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Performance Characteristics of Argentometric Method of Cyanide Determination

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ABSTRACT

The performance characteristics of the argentometric method of cyanide determination was investigated using the calibration curve method. The assessment offer linearity within the range $1.7x10^{-3}$moles to $3.5x10^{-3}$moles with a sensitivity of 0.6millimoles of cyanide per dm^3 of 0 .0200 $moldm^{-3}$ $AgNO_3$. It gave a detection limit of 0.7 millimoles (0.02gCN).The interference studies within the linear range shows that halides (Cl^-, Br^-, I^-) do not interfere in the analysis when there is excess of CN^- in the sample.

The assessed method was applied to determine cyanide in cassava samples and pack cyaniding compositions and residues.

Keywords: *pack cyaniding, calibration curve*

1. INTRODUCTION

Methods of cyanide determination in samples have been developed and more are still being developed or existing methods are being improved upon. These methods include those applicable for determining cyanide at trace concentrations especially in water samples. These are mainly instrumental methods like the rapid and sensitive gas chromatographic method in which cyanide ion is reacted with Bromine to form CNBr in an acidic medium and extracted into benzene.

The benzene extract is then injected into a gas chromatograph and the CNBr gives a narrow peak which results in linear calibration plot [1]. Another one is the fibre optics Flourimetric method. In this method, ascorbic acid is used in a calcein Cu-CN system and gives a detection limit of 0.2ppb while in a flow injection system cyanide is determined selectively at concentration in the range $2x10^{-6}$ mol/L by injection of 20µl samples at a rate of 360 samples per hour. By the use of continuous flow, cyanide could be determined at levels down to $5x10^{-7}$ mol/L [1].

A simplified colorimetric method was developed by replacing pyridine/barbituric acid as a colour reagent with isonicotinic/barbituric acid which was found to be more effective than the former [2]. In this method, cyanide ion is first oxidized to a cyanogen halide and of the colour reagent added at room temperature for colour development and the absorbance taken at 600nm.

A comparative study was undertaken comparing the electrochemical method with the colorimetric method [1]. It was observed that in the electrochemical method, a solution can be assayed for cyanide using an ion selective electrode and a double junction glass reference electrode with a suitable cyanide electrode. The potential difference could be measured with a pH meter/multimetre available in simple laboratories [1]. But interferences due to the presence of Cl^-, Br^-, I^- at high concentrations require the running of blank measurement for each analysis. The electrochemical method was found to be simple but complicated and cannot be used for samples containing less than 20 mg HCN Kg^{-1} because of the need for blank determination in each analysis. The average deviation of electrochemical results from the colorimetric method is 8.5% [1].

A picric kit for the determination of cyanogens in all cassava products within the range of 10-800 mg HCN equivalent Kg^{-1} even in the field has also been developed [3]. A titrimetric method of cyanide quantification using silver nitrate with the difficulty of the precipitate redissolving was improved upon by adding ammonia solution in which it is readily soluble and a little potassium iodide as the indicator before titration is commenced or by employing diphenyl carbazide as an absorption indicator in which the end point is marked by the pink colour becoming pale violet i.e. almost colourless [4].

Analytical techniques available for determination of CN^- in plants and biological fluids include amperometery [13], voltammetery [15], polarography [20], potentiometery

[22], piezoelectricity [16], gas chromatography [21], visible spectrophotometry [18], mass spectrometry [14], HPLC [12] and flow injection [11, 19].

The variety of analytical methods reported for CN^- in blood may indicate the difficulty of its analysis in that there is no universally preferred method [17]. Available methods are expensive, laborious, and require technical expertise and sophisticated equipment [11]. These equipment are usually difficult to find in simple laboratories. This work was done to address this difficulty in our laboratory and could address similar challenges in other simple laboratory.

Cassava is known to contain the cyanogenic glucosides-linamarin and lotaustralin in the ratio 93:7 in the leaves [5]. Cyanogenic glucoside of 1500 mg HCN equivalent Kg^{-1} dry weight of fresh root of bitter cassava has been reported [6]. Other works have also reported that more cyanogens are concentrated in the peel of the sweet cultivar and the leaves containing about 200 mg HCN Kg^{-1} [7]. Also, cyanogenic concentration of between 193.3-951.5 mg HCN Kg^{-1} has been reported [8].

2. MATERIALS AND METHOD

Chemicals used for the investigation of the Silver Nitrate titration method were BDH analytical grade chemicals. While cassava (*Manihot esculenta crantz*) samples were from the Teaching and Research farm of the Federal University of Technology Akure.

In this work, the leaves of the bitter cultivar of cassava were processed, analysed and used for pack cyaniding using the argentometric method of cyanide determination.

The present study first presents an investigation of the performance characteristics of the silver nitrate titration method of cyanide quantification to determining its detection limit, precision and sensitivity using the calibration curve method. After which it was used to monitor cyanide in the pack cyaniding of mild steel samples.

Standard solutions of potassium cyanide of 0.005M concentration serially diluted were titrated with 0.0200M silver nitrate solution to determine the detection limit, sensitivity, and the precision of the method using the calibration curve method. The calibration curve method was used in the determination of the detection limit and sensitivity of the silver nitrate titration of cyanide. The plot of the volume of silver nitrate used in cm^3 against concentration of potassium cyanide in moles is shown in figure 1.

3. EXTRACTION OF CYANOGENS

Cyanogens were extracted from cassava leaves by blending 50g each of processed cassava leaves with cold dilute ortho phosphoric acid (0.1000M) in a household blender and centrifuged. The cold ortho phosphoric acid prevents the evaporation of cyanide [9] and inhibits the endogenous linamarase from acting on linamarin and stabilizes the cyanohydrin till hydrolysis [10]. The extracts were hydrolyzed in boiling tubes using 4.0M H_2SO_4 in a water bath at 100^0C for 55 minutes.Then allowed to cool to room temperature and 3.6M NaOH was added for the spontaneous breakdown of cyanohydrin to release and fix CN^- in NaOH.

A portion of the aliquot was titrated with 0.0200M $AgNO_3$ using KI as the indicator and 2M NH_4OH added as solubilizer. The results of the application are shown in Table 1.

4. RESULTS AND DISCUSSION

Table 1: Concentration of Cyanide ion in different parts of Cassava plant

Cassava Sample	Fresh leaves	Fresh peels	Fresh tuber tissue	Fresh whole tuber tissue	Dried leaves	Dried peels	Dried whole tuber
mgCN in 50g sample	300±6	268±9.2	342±2.6	266±3.2	160±3.2	140±1.0	232±4.2

The plot of volume $AgNO_3(dm^3)$ Vs Concentration of KCN (in moles) in figure 1 shows linearity from concentrations of $1.7x10^{-3}$ mol dm^{-3} to $3.5x10^{-3}$mol dm^{-3}. This implies that at concentrations below $1.7x10^{-3}$ $moldm^{-3}$ this method will not be reliable. The method showed sensitivity of 0.6millimoles of CN^- dm^{-3} of 0.0200 $moldm^{-3}AgNO_3$ and detection limit at thrice standard deviation of 0.7millimoles (0.02g).The interference studies within the linear range showed that halides (Cl^-, Br^-, I^-) do not interfere with the analysis as in the electrochemical method which require the running of blank measurement for each analysis. Figures 2 to 6 show plots of the interference studies which validate the

simplicity of the method void of the complicity of running blank for each sample analysed.

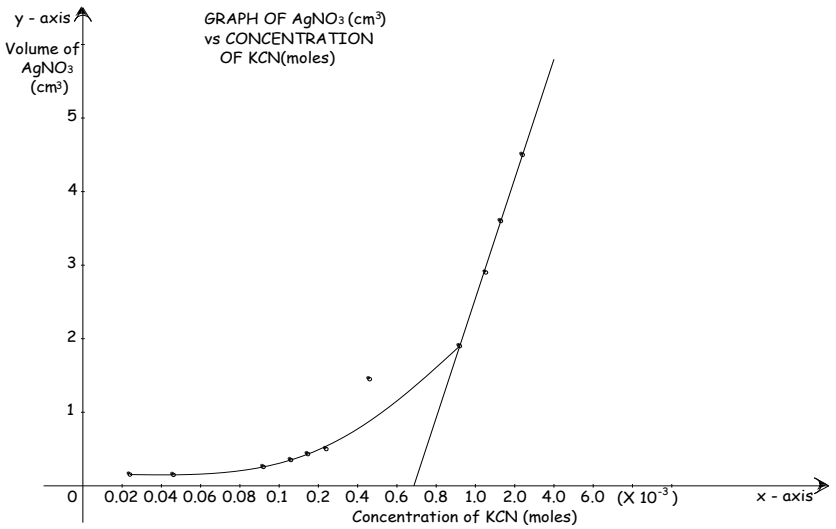

Figure 1: Plot of $AgNO_3$ (dm^3) Vs Concentration of KCN (moles)

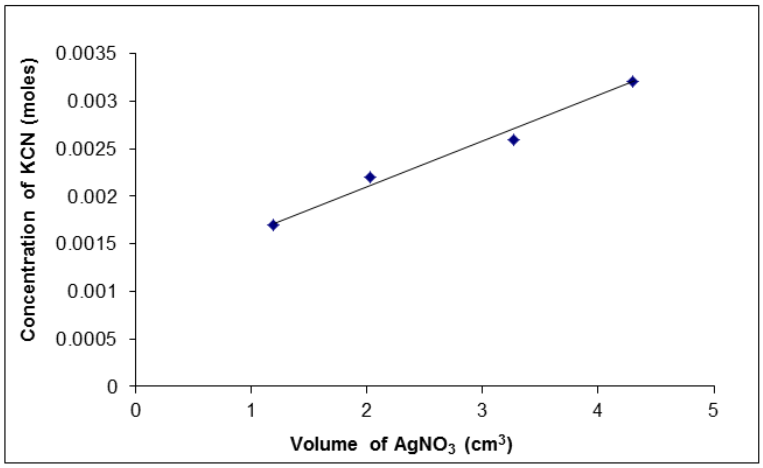

Figure 2: Graph of volume of 0.200M $AgNO_3$ used (cm^3) against KCN concentration in moles

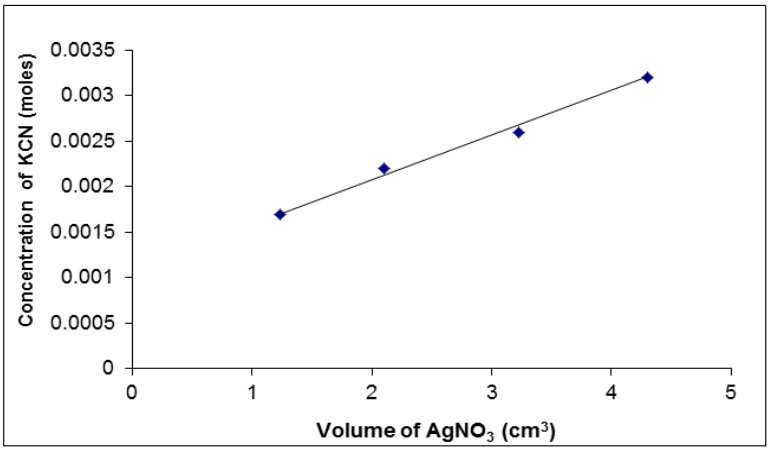

Figure 3: Graph of volume of 0.200M $AgNO_3$ used (cm^3) against KCN standard concentration plus 1cm^3 0.00483moles $BaCl_2$

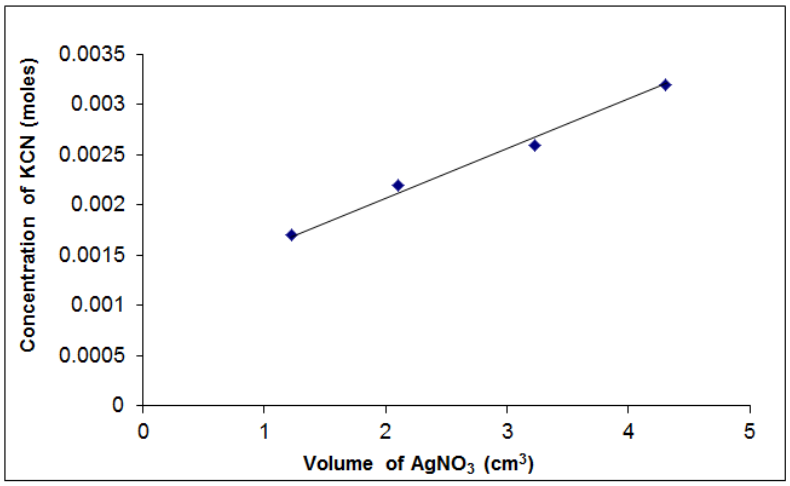

Figure 4: Graph of volume of 0.200M $AgNO_3$ used (cm^3) against KCN standard concentration plus 2cm^3 0.00483moles $BaCl_2$

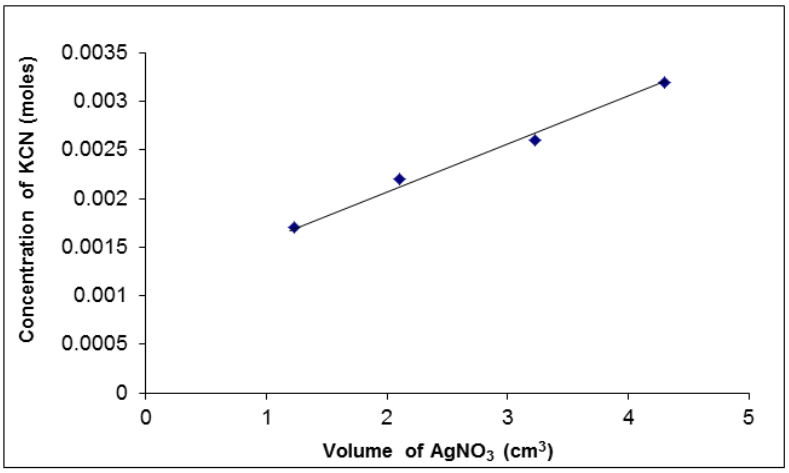

Figure 5: Graph of volume of 0.200M $AgNO_3$ used (cm^3) against KCN standard concentration plus 3cm^3 0.00483moles $BaCl_2$

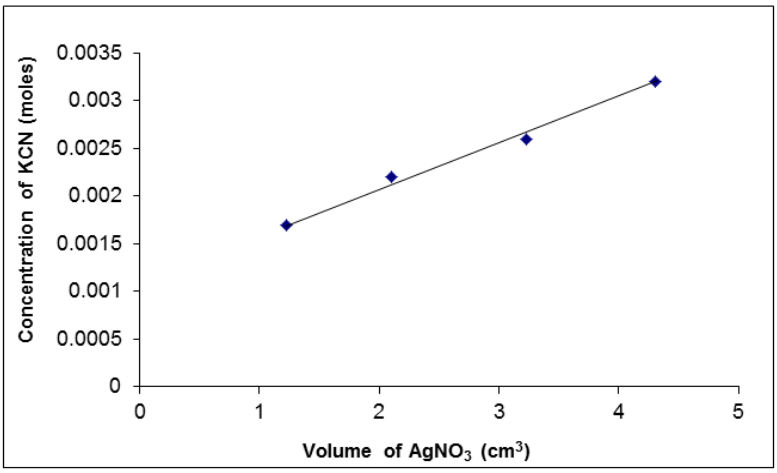

Figure 6: Graph of volume of 0.200M $AgNO_3$ used (cm^3) against KCN standard concentration

plus 4cm^3 0.00483moles $BaCl_2$

The results of the cassava samples showed the fresh tuber having the highest concentration of cyanide, 342.2 ± 2.6mgCN and the list concentration by the dried peels, 140±1.0mgCN. While the dried pulverized leaves to be used in pack cyaniding had cyanide concentration of 160 ±3.2mg/50g. The application of the assessed method was to monitor the usage of cyanide from cassava for pack cyaniding of mild steel indicated no presence of cyanide. The non detection of cyanide in the pack cyaniding residue is suspected to have resulted from either the cyanide being used up during pack cyaniding or the concentration of cyanide could be at trace level which could not be detected using this method.

5. CONCLUSION

The linear range of this method was found to be between $1.7x10^{-3}$ mol dm^{-3} and $3.5x10^{-3}$mol dm^{-3}. The sensitivity was 0.6millimoles of CN^- cm^{-3} of 0.0200mol$dm^{-3}$$AgNO_3$ and detection limit at thrice standard deviation was 0.7millimoles (0.02g).

There was no interference by halides (Cl^-, Br^-, I^-) requiring the running of blank measurement for each analysis.
The simplicity of the method and immunity to halides interference within the linear range makes it a reliable method in the absence of modern instrumental method of analyzing cyanide.

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