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Direct Detection of Residual Cyanide in Cassava Using Spectroscopic Techniques

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Fluorescence, infrared, scanning electron microscopy (SEM), UV–visible, and X-ray diffraction (XRD) techniques have been applied to monitor the effect of processing mode on the residual cyanogens in cassava roots. The processed samples' infrared spectra have shown that only the boiled sample contains residual cyanide. SEM micrographs have revealed that irregularly shaped granules of about 100-μm size contain cyanide, while spherical granules of about 10-μm size do not. X-ray diffraction patterns have shown that the intensities of peaks are not affected by the presence of cyanide in the cassava samples. Fluorescence and UV–visible studies have detected the presence of cyanide converted to cyanate in water used for soaking processes. The thermal behavior of cassava samples with respect to the cyanide content and the role of oxygen and different ions present in water used for soaking processes are also discussed.

KEYWORDS: Cassava; cyanide; infrared spectra; SEM; UV–visible spectra; fluorescence spectra

INTRODUCTION

Cassava (*Manihot esculenta Crantz*) roots form an important staple food for more than 500 million people, mostly in humid tropics such as Africa, Asia, and Latin America. Cassava is a carbohydrate with a high content of cyanogenic glycosides (*1–5*). Therefore, the consumption of uncooked cassava is unsafe due to the potentially toxic concentrations of cyanogenic glucosides that are reduced to low levels through cooking (*6*). The most popular processing modes used in reducing the cyanogen levels of cassava are drying, steaming, soaking, boiling, and fermentation. All these processes reduce the total cyanide content of cassava (*7*).

There are two types of cyanide in cassava. The free cyanide, that is non-glycosidic, and the bound cyanide, that is glycosidic (*6*, *7*). The bound cyanide in processed cassava is the major source of dietary cyanide exposure (*8*). Thus, there is a concerted effort to try to make cassava consumption safer. One approach is to breed plants with low cyanogenic potential or develop simple methods to test for the presence of cyanide.

Hoover (*9*) reviewed the present knowledge on the composition, structure, and physicochemical properties of native tuber and root starches and highlighted the lack of information on most of the starches because many researchers have used only one technique for determining the properties of tuber and root starches. He suggested that using different techniques collectively might be a more advantageous approach to obtain a deep insight into the physicochemical properties of these starches. In an international workshop held in 1993, it was also recognized that an important contributor for safety in cassava consumption is the availability of analytical methods to monitor the level of cyanogens (*3*). Among the many analytical methods published in the literature, most of them are time-consuming and require some sample preparation and skilled operators, and the reliability and accuracy of such methods have often been questioned (*3, 7, 10, 11*). The presence of cyanide at very low concentration is not always detected by most of the standard methods. A method that can use the root samples directly for analysis and provide a quick estimate of the cyanogenic potential is ideal.

Vetter (*12*) reviewed the different methods used so far to detect cyanide, including the indirect classical photometrical method and the most recent direct chromatographic method. The objective of this work is to complete the work done by Vetter (*12*) by presenting spectroscopic methods that can assess quickly and qualitatively the release of cyanogenic compounds. The methods reported herein are able to directly detect cyanide at low concentration in a processed cassava sample. Infrared, scanning electron microscopy (SEM), and X-Ray diffraction (XRD) techniques were applied to study the residual cyanide present in the processed cassava sample, while fluorescence and

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Table 1. Assignment of ATR-IR Bands for All the Tuber Piece Samples

approximate band position (cm^{-1})					
fresh tuber piece	air-dried tuber piece	soaked tuber piece	boiled tuber piece	deuterated tuber piece	vibrational assignment
3319	3293	3283	3328		ν_{OH}
2915	2921	2921	2922	2915	ν_{CH}
2853	2887	2846	2848	2847	ν_{CH}
2110			2130		ν_{CN}
1742		1735	1735	1732	ν_{COO}
1638	1633	1633	1633		ν_{CO}
1334	1335	1334	1365		$\delta_{OH} + \delta_{CH}$
1150	1147	1147	1150	1150	δ_{COC}
1076	1076	1079		1076	$\delta_{CO} + \delta_{CC}$
1012	994	998	998	1004	$\delta_{CO} + \delta_{CC}$
919	926	926	896	923	ring vibration
	855	858	855	858	δ_{CH}
	763	760		760	ring breathing
	702	702	699		ring vibration

UV–visible techniques were employed to monitor the appearance of cyanide in water used for boiling or soaking the cassava sample. Attenuated totally reflectance infrared (ATR-IR) spectroscopy has also been used to identify cyanide in water used for soaking. No fluorescence or ultraviolet techniques have been used before in cyanide detection. All these techniques do not show any correlation between the size and shape of the cassava granules and the presence of cyanide in the granules.

MATERIALS AND METHODS

Cassava Root. Fresh cassava root was bought at the store. Its origin was not specified. The cassava samples were cut into ~2 mm thick discs. The changes in molecular composition and in concentration of free cyanide (nonglycosidic) and bond cyanide (cyanogenic glycosides) were studied under different conditions and for different objectives.

To monitor the changes in concentration of cyanide in fresh cassava roots during boiling, air-drying, and soaking processes, three samples were cut from a fresh cassava root. The first sample was sun-dried for one month. The second sample was soaked in tap water at room temperature for one month. The third sample was boiled for 30 min and then soaked in tap water for one month. The water of the second and third samples was removed and replaced by fresh water every day.

To assess the influence of heat treatment on the cyanogenic loss, an experiment was carried out using one sample of cassava to monitor the cyanide escaping through heat. After recording the ATR-IR infrared spectrum of one piece, we divided this piece into three parts: one part was oven-dried for 20 min at 60 °C, one was boiled in water for 15 min, and one was boiled in water for 15 min and then oven-dried for 15 min.

Conflicting results on the oxidation process taking place in the removal of cyanide in cassava have been reported in the literature (*3, 5, 7, 8, 13*). An experiment was carried out to explore the role of oxygen, carbon dioxide, and ion traces in the removal of cyanide. Five samples were cut from a fresh cassava root. One sample was put in oxygenated water. The second and third samples were respectively soaked in deionized water and previously heated deionized water (to eliminate O_2 and CO_2) at room temperature. High purity deionized water was obtained from a Millipore Milli-Q-System (Waters, Millipore, Medford, MA). The fourth and fifth samples were put in tap water and previously boiled tap water, respectively, for 4 h. About 200 mg of each sample was placed in 50 mL of adequate water.

Infrared Spectra. The infrared spectra of the samples were obtained using a Spectrum One spectrometer from Perkin-Elmer. For transmission spectra, samples were prepared as KBr discs with 10% w/w of each sample. For ATR-IR spectra, an ATR DuraVision accessory was used to record the spectra of pure samples, without any preparation. The spectra were recorded between 4000 and 600 cm^{-1} at 4 cm^{-1} resolution, and 64 scans were accumulated. All the infrared spectra were normalized.

In order to facilitate assignments of the infrared bands associated with vibrations of oxygen sites, cassava samples were soaked in D_2O solutions. Mobile hydrogen atoms attached to oxygen are expected to be exchanged by deuterium after repeated deprotonation/protonation cycles performed in heavy water.

Scanning Electron Microscopy (SEM). Granule morphology was observed with a Hitachi scanning electron microscope (model S-4700). The samples of tuber pieces were coated with a thin layer of gold prior to being studied. All the scanning electron micrographs were obtained using an accelerating voltage of 5.0 kV and a magnification of 500×.

Powder X-ray Diffraction (XRD). X-ray spectra of the powdered samples were recorded using a Siemens D5005. The power was 40 kV/15 mA. The X-ray source was Cu K radiation of 1.54 wavelength. The powdered samples were maintained stationary while scattering angles from 4 to 80° were scanned in the reflection mode at a scanning rate of 1° min^{-1}.

Electronic Spectra. The tuber pieces were cut into ~2 mm thick discs and weighed. About 200 mg of each intact tuber piece was placed into 50 mL of adequate water. The cyanide released from the tuber piece goes through the aqueous medium by diffusion. Electronic spectra are then run over time. Absorption spectra were performed in a 1 cm quartz cuvette using a CARY BIO 300 spectrometer from Varian. Fluorescence spectra were similarly collected on a Varian Eclipse spectrometer. Deionized water was used as a blank.

RESULTS AND DISCUSSION

Effect of Processing Mode on the Structure of Cassava Tuber Pieces. ATR-IR spectra of powdered starch (obtained from Fischer), a fresh tuber piece, and powdered air-dried, soaked, and boiled tuber pieces were obtained in order to verify how the processing modes might affect the structure of cassava. The corresponding peak assignments are given in **Table 1** according to literature values and our deuteration experiments (*4, 8, 14, 15*). The ATR-IR spectra are very similar, showing that the major carbohydrate in our samples is starch, in agreement with the results of Hoover (*9*) and Demiate et al. (*13*). The presence of free and bound cyanide is evidenced in the fresh sample by an infrared broad peak at around 2110 cm^{-1}. The carbohydrate region (1300–800 cm^{-1}) remains unchanged in all samples. As a result, it roughly appears that the processing modes (boiling, soaking, and sun-drying) do not significantly affect the initial chemical composition of cassava. This result is consistent with the X-ray diffraction results shown later.

Analysis of Residual Cyanide after Different Processing Modes. The loss of cyanide from the cassava sample was simultaneously examined using infrared, XRD, and SEM techniques.

Figure 1 shows the transmission infrared spectra of the sun-dried, soaked, and boiled cassava in the 2600–600 cm^{-1} region. These spectra are in agreement with those reported in the

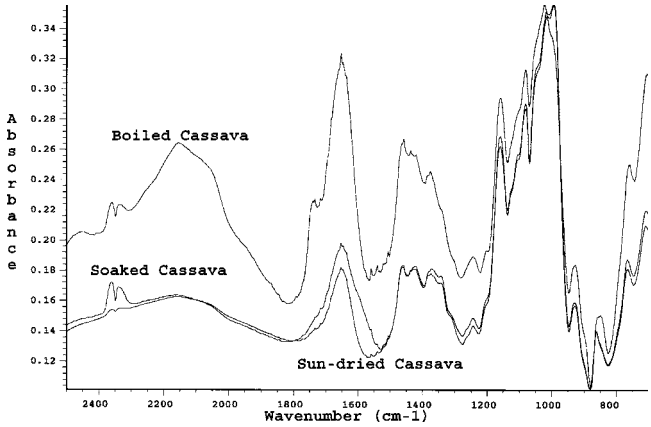

Figure 1. Transmission infrared spectra (normalized) of boiled, soaked, and sun-dried cassava. The spectra were obtained with pellets each containing a mixture of 10% by weight of a crushed tuber piece of cassava with KBr.

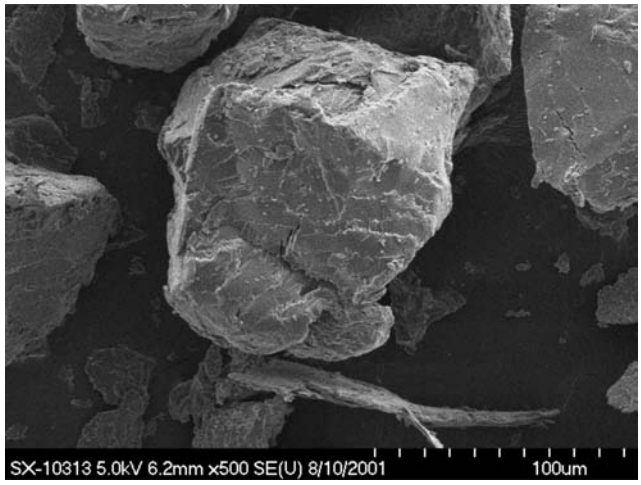

Figure 2. Scanning electron micrograph of a boiled and crushed tuber piece of cassava.

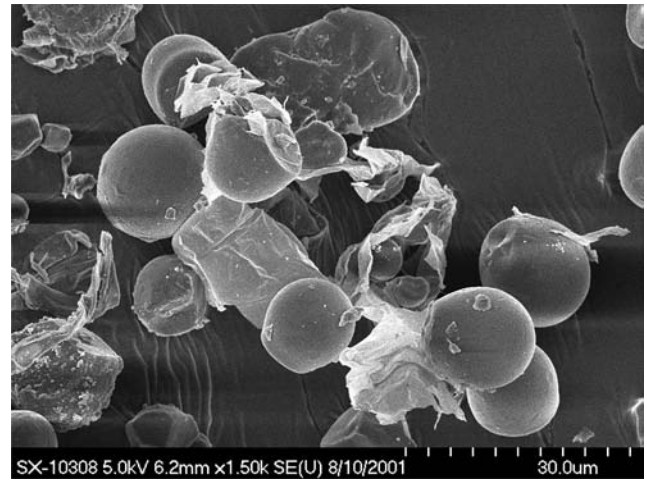

Figure 3. Scanning electron micrograph of a sun-dried and crushed tuber piece of cassava.

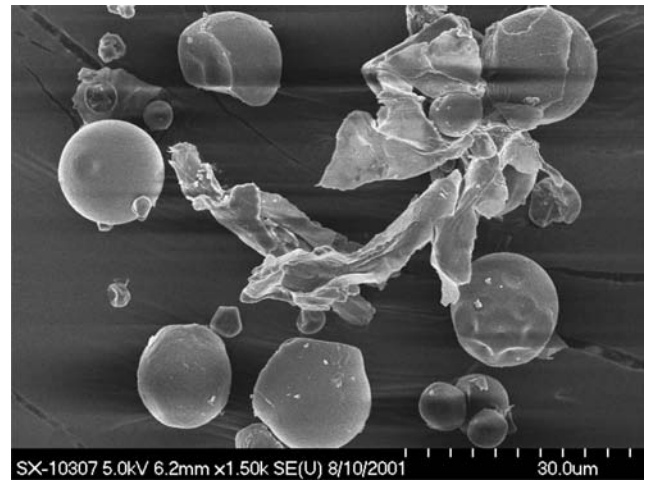

Figure 4. Scanning electron micrograph of a soaked and crushed tuber piece of cassava.

literature by Demiate et al. (*13*) and Gunaratne and Hoover (*5*). The band at 2130 cm^{-1} on the infrared spectra indicates the presence of bound cyanide (*15*). When we compare all the processed samples, we observe that only the boiled sample contains bound cyanide. The infrared technique was able to detect residual cyanide at relatively very low concentrations.

But a deeper analysis of the infrared spectra shows that the infrared spectra of our processed samples contain an additional band at around 1731 cm^{-1}. This band is probably due to a residual carboxylic acid that could not escape. According to the intensity of this band, gelatinization of starch in cassava may explain the higher carboxylic acid levels in the boiled sample than in the other sample. This acid may be a part of the molecular structure of cassava, because it remains after heat treatment, as the other bands of starch do. Demiate et al. (*13*) have also observed the presence of this band. The carboxylic acid may have been generated by an oxidation process. Future research is needed to unambiguously clarify the origin of this band at 1731 cm^{-1}.

In order to find a correlation between the presence of cyanide and the SEM technique, we present **Figures 2–4**, showing the micrographs obtained for the sun-dried, soaked, and boiled cassava (*4*, *16*). The grinding methods used when preparing the three samples for the SEM experiments were similar. The particles of the boiled sample have an irregular shape with a size of more than 100 μm (**Figure 2**); they contain fissures. When the samples are sun-dried (**Figure 3**) or soaked (**Figure 4**), the particles are spherical, with a smaller size of about 10 μm. The particles have imploded and become smaller because they have released cyanide. The size and shape of our air-dried, soaked, and boiled samples are in agreement with those reported by Hoover (*9*).

The degree of crystallinity of tuber and root starch from cassava (*Manihot esculenta Crantz*) has not been thoroughly investigated (*9*). X-ray diffraction analysis was performed to reveal the presence of molecular order postprocessing and the occurrence of any change in order of the samples due to the processing mode. For the first time to our knowledge, the X-ray diffractograms of boiled, soaked, and sun-dried samples of cassava root are presented (**Figure 5**). The diffractograms are typical of amorphous systems, exhibiting a broad pattern regardless of their processing mode. The broad pattern contains two weak peaks centered at around $\theta = 15$ and 20° (*16*). The intensity ratio I15/I20 seems to be smaller for the air-dried sample, which has been found to contain no cyanide by the infrared and SEM techniques. This result may suggest that the air-drying process brings more order to the structure of cassava. Since carbohydrates are amorphous, the X-ray diffraction patterns are not well-defined.

Analysis of Residual Cyanide in the Water Used for Soaking. UV–visible and fluorescence techniques simultaneously monitored the appearance of cyanide in deionized water

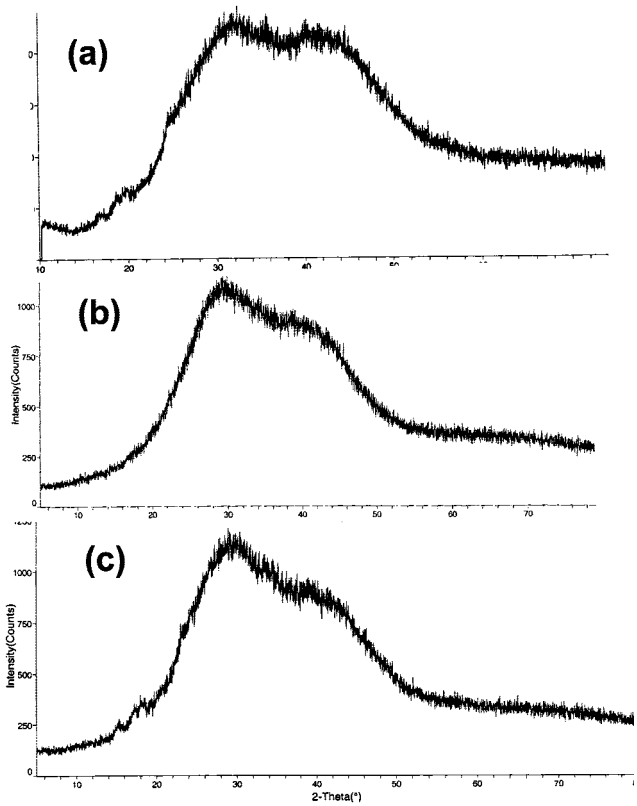

Figure 5. X-ray diffractograms of (**a**) air-dried; (**b**) boiled; and (**c**) soaked powdered samples of cassava.

during the soaking process. Ten grams of cassava sample were soaked in 1000 mL of deionized water (initial pH 6.93) for two weeks. Infrared spectra of the cassava sample were recorded to ensure that the sample contained cyanide before the soaking process. Aliquots were taken over time, and their pH, UV–visible, and fluorescence emission spectra were recorded over time for two weeks. The pH of deionized water decreased from 6.93 to 4.3 after two days. As there are no reported values for cyanide from cassava in the literature, UV–visible and fluorescence spectra of standards such as KCN and KOCN were also recorded for species identification. Taking into account the fact that the pK_a for HCN is 9.2, we do not expect the presence of CN^- species in deionized water at our work conditions (pH < 7). The flask used for this experiment was kept closed all the time, except when we had to take aliquots or measure the pH. We may have lost some cyanide in the form of a gas.

UV–Visible Spectra. During the soaking process, a peak maximum was found at around 265 nm (**Figure 6a**). After two hours, the solution was saturated (**Figure 6b**). To identify the absorbing species, we recorded the spectra of KCN and KOCN aqueous solutions (*17*). We were not able to detect the absorbance of KCN. But Masao et al. found a weak peak maximum at around 210 nm for a HCN aqueous solution (*18*). KOCN gave rise to a peak at 250 nm. The emerging peak at 265 nm in water used for soaking was probably due to cyanate, with a red shift due to the absence of K and the presence of an unknown cation in cyanide from cassava, but this suggestion must be confirmed by the fluorescence spectra.

Fluorescence Spectra. The absorption spectra show a peak maximum at 265 nm; thus, this wavelength was chosen as the wavelength of excitation. The fluorescence emission spectra of KCN exhibited a peak maximum at around 284 nm while those of KOCN showed a peak maximum at 370 nm.

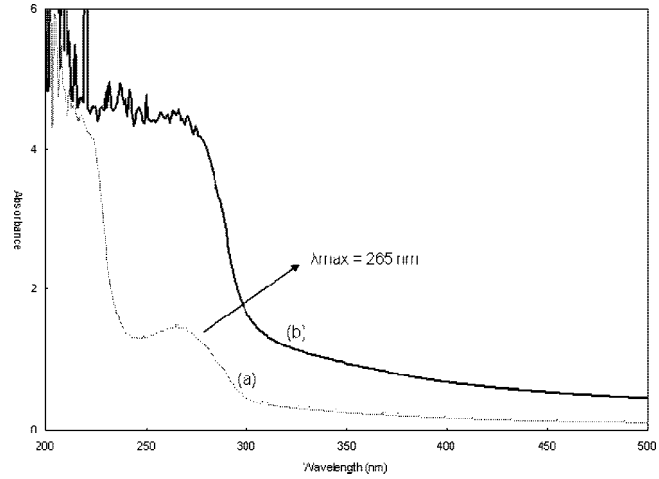

Figure 6. Absorption spectra of water used for soaking: (**a**) after 1 h; (**b**) after 2 h.

The initial (after 5 min of soaking) fluorescence emission spectra (**Figure 7**) exhibit four broad bands with maxima at 284 (very weak), 358 (very strong), 421 (very weak), and 460 (very weak) nm. The comparison of the fluorescence emission spectra of KCN and those of cyanide in soaking water showed that the peak at 284 nm was due to CN^- ion. But that peak at 284 nm disappeared after 1 h.

The strong fluorescence emission intensity around 358 nm initially increases and then decreases over time, without a shift of the peak maximum. The comparison of the fluorescence emission spectra of KOCN (peak maximum at 370 nm at pH 7) with those of cyanide in soaking water showed that the peak at 358 nm was due to cyanate ion (OCN^-) produced by the reaction between cyanide and oxygen contained in the water used for soaking. The reaction $2KCN + O_2 \rightarrow 2KOCN$ is the probable mechanism of production of the OCN^- species. The small red shift of 12 nm may be due to the absence of K and the presence of an unknown cation in cyanide from cassava.

The initial increase of intensity is due to the increasing appearance of cyanide released by the starchy part of the cassava over time. After 2 h of soaking, we observed that the viscosity of the solution increases with increasing concentration of cyanate and the pH decreases. High viscosity and a decrease in pH are the possible explanations of the decrease of the fluorescence emission intensity observed after 2 h of soaking. It is known that the major carbohydrate in cassava is starch. Starch and cyanide go into water by diffusion. Starch in water increases viscosity, as other investigators have reported previously (*19*). The viscosity effect and low pH are known to affect the fluorescence emission intensity of cyanate compounds (*19*). We have worked in an almost closed bottle under the hood, but we may have lost some cyanide under the form of HCN gas.

The peak at 421 and 460 nm increased over time while remaining less strong than the peak at 358 nm. But when that solution (obtained after 2 weeks of soaking time) was diluted in water, the peak at 460 nm disappeared (**Figure 8**), while the peak at 421 nm remained and became stronger but less intense than the peak at 358 nm. We believe that the peak at 421 nm may be due in part to the presence of an unknown cation attached to cyanide ion. This insight may help us determine under which form the cyanide is present in the cassava, because this question is still open to debate.

Influence of Heat Treatment on the Cyanogen Loss. To assess the influence of heat treatment on the cyanogenic loss, an experiment was carried out using one variety of cassava to

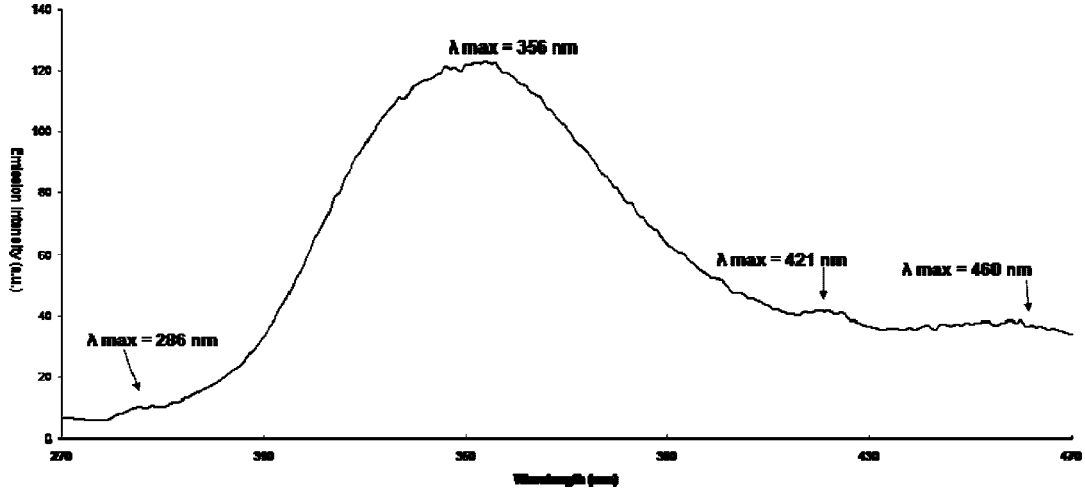

Figure 7. Effect of increasing concentrations of cyanide in the water used for soaking.

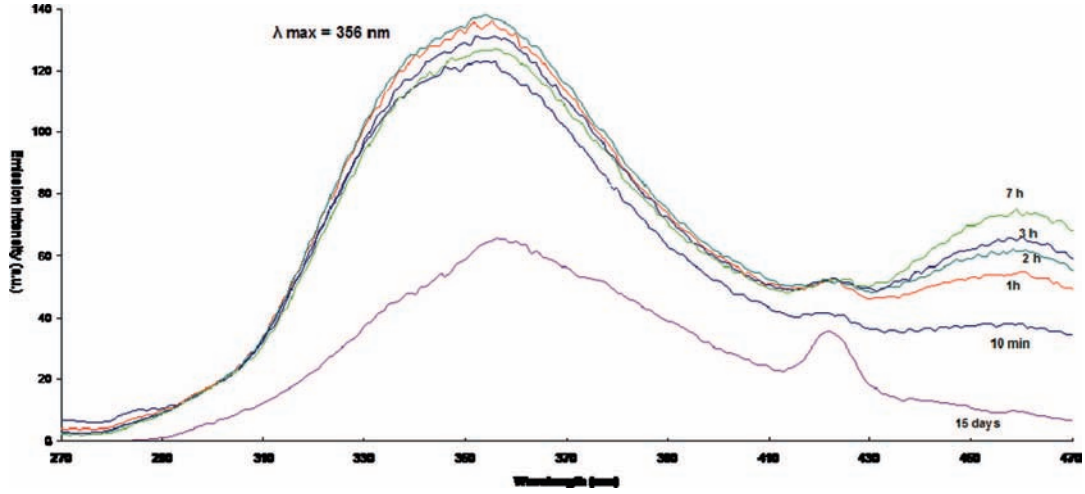

Figure 8. Fluorescence emission spectra of cyanide in water where the tuber piece was soaked for 10 min, 1 h, 2 h, 3 h, 7 h, and 15 days.

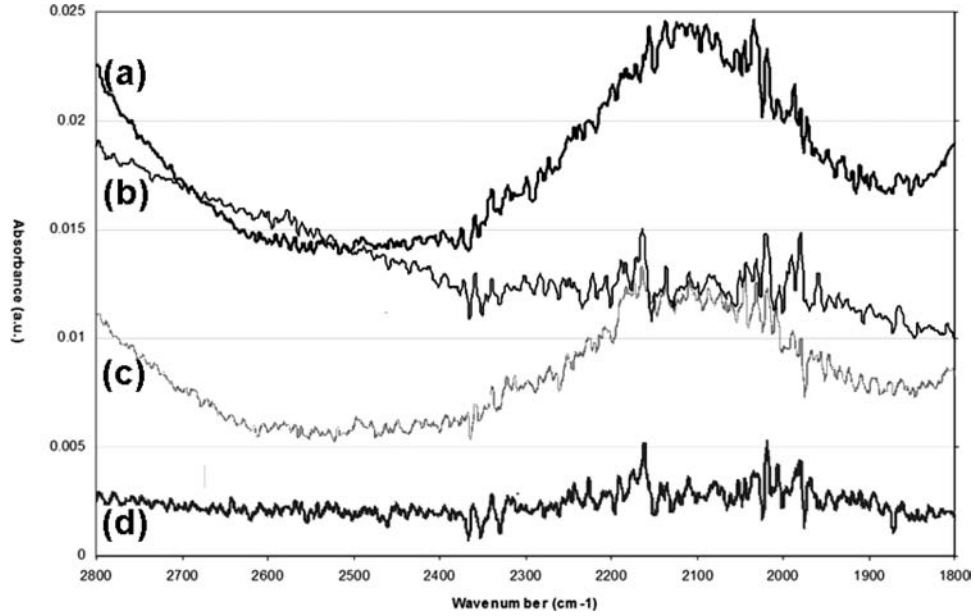

Figure 9. Four different infrared spectra of cassava upon thermal treatment: (**a**) a fresh tuber piece; (**b**) an oven-dried tuber piece; (**c**) a boiled tuber piece; and (**d**) a boiled/oven-dried tuber piece.

monitor the HCN escaping with the addition of heat. After recording the ATR-IR spectrum of one tuber piece to verify the presence of cyanide, three samples were prepared from this cassava tuber piece: the first was oven-dried for 15 min at 60 °C, the second one was boiled in water for 15 min, and the third one was boiled in water for 15 min and then put in an

Table 2. Percent of Cyanide Removed over Time

tuber piece of cassava in	% of cyanide removed after 2 weeks	% of cyanide removed after 4 weeks
hydrogen peroxide (H_2O_2)	58	82
tap water	86	92
preheated tap water	79	90
deionized water	27	84
preheated deionized water	26	87

oven for 15 min. **Figure 9** shows the ATR-IR spectra of the three parts of a tuber piece of cassava after the thermal treatment.

The presence of cyanide is evidenced in the fresh tuber sample (**Figure 9**, spectrum **a**) by an infrared broad peak at around 2110 cm^{-1}. The boiled cassava still shows almost the same amount of cyanide as the fresh tuber sample (**Figure 9**, spectrum **b**). But when a sample is subsequently oven-dried (**Figure 9**, spectrum **c**) or directly oven-dried (**Figure 9**, spectrum **d**), it shows no trace of cyanide. Therefore, cyanide has been completely removed without changing cassava's chemical structure.

This result shows that (**a**) "dry" heat removes free and bond cyanide and (b) the effect of temperature on cyanide content in cassava depends on the mode of processing. Briefly, the processing modes did not significantly affect the chemical composition of the cassava sample. The ATR-IR technique can use the cassava root directly for analysis and provide a quick estimate of the cyanogenic potential. In addition, this technique requires no sample preparation.

Influence of Oxygen, Carbon Dioxide and Ion Traces on Cyanogenic Loss. The following experiment was carried out to explore the role of oxygen, carbon dioxide, and mineral traces in the removal of cyanide. Five samples were cut from a fresh cassava root. The first sample was soaked in hydrogen peroxide solution (3%). The second and third samples were soaked in deionized water and preheated (to eliminate dissolved O_2 and CO_2) deionized water at room temperature, respectively. The fourth and fifth samples were soaked in tap water and preheated tap water, respectively. About 200 mg of each sample was used in 50 mL of adequate water. In our study on cyanogen elimination during processing, the initial and final levels only are quantified. All the experiments were conducted under the hood at room temperature (the preheated solution was allowed to cool down before soaking the sample in it) and under a controlled atmosphere. Cyanogen elimination during processing was monitored at the initial and final stages.

Table 2 shows the percent of cyanide remove in cassava over time. The results show that hydrogen peroxide, deionized water, and preheated deionized water release less cyanide than tap water. According to these results, it seems that oxygen (alone) and heat do not play a major role in cyanide removal, while ion traces contained in tap water speed up the cyanide removal in cassava.

This study highlights the major changes occurring in the infrared spectra and SEM micrographs of cassava as a result of different modes of processing. Soaking in water and sun drying were very effective in reducing bound cyanide. The ATR-FTIR technique can use the tuber pieces directly (without preparation) for analysis and provide a quick estimate of the cyanogenic potential. This technique will be helpful to plant breeders, who often deal with large numbers of samples. There is a correlation between the size and shape of cassava granules given by the SEM micrographs and the presence of cyanide. The processing modes did not significantly affect the structure of the cassava samples, as reflected by the infrared and XRD spectra. Future work will study cyanogenic differences between cassavas from different regions. The mechanism of metal/cyanide binding will also be investigated.

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