GREEN SYNTHESIS AND CHARACTERIZATION OF SODIUM CYANIDE FROM CASSAVA (*Manihot esculenta* CRANTZ)

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E. B. AttahDaniel[1]*, P. O. Enwerem[2], P. G. Lawrence[1], C. U. Ofiwe [3], S. O. O. Olusunle[4] and A. R. Adetunji[5]
[1]Department of Chemical Sciences, Federal University Wukari, PMB 1020, Taraba State, Nigeria
[2]Department of Chemistry, River State University, PMB 5080, Mkpoluorowurukwo, Port Harcourt, Nigeria
[3]National Agency for Science & Engineering Infrastructure, Centre of Excellence,
Nanotechnology and Advanced Material, Akure x, Ondo State, Nigeria
[4]Engineering Materials Development Institute, PMB 611 Akure, Ondo State, Nigeria
[5]Department of Materials and Metallurgical Engineering, Obafemi Awolowo University, Ile Ife, Nigeria
*Corresponding author: attahdaniel@fuwukari.edu.ng

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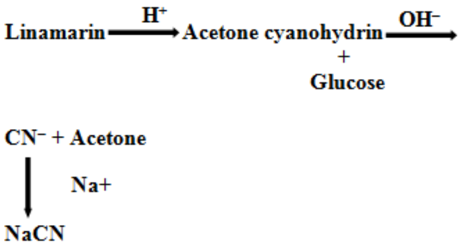
Abstract: This study was carried out to develop a green, simple and cost-effective route for synthesis of sodium cyanidevia aquohydrolysis of linamarin a cyanogenic glucoside found in cassava (*Manihot esculenta* Crantz). Two procedures were employed and compared, the acid hydrolysis method and direct (aquo) hydrolysis. The CN^- ion released was reacted with Na^+ via ion exchange to replace the hydroxyl ion (OH^-) and yielded NaCN. The NaCN was crystallized via evaporation in an air ventilated oven by maintaining the temperature of the reaction solution at 100°C. The crystalized salt was quantified using the modified Vogel's Argentometric method of cyanide quantification. The concentrations were found to be 10.56 mg/g for whole tuber, 13.92 mg/g for tuber tissue and 4.5 mg/g for cassava peels. Analyte grade sodium cyanide purchased off shelf was used as a reference. The crystals were characterized using, X-ray diffraction analysis; the X-ray diffractogram confirmed the products from acid hydrolysis was a cyanogen (CN_2CN_2) while the product from direct hydrolysis was sodium cyanide. The X-ray diffraction peaks of the NaCN from the direct hydrolysis was compared with the X-ray diffractogram of the reference analyte grade NaCN and the peaks were comparable. The crystals were also characterized using the EDXRF. They showed the presence of impurities in the analyte grade and the aquo hydrolysis synthesized salt. We deduced that sodium cyanide synthesized via direct hydrolysis revealed superior purity and possess competitive characteristics when compared with the analyte grade sodium cyanide. This leads to the conclusion that our aim of developing a green, simple and cost-effective synthesis route for producing NaCN was achieved.

Keywords: Cyanide, cyanogen, cyanogenic glucoside, cassava direct hydrolysis, Linamarin, sodium

Introduction

Cassava (*Manihot esculenta* Crantz) is a perennial root crop grown in areas between latitudes 30°N and 30°S of the equator (Akinpelu *et al.*, 2011). It grows in a wide range of climatic conditions and performs better than most other crops under drought conditions. More than half a billion people consume cassava, which is mainly grown for its roots and leaves. Nigeria is the largest producer of cassava (as the major food crop) producing more than 45 million metric ton annually (Akinpelu *et al.*, 2011, International Fertilizer Development Center (IFDC), 2014). Cassava contains cyanogenic glucosides linamarin and laustostralin (in the ratio 93:7). There are two types of cassava varieties, the sweet type (very low cyanide content) and the bitter type with high cyanide content. The bitter variety contains high amount of Linamarin which is manufactured in the leaves and translocated as the glucoside linustatin and stored in the roots (Bokanga, 1993). The glucosides upon hydrolysis release hydrocyanic acid (HCN) which is poisonous. The hydrolysis of the glucoside linamarin is initiated by the enzyme Linamarase when the plant tissue is raptured or peeled (AttahDaniel *et al.*, 2013).

AttahDaniel *et al*. (2013) used an acid hydrolysis method developed by Bradburry and Holloway (1988) to synthesize NaCN from cassava fresh leaves, fresh peels, fresh tuber tissue, fresh whole tuber, dried leaves, dried peels and dried whole tuber. The quantity of product obtained in that work were 2.84, 2.75, 2.94, 2.64, 2.31, 2.14 and 2.59 g, respectively.



------ eqn. 1

Fig. 1: NaCN synthesis via acid hydrolysis of Linamarin (AttahDaniel *et al.*, 2013a)

The production of sodium cyanide (NaCN) for industrial purposes before now involved very energy intensive, time consuming and costly processes to first produce HCN and then react it with ammonia (NH_3). The ammonia production also involves energy and time consuming and costly process.

Methods used to produce HCN include the Andrussaw and Degussa processes. These two methods use methane and ammonia as the raw materials (AttahDaniel *et al.*, 2013a).

$$CH_4 + NH_3 + 1\tfrac{1}{2}O_2 \xrightarrow[\substack{2atm/1000 - 1200^{\circ}C \\ \text{(Andrussaw process)}}]{Ph/Rh \text{ or } Pt/Ir} HCN + 3H_2O + 144KCalmol^{-1} \quad \text{--------- Eqn. 2}$$

$$CH_4 + NH_3 \xrightarrow[\substack{1200\text{-}1300^{\circ}C \\ \text{(Degussa process)}}]{Pt} HCN + 3H_2 + 144KCalmol^{-1} \quad \text{------- Eqn. 3}$$

In metallic cyanides, e.g. sodium cyanide (NaCN), the group -C≡N is present as the negatively charged ion CN^-. At normal temperature, the CN^- ion is rotationally disordered and is thus effectively spherical with a radius of 1.92Å; hence, NaCN has the NaCl structure (AttahDaniel *et al*., 2013a).

Kerry and Marv, (2002) reported that Sodium cyanide (CAS No. 143-33-9) was first produced in 1834 by F. and E. Rogers, who heated Prussian blue (highly colored mixed oxidation state Fe II and Fe III derivatives) and sodium carbonate together (King, 1994). The mixture was cooled and sodium cyanide was extracted with alcohol. The compound then had no intended purpose until J. S. MacArthur and the Forrest brothers patented a process for extracting gold and silver from ores in 1887. From 1900 to 1961 the Castner process, was used to make sodium cyanide (Kerry and Marv, 2002).

$$2Na + 2C + 2NH_3 \longrightarrow 2NaCN + 3H_2 \quad \text{------ eqn. 4}$$

Equation 5 based on the neutralization of sodium hydroxide (aqueous) and hydrogen cyanide (gas) shows the process employed in the production of NaCN (Kirk- Othermer, 1993).

$$HCN + NaOH \longrightarrow NaCN + H_2O \quad \text{-------- eqn. 5}$$

This method will be adopted to produce NaCN in this work via acid hydrolysis and direct hydrolysis from cassava.

Cyanides are used for gold and silver extraction from ores (Figueroa *et al*., 2015), surface hardening of ferrous materials like in cyaniding and nitriding (Adetunji *et al*., 2008). Adetunji *et al*., 2008 used cassava leaves powder for the strengthening of the surface ferrous materials. Their study showed that there was C diffusion into the case of mild steel at elevated temperature (900^oC) and low temperatures (450 and 500^oC). Cyanides are also used in making insecticides and rodenticides, as chelating agents, and in the manufacture of dyes and pigments (ATSDR, 2006). Cyanogens are used in organic syntheses, as fumigant, as fuel gas for welding and cutting heat-resistant metals, and as a rocket and missile propellant with ozone or fluorine (HSDB, 2004).

Materials and Method

Acid hydrolysis

Acid hydrolysis was carried out by grating 50 g each of fresh cassava samples and blended with 160 cm^3 of 0.1000M of cold dilute ortho phosphoric acid H_3PO_4 in a blender (AttahDaniel *et al*., 2013b) and centrifuged (and when necessary filtered). The cold dilute ortho phosphoric acid was used to control the temperature of the reaction system because of the high volatility of cyanide (about 1.1 x106 mg/m3 at 25^oC). 8 mL of each of the extracts of samples, were pipetted into a boiling tube and 8 mL of 4.0M H_2SO_4 was added to each, corked and placed in a water bath at 100^oC for 55 min. The tubes were then removed and allowed to cool at room temperature. 20 mL of 3.6M NaOH was then added to the mixture in the stoppered boiling tube and allowed to stand for ten minutes for complete breakdown of cyanohydrins to release cyanide ion which reacted with NaOH to form NaCN via ion exchange. The whole volume was transferred into a 50 mL standard flask and made up to mark with 3.6M NaOH. The aliquots were quantified using Denige's Argentometric titration method of quantification of cyanide (modified by AttahDaniel *et al*., 2013c). 5 mL of each of the aliquots was pipetted and diluted to 25 cm^3 in a conical flask. 8 mL of 2M NH_4OH was added and 2 mL of 5% KI added as the indicator. The flask was then placed on a black background and titrated with 0.0200M $AgNO_3$ in drops until the end point (when one drop produces a permanent turbidity).

Direct hydrolysis

Aquo (direct) hydrolysis was carried out by grating 50 g of each fresh cassava sample and blended with 160 mL of icy distilled water in a blender and centrifuged (and when necessary filtered). This was based on the property of cyanide to sink and mix with water. The icy distilled water was used to keep the temperature of the reaction below 25^oC for the control of volatile cyanide as mention above within the reaction system. 8 mL of each of the extracts of samples were pipetted into a boiling tube. 20 mL of 3.6M NaOH was then added to the mixture in the stoppered boiling tube and allowed to stand for ten minutes for complete breakdown of cyanohydrins to release cyanide ion which reacted with NaOH to produce NaCN via ion exchange. The NaCN obtained in the two different procedures were crystalized in an oven by maintaining the temperature at 100^oC. The crystalline sodium cyanide produced from the acid hydrolysis method and aquo (direct) hydrolysis were characterized using X-ray diffraction and Energy Dispersive X-ray fluorescence.

EDXRF

X-ray fluorescence (XRF) analysis is a fast, non-destructive and environmentally friendly method with very high accuracy and reproducibility. Concentrations of up to 100% are analyzed directly, without any dilution, with an XRF spectrometer both very small concentrations of very few ppm and very high concentrations of up to 100% can be analyzed directly without any dilution process.

Elemental characterization (EDXRF)

The elemental analysis of the crushed finely homogeneous synthesized sodium cyanide samples were obtained using Skyray Instrument's Energy Dispersive X-ray Fluorescence (EDXRF) (EDX3600B) machine.

The Energy dispersive spectrometric feature of the EDXRF equipment allowed for a qualitative elemental analysis of our sample thereby giving us a picture of the elemental composition using spectrum (graphical) representation, with each energy peak labeled after the element it represents. Physical examination of the spectrum showed discrete and continuous patterns with the most prominent element as the highest peak and trace elements as low and almost grounded peaks.

XRD

In this study, we employed different techniques; energy dispersive X-ray fluorescence and X-ray diffraction analysis were used to characterize our samples for elemental and phase identification.

The X-ray powder diffractogram of the sodium cyanide samples were measured at room temperature on a GBC EMMA (Enhanced Mini-Material Analyzer) Diffractometer, GBC Scientific Equipment Ply Ltd, Australia; which has a Cu Target X-ray tube with wavelength of 1.54059 Å. The measurement was taken at a step size of 0.05^0, 2θ start angle of 5^0 and end angle of 65^0.

The formula used to calculate concentration of cyanide in mg/g is;

$$\text{mg/g} = \frac{C \; x \; V_d}{V_a \; x \; w}$$

Where C= Concentration in ppm from the curve; V_d = volume of digest solution; W = weight of sample taken to prepare digest solution; V_a = Volume of sample digest taken

Results and Discussion

Hitherto, production of sodium cyanide was achieved by the production of hydrogen cyanide (HCN) through the Andrussaw or the Degussa process by reacting methane and ammonia in the presence of a catalyst and huge energy input before and the HCN contacted with sodium hydroxide (NaOH) to yield NaCN. It could also be achieved via the Castner process by reacting sodium metal with carbon and ammonia to yield HCN and contacting the HCN with NaOH to yield NaCN. In this work we sought a simple, less use chemicals and less energy consuming route using natural materials (water and cassava waste). In the acid hydrolysis method using dilute cold orthophosphoric acid and icy water for the release of CN^- from the hydrolysis of Linamarin also ensures non-usage of toxic chemical like ammonia and green chemistry practice.

The study was designed based on the synthetic route followed by AttahDaniel *et al.* (2013) to synthesize sodium cyanide (NaCN) from cassava *(Manihut ecsulenta* Crantz) via acid hydrolysis. The route was followed to provide for further modify the route. The modification was embarked upon develop a green, simple and cost-effective process for producing NaCN from cassava (*Manihot esculenta* Crantz) in Nigeria being the largest producer of cassava in the world. Icy distilled water and the endogenous enzyme linamarase were employed for hydrolysis of the cyanogenic glucose linamarin and the CN^-ion yielded during hydrolysis was then reacted with NaOH(aquo (direct) hydrolysis) to yield NaCN. The reaction of $CN^-$with NaOH was based on the property of hydrogen cyanide to mix well and sink with water and its dissociation in aqueous media. The reaction products were quantified using Denige's argentometric method of cyanide determination studiedand modified by AttahDaniel *et al.* (2013). The modified method showed linearity from concentrations of 1.7x10-3 mol dm^{-3} to $3.5x10^{-3}$mol dm^{-3} (which implies that within the linear range the method is reliable but at concentrations below 1.7x10-3 molodm-3 the method is not reliable and cannot be used). Themethod showed a sensitivity of 0.6 millimoles of CN^-/cm^3 of 0.0200 mole/dm^3 $AgNO_3$, and detection limit of 0.7 millimole (0.02 g) cyanide in sample. The procedure involved the use of $AgNO_3$ for titration, potassium iodide (KI) and ammonium hydroxide (NH_4OH) as indicator and solubilizer, respectively.

AttahDaniel *et al.* (2013), obtained 2.84 g of NaCN from fresh leaves sample which is about 5.68% of the total weight of sample while the fresh peels had 2.75 g NaCN/50 g sample, also about 5.50% of the sample weight. 2.94, 2.64, 2.31, 2.14 and 2.56 g NaCN were obtained for samples of fresh tuber tissue, fresh whole tuber tissue, dried leaves, dried peels and dried whole tuber respectively and their respective percentage yields were; 5.90, 5.27, 4.61, 4.27 and 5.11%.

In this work using the acid hydrolysis method, we found the weights (Table 1) of NaCN crystals for cassava peel (C_p), cassava fresh tuber tissue (C_F) and Fresh whole cassava tuber (C_{FP}) as 5.04 g which is 10.08% of the total weight of sample, 5.03 g equivalent to 10.06% of the total weight of sample and 4.73 g as 9.46% of the total weight of sample, respectively. While for the direct hydrolysis method, the weight (Table 2) of crystals for the cassava peels (Cp) was 2.39 g, cassava fresh tuber tissue (C_F) 2.93 g and Fresh whole cassava tuber (C_{FP}) 1.96 g with percentage yields of 5.5, 5.86 and 3.92%, respectively.

Table 1: Concentration in Mg/HCN and quantity of NaCN obtained from direct hydrolysis

Cassava sample	CP2	CF2	CFP2
mgCN IN 50 g sample	165	456	504
% yield CN^-	0.33	0.91	1.01
Weight of NaCN salt (g)	2.39	2.93	1.96
% yield of NaCN (%)	5.50	5.86	3.92

Table 2: Concentrations in mg/HCN and quantity of NaCN obtained from acid hydrolysis

Cassava sample	CP 1	CFI	CFP1
mgCN in 50 g sample	225	696	528
% yield CN-	1.40	1.39	1.056
Weight of NaCN salt (g)	5.04	5.03	4.73
% yield of NaCN (%)	10.08	10.06	9.46

Figures 1 to 3 show the X-ray diffraction pattern for analyte grade NaCN, NaCN direct hydrolysis and NaCN from the acid hydrolysis, respectively.

From the patterns, the samples; Analyte grade NaCN, NaCN from direct hydrolysis and NaCN from acid hydrolysis showed similar XRD patterns at 2θ angles of 32.514^o, 32.3^o, 32.339^o and 38.693^o, 38.55^o, 38.814^o, respectively. Analyte grade NaCN and NaCN from direct hydrolysis shared similar peaks at (30.578^o, 30.75^o), (32.514^o, 32.3^o), (33.693^o, 33.15^o) and (38.693^o, 38.55^o), respectively. Analyte grade NaCN, and NaCN from acid hydrolysis shared similar peak projections at angles (32.514^o, 32.339^o) and (38.693^o, 38.814^o). NaCN from direct hydrolysis and NaCN from acid hydrolysis also shared similar peak projections at (19.05^o, 19.251^o), (29.35^o, 29.252^o), (32.3^o, 32.339^o), (34.394^o, 34.101^o), (38.55^o, 38.814^o), respectively.

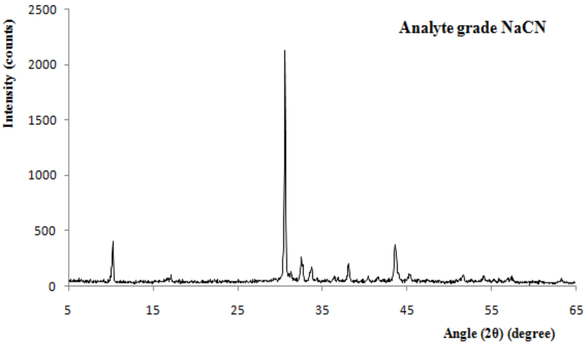


Fig. 1: X-ray diffraction pattern of analyte grade NaCN

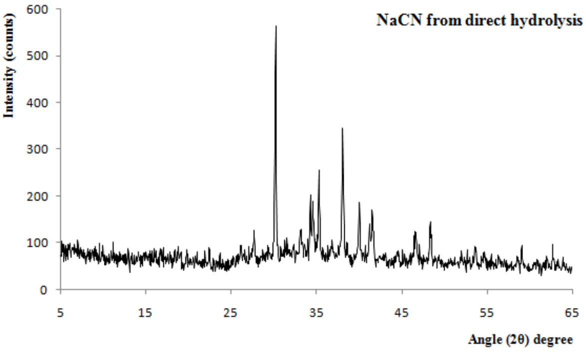


Fig. 2: X-ray diffraction pattern of NaCN from direct hydrolysis

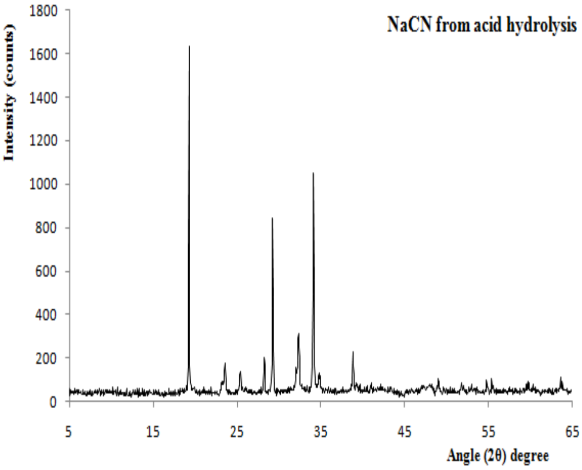


Fig. 3: X-ray diffraction pattern of NaCN from acid hydrolysis

The sample phase search was achieved using the GBC X-ray analysis TRACES Software (Version 6) which operates on the full ICDD PDF-2 database file. Two distinctive compound phases were identified to match the samples phases. These phases are sodium cyanide (ICDD reference code 00-003-0638) and cyanogen (ICDD reference code 01-072-0497). Analyte grade NaCN phase matches strongly with sodium cyanide reference phase at 2θ angles of 30.1674° and 31.7035°, with maximum relative intensity at 30.1674°. NaCN from direct hydrolysis shared its maximum relative intensity of 30.1674° with the sodium cyanide reference phase while NaCN from acid hydrolysis corresponded more with the cyanogen reference phase.

Figures 4 – 6 show the X-ray fluorescence patterns of analyte grade NaCN, X-ray fluorescence pattern of NaCN from direct hydrolysis and X-ray fluorescence pattern of NaCN from acid hydrolysis, respectively.

The EDXRF has a limitation (inability to detect the first twelve elements). These twelve elements, carbon, nitrogen and sodium, elements that combined to form NaCN. However, the EDXRF results were adopted to determine impurities in the NaCN. The elements found as impurities and their concentrations for analyte grade NaCN included; Mg 0.1261, P 0.0099, S 0.0216, K 0.0831, Ca 0.0276, V 0.00065, Cr 0.0056, Co 0.0028, Fe 0.2082, Ni 0.0877, Cu 0.1043, Zn 0.1514, W 0.14604, Nb 0.0580, Mo 0.1151, Sn 1.5159 and Sb 1.3425.

Impurities found for the NaCN crystals from the direct hydrolysis method were Mg 0.0215, Al 0.0012, P 0.0081, S 0.0038, K 0.0904, Ca 0.0991, V 0.0103, Cr 0.0042, Mn 0.0026, Co 0.0028, Fe 0.2353, Ni 0.0965, Cu 0.0553, Zn 0.1930, As 0.0643, Pb 0.0031, W 0.2018, Au 0.0282, Nb 0.0182, Mo 0.1382, Cd 0.0002, Sn 2.0683, and Sb 1.8077. While impurities in the NaCN crystals from acid hydrolysis were Mg 0.1005, Al 0.3168, Si 0.0326, P 0.1496, S11.0365, K 0.2709, Ca 0.0381, V 0.0059, Cr 0.0025, Mn 0.0055, Co0.0030, Fe 0.1987, Ni 0.0890, Cu 0.0541, Zn 0.1454, Pb 0.0227, W 0.1912, Nb 0.0246, Mo 0.1748, Cd 0.0003, Sn 2.0677, Sb 1.7944.

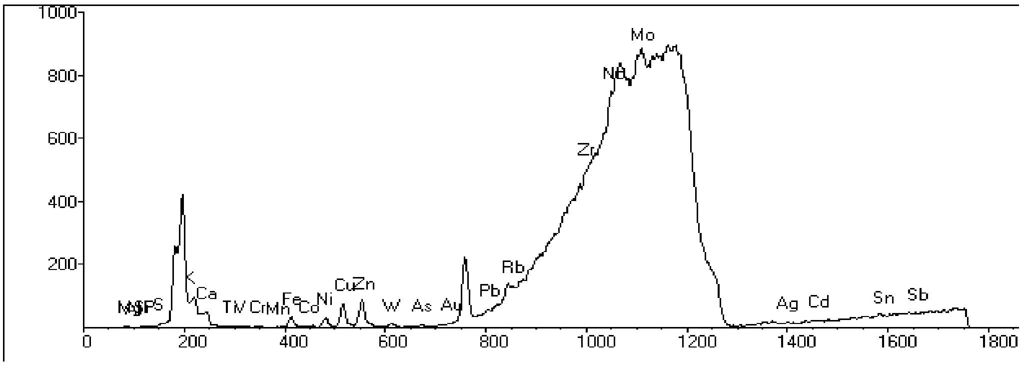


Fig. 4: X-ray fluorescence pattern of analyte grade NaCN

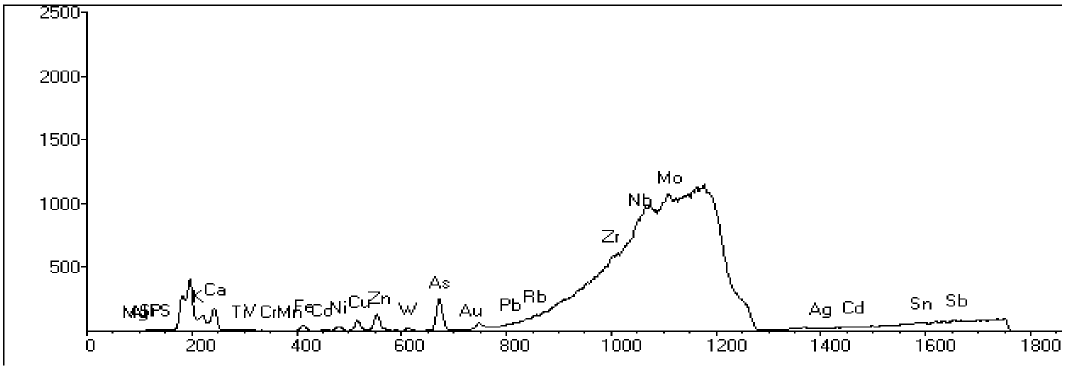


Fig. 5: X-ray fluorescence pattern of NaCN from direct hydrolysis

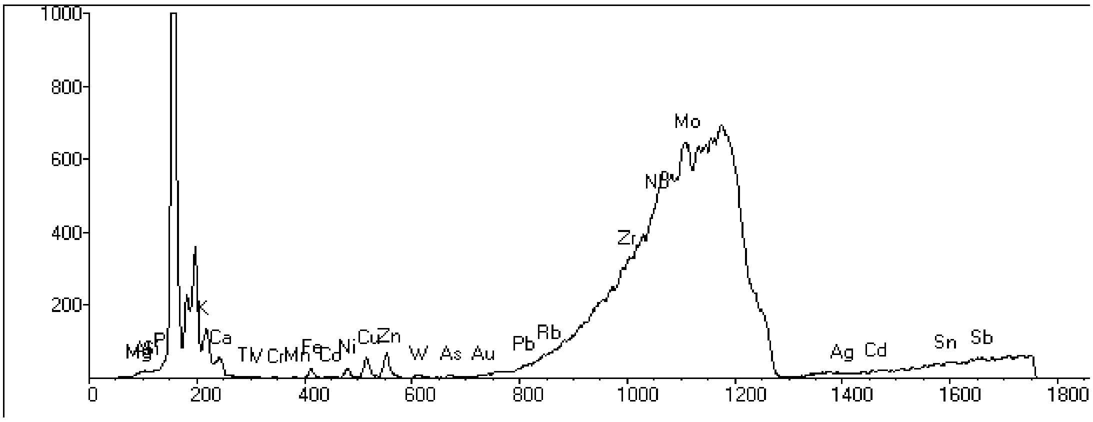


Fig. 6: X-ray fluorescence pattern of NaCN from acid hydrolysis

From the patterns in Figs. 4 and 5, we can say that the NaCN prepared from direct hydrolysis has less impurities compared to analyte grade NaCN and NaCN from the acid hydrolysis method. For example, the Sulphur content of analyte grade NaCN is 0.0216; the Sulphur content of the NaCN from direct hydrolysis is 0.0038 while the NaCN for the acid hydrolysis has a Sulphur content of 11.0365 (Fig. 6). The high Sulphur content in NaCN from acid hydrolysis could have resulted from the use of more reagents such as phosphoric acid, Sulphuric acid and sodium hydroxide which may also contain other impurities.

Conclusion

We can conclude from this study that through aquo (direct) hydrolysis, NaCN was synthesized and characterized. The characterization results showed minimum impurities using natural raw materials andfewer chemicals. Therefore, a green synthetic pathway for the synthesis of NaCN has been developed for the production of NaCN in cassava producing countries like Nigeria and other tropical countries producing cassava. The results from the X-ray diffraction identified that acyanogen was formed from acid hydrolysis and not NaCN. Comparison of the X-ray diffraction and EDXRF patterns results showed that NaCN from aquo (direct) hydrolysis compared favorably with superior purity to the analyte grade NaCN. Above all we can conclude that the acid hydrolysis method has been successfully modified and ascertained for the green synthesis of cyanide while cyanogen can be produced from acid hydrolysis of Linamarin in cassava.

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Conflict of Interest

Authors declare there is no conflict of interest related to this study.

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