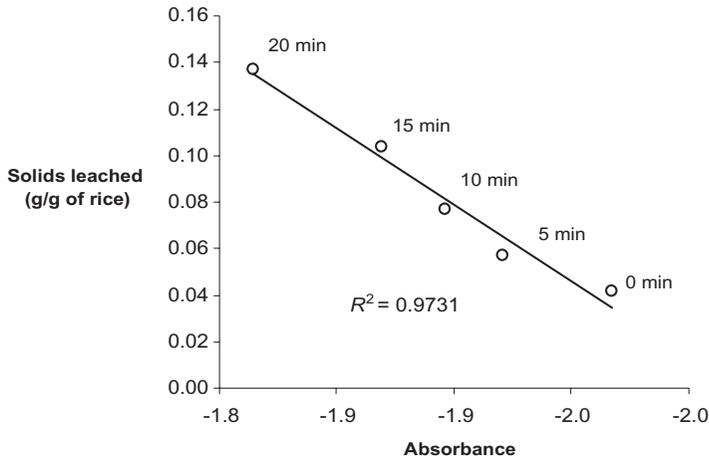


FIG. 2. CORRELATION BETWEEN SOLIDS LEACHED DURING RICE COOKING FOR DIFFERENT COOKING TIMES AND THE ABSORBANCE, AT 650 nm, OF THE COOKING MEDIUM

The regression line has a coefficient of determination of 0.9731. Rice of the Wells variety milled for 30 s was used for this experiment, and each point is the average of triplicate experiments.

TABLE 1.
CALIBRATION CURVES* USING RICE STARCH AND RICE FLOUR USED FOR PREDICTION STUDY PRESENTED IN FIG. 3

	Equation	R^2
Rice starch	$y = -3.1048\text{Ln}(x) + 14.406$	0.9995
Rice flour	$y = -2.8212\text{Ln}(x) + 12.985$	0.9969

* "y" represents the concentration of solids in 400 mL of water and "x" is the transmittance at 650 nm.

Method Validation

The applicability of these findings was tested by generating calibration curves and using them to predict the solids leached during rice cooking. Calibration curves, which were developed with rice starch and commercial rice flour, related the absorbance at 650 nm with the concentration of solids in water (Table 1). Both calibration curves were used to predict the weight of solids leached from the rice kernels during variable cooking durations using the absorbance of the cooking medium.

Examination of the validation plot (Fig. 3) visually exhibits a good agreement between measured versus predicted values. One component of a valida-

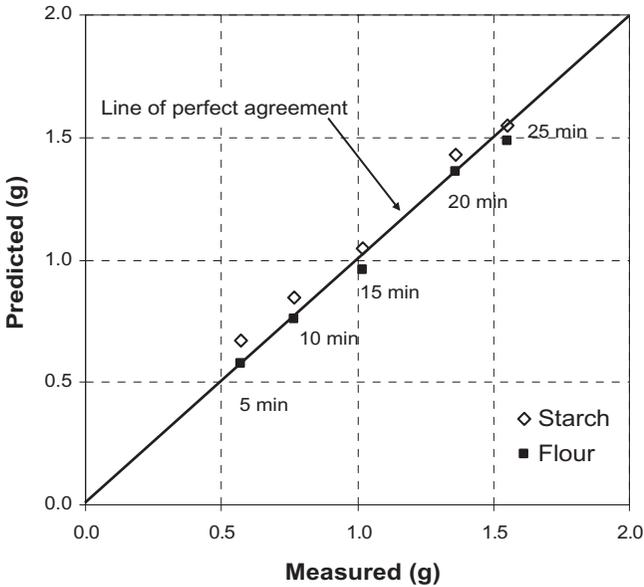


FIG. 3. VALIDATION PLOT OF PREDICTED VALUES VERSUS MEASURED VALUES OF SOLIDS LEACHED DURING RICE COOKING OF RICE XP723

Predictions were made using calibration curves (Table 1), developed with commercial rice starch and rice flour, that correlated the absorbance at 650 nm, with the solid content in suspension. Measured values were obtained gravimetrically by triplicate experiments.

tion plot is the “line of perfect agreement.” This 45-degree angle line connects measured and predicted values when they both agree perfectly.

Both calibration curves were able to predict, to some extent, the solids leached after variable cooking durations. However, a closer examination of the data using an error plot (Fig. 4) showed that the calibration curve made with rice flour had a tendency to underpredict the amount of solids leached. The error of the predicted values oscillated between -0.9 and 5.9% . Still, the error points are not randomly distributed above and below the 0% error line.

The calibration curve developed with rice starch, on the other hand, failed to predict the solids leached to a much larger extent. The error generated by this calibration curve oscillated between -0.1 and -17.1% , with a nonrandom pattern and exceedingly biased toward overprediction.

Amylopectin and hot water soluble amylose are the main components of the solids in cooking water at molecular level (Jane and Chen 1992; Cameron and Wang 2005). Other components like whole and partially broken starch granules, proteins and lipids (Nierle *et al.* 1981) are also expelled from the

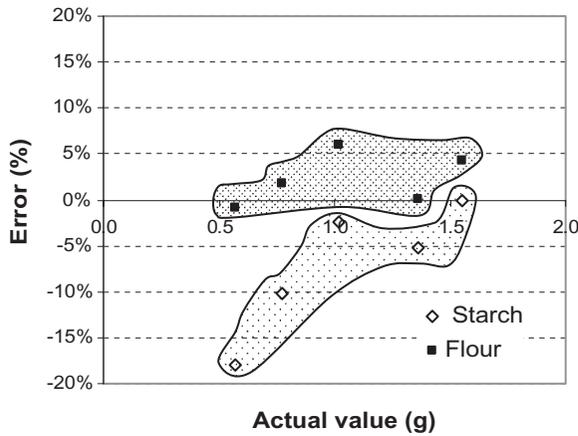


FIG. 4. ERROR PLOT FOR THE DATA PRESENTED IN FIG. 3
Error (%) was calculated as $100 \times (\text{actual} - \text{predicted})/\text{actual}$.

kernel during cooking. This would explain, in part, why the calibration curve made with rice starch tended to overestimate the amount of solids. Even when large starch molecules do not produce true solutions, the dispersion is more transparent than when other components like starch granules and lipids are present.

When rice flour was used instead, starch granules that were not dissolved and that drifted freely in the solution tended to disperse light more effectively, thus modifying the absorbance in a more realistic way. Free lipids may have also had an important function in the balance of transparency versus opacity of the water. Because lipids are insoluble in water, the aggregation of molecules may have led to the formation of small droplets that made the solution more opaque.

Effect of Degree of Milling and Lipids

To have a better understanding of the factors that affect the absorbance, we studied how the degree of milling and surface lipids content would influence the absorbance of a suspension of rice flour. From Fig. 5, a clear pattern emerges, showing that the degree of milling affects the clarity of the suspension of rice flour in water. The 60 s milled rice flour suspension showed the smallest decrease in absorbance with concentration. As we decreased the degree of milling to 20 s, the suspension became cloudier, reaching the cloudiest point when brown rice (non-milled) was used. These results suggest that hydrophobic components of the rice kernel outer layers

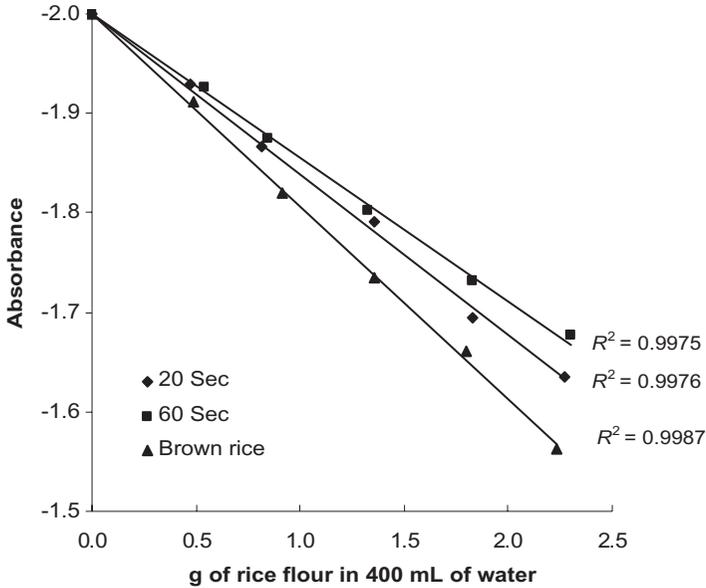


FIG. 5. PLOT OF THE ABSORBANCE AS A FUNCTION OF THE GRAMS OF RICE FLOUR SUSPENDED IN 400 mL OF WATER

Three rice flours were made by grinding brown rice, 20 s, and 60 s milled rice of the Wells variety.

have an effect on the way that particles interact in the suspension. Because lipids are concentrated in the outer layers of rice, we thought that lipids can be the factor influencing those interactions. To test it, we made suspensions at different concentrations of rice flour with the lipids removed. The absorbance for the different concentrations was measured and then compared with the data for non-deoiled flour. A visual comparison of the results (Fig. 6) indicates how the presence of lipids affects the transparency of the suspension. Starting with brown rice (Fig. 6), we can observe a clear difference on the transmittance for the deoiled versus the non-deoiled flours. Then, after removing the outer layers by milling the rice for 20 s, we see how less important the differences between both curves become. A longer milling duration (60 s), which virtually removes all lipids, shows almost no difference between the transmittance curves made with deoiled and non-deoiled flours. This experiment demonstrates the importance of lipids in the transparency of suspensions of rice flour in water even when the concentration of lipids in rice is very low. These findings are in agreement with the results reported by Bello-Perez *et al.* (1998) when studying the effect of fatty acids on clarity of starch pastes.

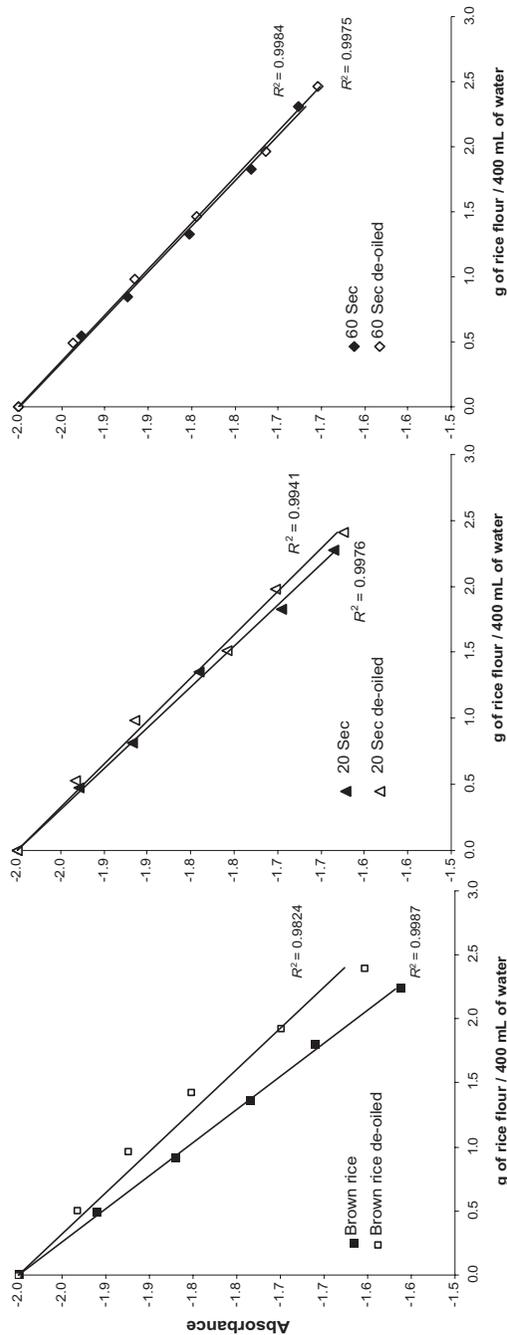


FIG. 6. ABSORBANCE AS A FUNCTION OF GRAMS OF RICE FLOUR SUSPENDED IN 400 mL OF WATER FOR REGULAR AND DEOILED RICE FLOUR FOR THREE DEGREES OF MILLING

Flours were prepared with Wells rice milled at three durations: 0 (brown rice), 20 and 60 s.

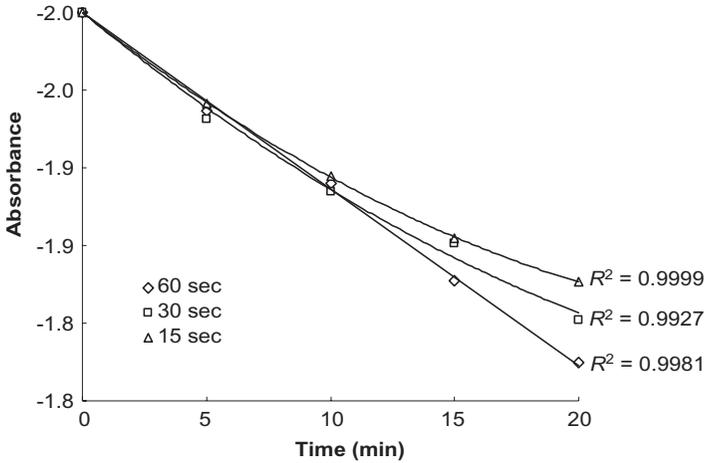


FIG. 7. ABSORBANCE AS A FUNCTION OF TIME OF THE COOKING MEDIUM OF RICE XP723 MILLED FOR 15, 30 AND 60 s, AND COOKED IN EXCESS WATER (10 g IN 400 mL).

Effect of Outer Layers on Solids Leached

Additional evidence of how components present in the outer layer of rice may influence the solids leached during cooking is shown in Fig. 7. The experiment consisted of cooking in excess water XP723 rice that was milled for different durations (15, 30 and 60 s) and the transmittance followed during the cooking process. Solids released by the 60-s milled rice showed a linear response with the absorbance. Then, as the degree of milling decreased, the transmittance started bending upwards after 5 min into the cooking process. For milling durations of 15 and 30 s, the behavior of the absorbance as a function of time becomes parabolic instead of linear. By taking the 60-s curve as a reference, the curve for 15-s milling duration shows a more evident deviation than the one at 30 s. This indicates that the outer layers of the rice kernel control, to some extent, the leaching of compounds to the water medium.

CONCLUSION

This study proved that the transmittance correlates fairly with the solids leached during rice cooking. However, the use of this method to predict the amount of solids leached during rice cooking has proved to be only partially successful because of the lack of a suitable standard. The use of commercial rice starch as a standard has shown to produce suspensions that are too transparent and, as a result, overestimates the results. On the other hand, rice

flour is a more realistic standard. However, the amount of lipids present in the material, that is a function of the degree of milling, has an influence on the transparency of the solution. With the knowledge acquired in this work, a standard for a particular variety of rice could be tailored. However, this standard would be applicable to that specific variety and it would be unreliable to unknown samples. The leaching of solids during rice cooking is a phenomenon influenced by several factors. The use of transmittance at 650 nm only is not capable of capturing the influence of all the factors involved. Therefore, the development of a method using other spectroscopic techniques that would be more sensitive to the influence of all those factors is currently in progress.

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