EFFECT OF COLD STORAGE ON OPTICAL PROPERTIES OF SOME CITRUS FRUITS
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ABSTRACT

The objective of this research was to compare the optical properties of some citrus fruits (orange, mandarin and lemon) before and after cold storage over the visible and near-infrared wave region (400–1000 nm). AvaSpec-2048 Standard Fiber Optic Spectrometer was used to acquire spatially resolved diffuse reflectance images from the samples of orange, mandarin and lemon. Seven effective wavelengths (480, 535, 675, 720, 840, 880, 978 nm) were selected to realize hyper-spectral tests. The obtained results show that for flesh and skin of fruits after cold storage, there was not any peak at 675 nm excluding orange skin, this attribute after cold storage fruits become over ripe that there was not chlorophyll content as before storage; cold storage had not any effect on chlorophyll content of orange skin. Results also show that there is a close correlation between the Plant Senescence Reflectance Index (PSRI) and fruit ripening.

Keywords: Spectrometer, Optical properties, Ripe, Chlorophyll, Cold storage

INTRODUCTION

Fruit quality is defined as a measure of characters or attributes that determine the suitability of the fruit to be eaten as fresh or stored for reasonable period. So cold storage is very important for keeping quality of citrus fruit. The hyper-spectral imaging technique has been implemented in several applications such as defect detection or quality determination on apples, eggplants, pears, cucumber and tomatoes **(Li et al., 2002;Liu et al., 2006)** as well as physical, chemical and

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mechanical properties estimation in various commodities (**Lu, 2004; Nagata et al., 2005**). In addition, a significant amount of research has been done in the area of spectroscopy and hyper-spectral imaging applied especially to fruit analysis. The successful attempts to evaluate internal properties non-destructively were accomplished using spectral technology for prediction sugar content (**Bellon et al., 1993**), soluble solids (**Park et al., 2003**), firmness and acidity (**Peirs et al.,2002**), moisture content (**Katayama et al.,1996**), and so many other applications. The absorption coefficient at a given wavelength (μ_a) can be interpreted as the linear combination of the extinction coefficients of main fruit components like water, chlorophyll, carotenes, sugars, etc. weighted by their average concentration. In a previous work aimed at quantifying the percentage volume of water and the chlorophyll-*a* content in the bulk of the intact fruit, it was shown that chlorophyll is the dominant contributor to μ_a at 670 nm (**Cubeddu et al., 2001**). Considering that in peaches and nectarines the chlorophyll content decreases with maturity, the hypothesis was made that the absorption coefficient μ_a at 670 nm (near the chlorophyll peak) could be an index for identifying fruit maturity at harvest. The absorption coefficient μ_a at 720 nm was significantly higher in brown heart pear tissue than that in sound tissue and the scattering coefficient l0s at 720 nm was influenced by translucency of water-soaked tissue, as in over-ripe fruits and bruised regions (**Zerbini et al., 2005**). The samples containing higher moisture content had lower reflectivity across their spectra. In case of unripe fruit, the reflectance curve had three broadband absorption regions around 500, 680, and 960 nm in addition to small absorption region at 840 nm. The regions around 500 and 680 represent anthocyanin and chlorophyll pigments which represent the color characteristics in the fruit (**Seeram et al., 2006**). The absorption regions in the NIR at 840 and 960 nm represent sugars and water absorption bands. The reflectance from both ripe and overripe fruits was consistently lower than that from the unripe one over the entire spectral region. The chlorophyll

absorption band at 680 nm was absent in case of ripe and overripe fruits due to the degradation of chlorophyll in these fruits. Meanwhile, the relative reflectance at anthocyanin and sugar absorbency bands (at 500 and 840 nm, respectively) were much lower than those in unripe ones, meaning that the anthocyanin and sugars in the ripe and overripe fruits are much higher. Absorption due to carotene in the fruit tissue, has an absorption peak at 480 nm (**Merzlyak et al., 2003**). Large differences in the absorption spectra were observed for the tomatoes of three ripeness stages (green, pink, and red), and their ripeness was correctly classified using the ratio of the absorption coefficient at 675 nm (for chlorophyll) to that at 535 nm (for anthocyanin) (**Qin and Lu, 2008**). Considering that in orange, mandarin and lemon the chlorophyll content decreases with maturity, the hypothesis was made that the absorption coefficient μ_a at 675 nm (near the chlorophyll peak) could be an index for identifying fruit maturity at harvest. The presence of water in the fruit caused a raise at the characteristic absorption bands that appear as localized minima. The samples containing higher moisture contents had lower reflectivity across their spectra. The absorption valleys around 500 and 680 represent carotenes and chlorophyll pigments which represent the color characteristics in the fruit (**Abbott et al, 1997**). The absorption valleys in the NIR at 840 and 960nm represent sugar and water absorption bands. On the other hand, the reflectance from bruised surface, even from the recent ones, was consistently lower than that from the normal tissue over the entire spectral region (**El Masry et al. 2008**). The difference in reflectance between the bruised and un bruised tissue was the greatest in the NIR region, while it decreased dominantly in the visible region, and the spectral images had higher levels of noise with low reflectance especially in case of red and reddish background colors. This wavelength was found to be useful for predicting the firmness of apples (**Moons et al., 1997**) and the SSC of melons (**Sugiyama, 1999**). Wavelengths at 880and 905 nm were used for predicting the SSC of fruits (**Moons et al.,**

1997). **Lu and Peng (2006)** reported that the water absorption band was found to be at 950 nm using hyper-spectral imaging technique for peach fruits. It was found that the absorption coefficient at 670nm (μ_a 670), the absorption peak of chlorophyll-a is linked to fruit biological age, and decreases as fruit ripen **(Tijskens et al., 2006)**. In nectarines the conversion of μ_a 670 to a biological shift factor was successfully used to predict fruit softening rate during shelf life **(Tijskens et al., 2007)**, allowing the selection of fruit for different market destinations **(Eccher Zerbini et al.,2009)**. The absorption curve pattern for oranges is very similar to that of other fruit, such as the mandarin, mango, apple, cherry, peach and kiwifruit **(Lu et al., 2000)**.So the main objective of the present study was to compare the optical properties of some citrus fruits (orange, mandarin and lemon) before and after cold storage over the visible and near infrared wave region (400-1000nm).

MATERIALS AND METHODS

In the present study, the optical properties of some citrus fruits were compared before and after cold storage .The practical experiments were carried out from 13th march to 4th of April 2012 at Debrecen University, Centre for Agricultural Sciences and Engineering, Faculty of Agricultural and Food Sciences and Environmental Management, Institute of Water and Environmental Management, Hungary.

Materials:

The used citrus fruits:

The following citrus fruits were used in the present study with the following specifications:

- Orange: ٢٦ 3 cm^3 volume, 95 % percentage of sphericity and 228 g mass.

- Mandarin: 162 cm^3 volume, 84 % percentage of sphericity and140 g mass.

- Lemon: 110 cm^3 volume, 74 % percentage of sphericity and100 g mass.

The Spectrometer system:

A laboratory AvaSpec-2048 Standard Fiber Optic Spectrometer system was constructed as shown in (Fig. 1).
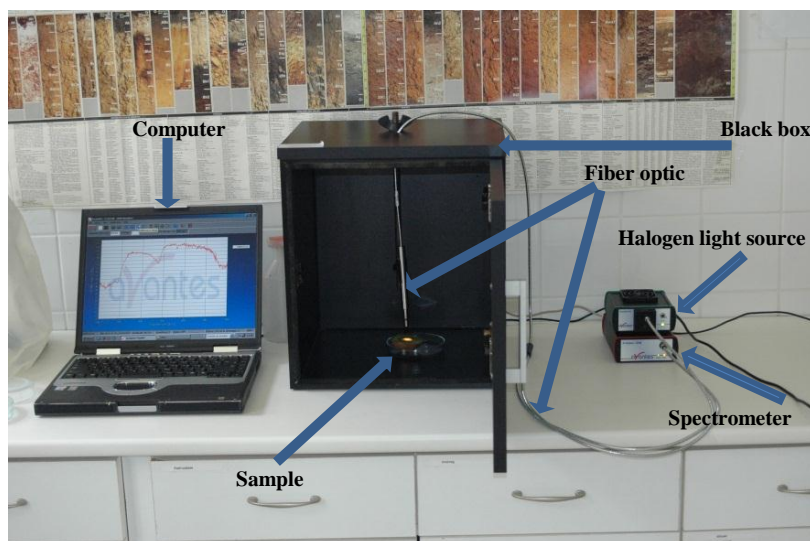

Fig. 1: AvaSpec-2048 Standard Fiber Optic Spectrometer system construction in operation.

The reflectance spectra were measured by AvaSpec 2048 Fiber Optic Spectrometer within 400-1000 nm interval. The AvaSpec 2048 system consists of a spectrometer (detector) and connected by an 8 μm core diameter fiber optic standard AvaLight-HAL halogen light source. The light source has about 1 μWatt light energy input to result the permanent light intensity in the whole measure range. The accurate measurement was provided by a special spectral sampling black box since the samples were isolated from the variable external light.

Before the spectral measurement begin, the AvaSpec 2048 Spectrometer had to be calibrated by white and black references. The special type of reference unit is WS-2 reference tiles, was made out of white diffuse PTFE (polytetrafluoroethylene) based material, meeting the highest demands with regard to high grade diffuse reflectance. In case of calibration the distance of the reflection probe and reference tiles, these samples were three cm.

The spectral data in the AvaSoft USB2 were processed, which is the own software of AvaSpec 2048 Spectrometer and Microsoft Office Excel™. Some parameters could be investigated based on spectral curves in the visible (VIS) and near infrared (NIR) ranges.

Methods:

Fruit samples before and after cold storage:

Three fresh healthy citrus fruits without symptoms of damage were obtained to investigate the spectral properties of fruits before and after cold storage. First measurement done immediately before storage in refrigerator about three weeks under about 3º C., these test fruits were placed at room temperature around (22 ± 1º C) for around one day before second measurement. The measurement was performed on each sample in a Petri dish after cutting it to slices thickness about 1.5 cm for every slice as shown in (Fig 2).

Experimental procedure:

Seven effective wavelengths in the short-wave near infrared region (480,535,675,720, 840,880, 978 nm) were selected to realize multispectral imaging tests. Absorption coefficient (µa) at 480 nm (for carotene), at 535 nm (for anthocyanin), at 675 nm (for chlorophyll), at 720 nm (for bruised regions), at 840 nm (for sugar), at 880 nm (for starch), at 978 nm (for water content), technique provides a convenient and efficient means for measuring the optical properties of fruits.
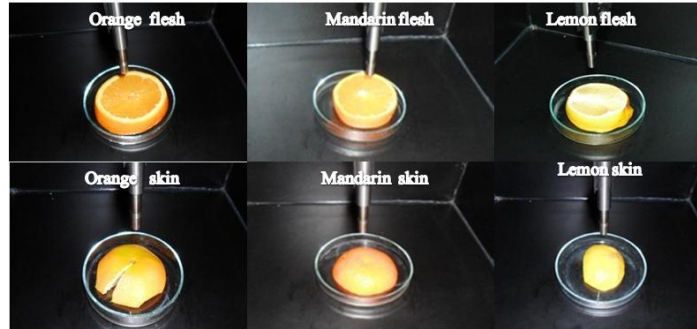
Fig. 2: Slices of orange, mandarin and lemon under measurement operation.

Measurements:

Absorption coefficient:

Absorption coefficients (μ_a) of all fruits were collected in a range of (400-1000 nm) with AvaSpec-2048 Standard Fiber Optic Spectrometer, Spectral data were interfaced to a personal computer for further processing. The height between bottom end of sensor and the samples were about 3 cm and radiation diameter on slices was about 2.3 cm. All of the measurements were averaged from the data from three replicates.

Plant Senescence Reflectance Index (PSRI):

In order to numerically observe the effect of cold storage on citrus fruits, Plant Senescence Reflectance Index values were created from the reflectance values at the studied wavelengths using the following equation **(Merzlyak et al., 1999)**

$$PSRI = \frac{\rho_{678} - \rho_{500}}{\rho_{750}}$$

RESULTS AND DISCUSSIONS

1. Spectral properties of orange, mandarin and lemon fleshes before and after cold storage

Fig. 3 shows that there is high decreasing (μ_a) in lemon flesh lines than other fruits range 400 to 535 nm. This mean that anthocyanins and carotenes were at low amounts, lemon flesh not reach final ripe stage enough as shown in Fig. 3 the (μ_a) of the three fruits orange flesh, mandarin flesh and lemon flesh before cold storage all peaked at 675 nm, which was attributed to chlorophyll content in the fruit tissue. The orange had smooth curve pattern (μ_a), had small peak and other fruits had clear peaks at 675 nm. This result attribute to that orange had reached ripe stage and lower chlorophyll content in the measurement than mandarin and lemon. About other effective wavelengths there are no observations excluding at lemon that had low (μ_a) at 978 nm than other fruits because of containing less water in flesh than orange and mandarin.

After cold storage curve pattern were smooth, there was not any peak at 675 nm, this attribute after cold storage fruits become over ripe that there is not chlorophyll content as before storage. At 978 nm the curve pattern is higher than fruits before cold storage. This means that fruits had more water in tissue.

2. Spectral properties of orange, mandarin and lemon skins before and after cold storage

Fig . 4 shows that orange skin before cold storage have deep clear peak at 675 nm, which was attributed to high amount of chlorophyll in the skin and did not observe this in other skin of fruits, this mean that skin of orange have more chlorophyll content than other skin of fruits. Observed that skin of orange at 978 nm had lowest (μ_a) then mandarin skin and lemon skin respectively. This mean orange skin had less water than mandarin skin and lemon skin respectively. About other effective wavelengths there are no observations.

After cold storage all curve pattern were smooth, there is not any peak at 675 nm, except orange skin that had deep clear peak at
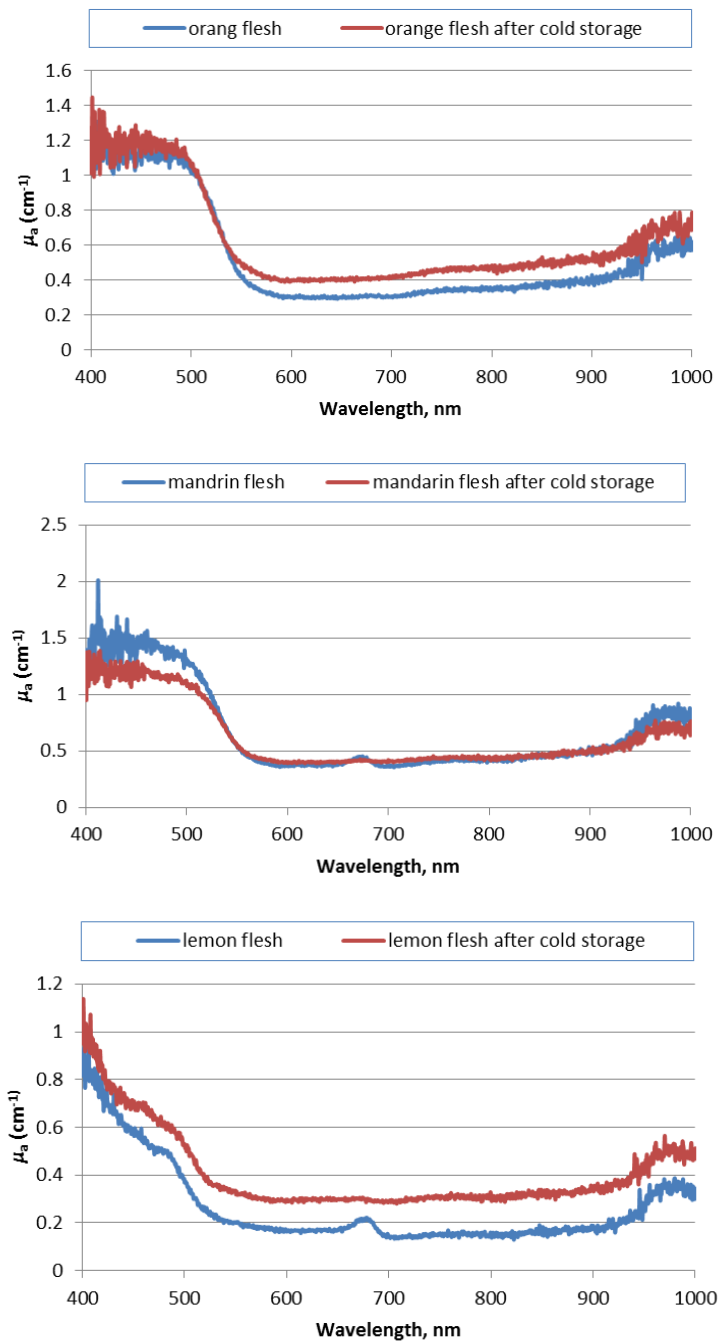
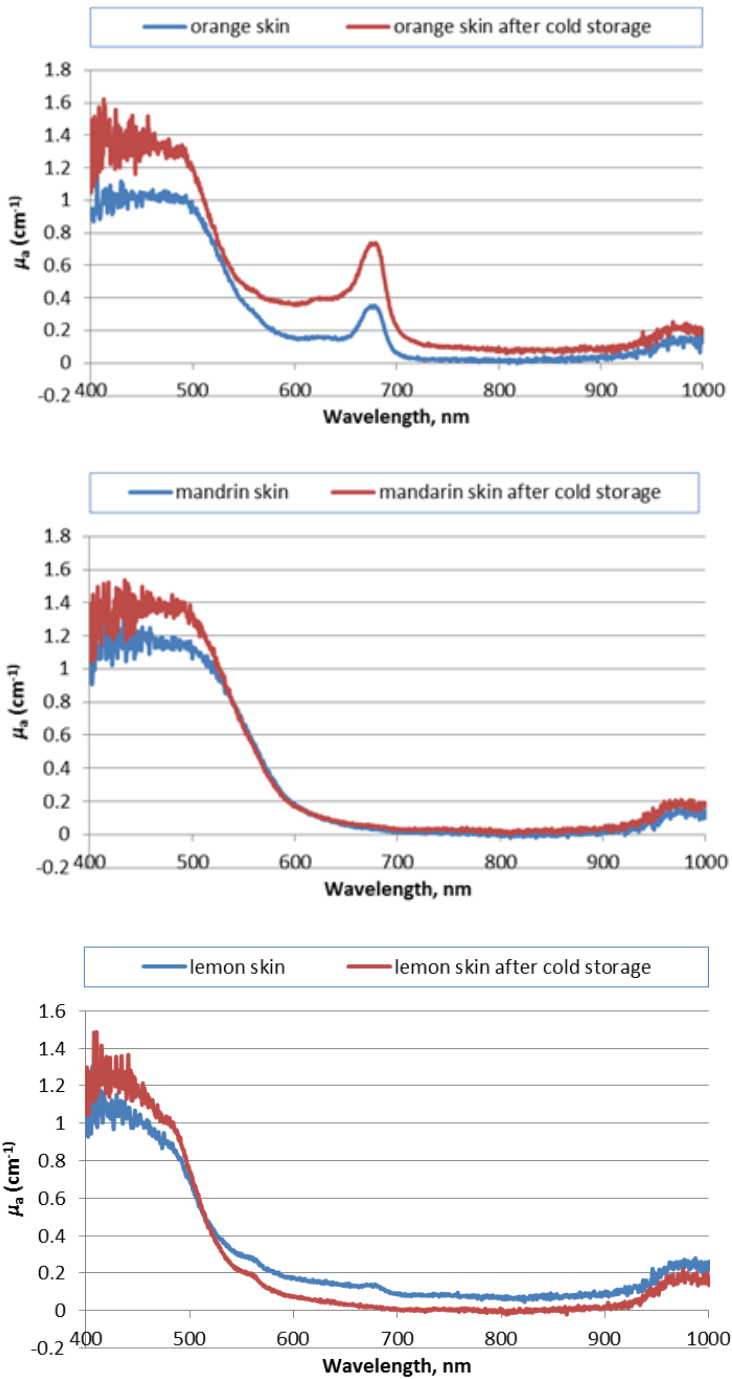**Fig. 3: Absorption coefficient (μ_a) of orange, mandarin and lemon fleshes before and after cold storage.**

Fig. 4: Absorption coefficient (μ_a) of orange, mandarin and lemon skins before and after cold storage.

675 nm, which was attributed to a high amount of chlorophyll content in the skin after cold storage this mean that cold storage had not any effect on chlorophyll content of orange skin.

3. Plant senescing Reflectance Index

Fig. 5 shows the plant senescing reflectance index values for the studied citrus fruits before and after cold storage. Results in Fig .5 shows that there is a close correlation between the plant senescing reflectance index and fruit ripening.

The same results also show that these indices were higher in the case of cold storage comparing with before cold storage due to the over ripening after cold storage.
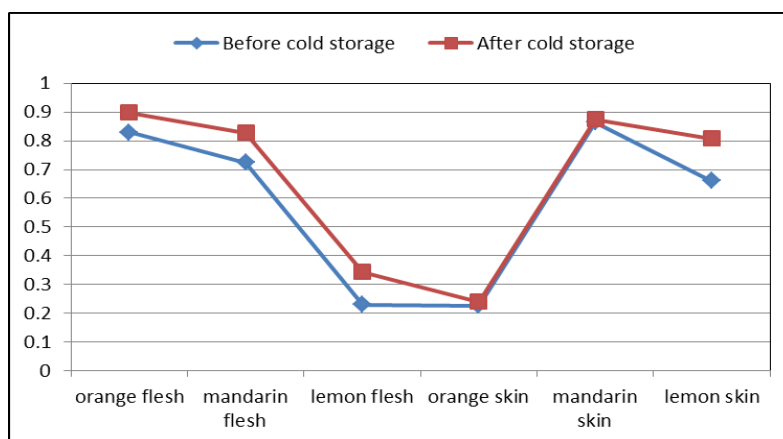

Fig .5: Plant senescing reflectance index before and after cold storage.

CONCLUSION

The developed hyperspectral methods provide opportunity to support a nondestructive technique for assessing the postharvest quality of citrus fruits. After cold storage curve patterns were smooth, there was not any peak at 675 nm excluding orange skin. This attribute after cold storage fruits become over ripe that there was not chlorophyll content as before storage, cold storage had not any effect on chlorophyll of orange skin.

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الملخص العربي

تأثير التخزين البارد على الخصائص البصرية لبعض الحمضيات

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يهدف هذا البحث لدراسة تأثير التخزين البارد على الخصائص البصرية لبعض
الحمضيات وذلك للبرتقال واليوسفى والليمون حيث تم اجراء دراسة وقياس تأثير
التخزين فى ثلاجة تحت درجة حرارة ٣ درجة مئوية لمدة ٣ اسابيع على محتوى
الكلوروفيل والماء فى لحم وقشر الحمضيات تحت الدراسة . وقد أوضحت نتائج
الدراسة بمقارنة النتائج المتحصل عليها قبل التخزين البارد وبعده عند أطياف ٦٧٥
نانومتر (الكلوروفيل) و٩٧٨ نانومتر (الماء) الي انخفاض الكلوروفيل عند معامل
امتصاص٦٧٥ نانومتر (النضج المتزايد) ومع انخفض محتوى الكلوروفيل عند ٦٧٥
نانومتر يحدث زيادة محتوى الماء عند ٩٧٨ نانومتر مع التخزين البارد. حيث أن
أنسجة لحم الحمضيات بعد التخزين تكون مشبعة بالماء، كما هو الحال في أكثر من
الفاكهة الناضجة، حيث الأنسجة تصبح لينة، وعصيرية، ويحدث بعض الرضوض في
مناطق من الثمرة ، حيث يحدث تمزق الخلايا ومحتوياتها الخلوية. بعد التخزين البارد
في قشر الحمضيات لم يكن هناك أي ملاحظة عند ٦٧٥ نانومتر باستثناء قشر البرتقال
لوحظ عدم انخفاض الكلورفيل فى قشر البرتقال رغم التخزين البارد لذلك التخزين
البارد ليس له أي تأثير على الكلوروفيل فى قشرالبرتقال . نخلص من هذه الدراسة الي
التوصية باستخدام جهاز سبكترومميتر لحساسيته وسرعة تقدير مدى نضج الفاكهة فى
ثوانى معدودة عند تقديره الكلوروفيل والماء فى الحمضيات تحت الدراسة بالأضافة الى
عدم اتلاف الكثير من الثمار عند الدراسة وبعد التخزين البارد للحمضيات تصبح
ناضجة أكثر حيث أنه يقل محتوى الكلوروفيل عما كان عليه قبل التخزين حيث يزيد
محتوى الماء بالأنسجة.

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