RESEARCH TO DETERMINE CONTENT OF CYANIDE IN CASSAVA AND BAMBOO SHOOT BY DIFFERENTIAL PULSE POLAROGRAPHY METHOD

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Dinh Thi Truong Giang, Mai Thi Thanh Huyen
Faculty of Chemistry, Vinh University

TÓM TẮT

NGHIÊN CỨU XÁC ĐỊNH XYANUA TRONG SẮN VÀ MĂNG BẰNG PHƯƠNG PHÁP CỰC PHỔ XUNG VI PHÂN

The electrolyte solutions, sweep rates, purges time, etc...were researched on the determination of cyanide. Distillation time of 90 minutes was recommended to use; some interferences of other anions including sulphide and sulphite were also investigated. Cyanide content ion of cassava and bamboo shoot has been determined by differential pulse polarography method using the quantitative technique of standard addition. The ranges of cyanide concentration in bamboo shoot were within 0.00045 -0.075 mg/g and from limit of detection to 1.7902 mg/g for cassava. Accuracy was assessed by analyzing artificial sample and the repeatability (expressed as the relative standard deviation in percentage) was 3%. Sensitivity of analysis was assessed by limit of detection (LOD = 0.017 mg/l) and limit of quantification (LOQ = 0.057mg/l).

Keywords: *Cyanide, cassava, bamboo, differential pulse polarography*

1. INTRODUCTION

Cassava and bamboo shoot are seen as two kinds of popular food in Vietnam. Shoot of bamboo can be processed into various types of food such asdried, salted or fresh bamboo shoot. However, both of cassava and bamboo shoot are two kinds of food containing toxin cyanide. It can be toxic to human health and can lead to death in doses 50-90mg/kg[1]. Depending on the parts of cassava roots and bamboo shoots and their processed products, concentrations of cyanide are different. There are many methods to determine cyanide such as volumetric methods, spectrophotometry UV - VIS, and differential pulse polarography method… [2], [3],[4]. The differential pulse polarography is considered a sensitive, selective method with high accuracy to determine low contents of cyanide in the samples. Therefore, the determination of cyanide content in cassava and bamboo shoot by

modern analytical methods as differential pulse polarography is necessary. This contributes to provide information, control quality of toxic ingredients in the cassava and bamboo shoot.

2. EXPERIMENTAL

2.1. Apparatus

The work was carried out on a 797- VA computrace multipolarograph (Switzerland). A three - electrode system was used throughout, consisting of saturated calomel electrode as reference electrode, drop mercury electrode (DME) as working electrode and platinum coil as auxiliary electrode. Data handling and storage were controlled by a computer using 797 VA - 1.3 software. Other equipments were used including cyanide distillation system, grinding food equipments, analytical balance Sartorius with 0.1 mg resolution. All glassware was soaked and washed with acid HNO_3 5%, then they were washed with ultrapure water before using.

2.2. Chemicals

The chemicals (KOH, H_3BO_3, KCN, $MgSO_4$, H_3PO_4, NaOH, Na_2S, $Na_2B_4O_7$) were suprapur grade chemicals (Merck). All working standard solutions of CN^- were prepared daily by diluting commercial 1000ppm stock standard solution (Merck). All solutions were prepared using ultrapure water obtained by passing deionized water through a Milli - Q water purification system.

2.3. Sample preparation

2.3.1. Preliminary digestion

Roots of high yield cassava, fresh normal, dried normal and boiled normal cassava were collected at Thanh Ngoc commune, Thanh Chuong district, Nghe An province, Vietnam. Roots of cassava were washed, naturally dried and peeled to collect white parts. Roots of high yield cassava were divided into 2 parts: the parts of head, tail (3cm), and body of cassava. Samples (15g) were crushed. After that, they were placed in the Erlenmeyer flasks (100ml) with closed button. Then they were added ultrapure water to 100ml, soaked for 1 day and were grinded both solution and residue.

Shoots of bamboo were collected at Long Son commune, Huong Son district, Ha Tinh province, Vietnam. Samples of fresh bamboo shoots were peeled, divided into 3 sections (the top, foot, middle), the length of each section was 5cm. Dried samples or salted samples (boiled three times with water) of bamboo shoot was a mixture of top sections, foot section and body section. They were cut and crushed, the process of digestion was done as cassava samples.

2.3.2. Sample distillation

5g $MgSO_4$, 15ml H_3PO_4 were added into the flask containing cassava samples and bamboo shoot samples after soaking and grinding (flask was placed on the water). The flasks were then heated for an hour and 30 min at 90^0C. The vapor of HCN was released and absorbed twice serially by 20 ml of NaOH 0.5M. Blank samples were prepared according to the process above.

2.4. Method of determination

Optimizing analysis by investigating to select electrolyte and parameters of measurement (sweep rate, initial purge time of N_2 for releasing O_2, pulse amplitude, etc…). Interferences of sulfide ion, sulphite ion and distillation time were investigated. After that, samples were analyzed by optimized procedure above. The accuracy of the analysis was evaluated by repeatability and analytical result of concentration of cyanide in the artificial sample. The

sensitivity of the method was described by the limit of detection and limit of quantification.

3. RESULTS AND DISCUSSION

3.1. Investigated results of measurement parameters and conditions

3.1.1. Electrolyte

Some electrolyte solutions were chosen for investigated as ammonium buffer, borax buffer, sodium hydroxide. The differential pulse polarograms of electrolyte solutions as background and electrolyte solutions containing cyanide were recorded. Selected suitable electrolyte solution for measurement of cyanide was borax buffer solution at pH =10.2, because there was no peak on polarograms for electrolyte solution and there was a symmetric peak of CN^- in borax buffer. Figure 3.1 shows polarograms of cyanide (CN^-) in the electrolyte solutions and electrolyte solutions containing 0.125mg/l; 0.25 mg/l CN^-

Table 3.1.Optimum measurement parameters

Working electrode	DME
Stirrer speed (rpm)	2000
Initial purge time (sec)	300
Pulse amplitude (mV)	50
Start potential (mV)	- 100
End potential (mV)	- 500
Sweep rate (mV/sec)	8.8

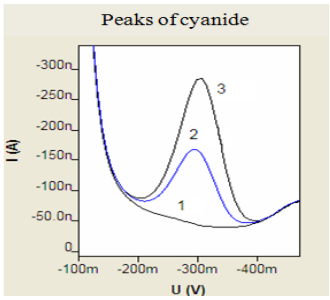

Figure 3.1.The differential pulse polarograms

(1): Containing borax buffer (pH=10.2)
(2),(3):Containing borax buffer (pH=10.2) and 0.125; 0.25mg/l CN^-

3.1.2. Measurement parameters

The sweep rate, initial purge time of N_2 for releasing O_2, pulse amplitude, start potential, end potential,stirrer speed, were changed to pick out optimum parameters after each recorded polarograms.Optimum measurement parameters were selected when they correspond with proportional polarograms, high peak current and good repeatability of measurements. The results of analysis were showed in the table 3.1.

3.2. Investigated results of effects

3.2.1. Effect of distillation time of samples

Samples containing cyanide were distillated at 90^0C for 15, 30, 60, 90, 120 minutes, respectively.The differential pulse polarograms were recorded for adsorption solution containing cyanide with optimum parameters in the table 3.1.90 minutes is chosen as optimum distillation time, because when distillation time was increased from 15 to 60 min, it was found that the peak height for CN^- was increased, but the peak height for CN^- was constant when distillation time was more than 60 minutes.

3.2.2. Effect of sunfide and sulphite concentration

Variation of the sunfide (S^{2-}) and sulphite (SO_3^{2-}) caused the peak height for CN^- to increase 8% with increasing sunfide and sulphite concentration when $[S^{2-}]/[CN^-]$ and $[SO_3^{2-}]/[CN^-]$ ratios were exceeded 5; 3, respectively. However, that ratios were smaller, peak heights were constant. According to some documents, the contents of S^{2-} and SO_3^{2-} in the shoot of the bamboo

and cassava are very low. In order to eliminate the the effects of $S^{2-}$and SO_3^{2-}, a $Pb(NO_3)_2$ solution in wet cotton was placed on the top of flask and around the joints while distilling samples.

3.3. Analysis of bamboo shoot and cassava

3.3.1. Analysis of bamboo shoot

Distillated solution (1.0 ml) of CN^- was diluted to 50.0 ml with 0.01M KOH in volumetric flasks. A mixture of diluted solution and 10.0ml borax solution (pH =10.2) was poured into cell. Typical polarograms of cyanide were recorded with operating parameters in table 3.1. The concentrations of CN^- were determined by standard addition (2 times). The results of analysis were showed in the figure 3.2 and table 3.2

Table 3.2.Concentrations of CN^- in the bamboo shoot

Bamboo shoot	C_{CN^-} (mg/l)	C_{CN^-} (mg/g)
The foot of fresh bamboo shoot	10.016	0.045
The middle of fresh bamboo shoot	20.822	0.056
The top of fresh bamboo shoot	28.270	0.075
Salted bamboo shoot	0.120	0.00045
Dried bamboo shoot	0.20	0.00094

As shown in table 3.2, the highest CN^- content in the top of fresh bamboo shoot was 0.075mg/g, whereas lowest CN^- content in salted bamboo shoot was 0.00045 mg/g. So we recommend users should not eat fresh unprocessed bamboo shoot.

3.3.2. Concentrations of CN^- in cassava samples

Distillated solution (5.0 ml) of CN^- was diluted to 10.0 ml with 0.01M KOH in volumetric flasks. A mixture of diluted solution and 10.0ml borax solution (pH =10.2) was poured into cell. Typical polarograms of cyanide were recorded with operating parameters in table 3.1. The concentrations of CN^- were determined by standard addition (2 times).The results of analysis were showed in the figure 3.3 and table 3.3.

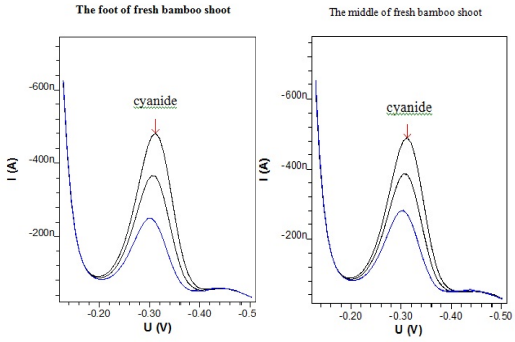

*Figure 3.2.*The differential pulse polarograms of CN- in the bamboo shoot

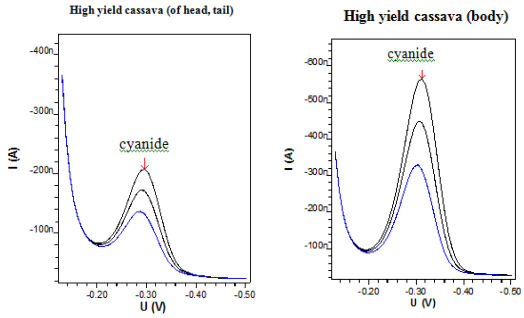

Figure 3.3. The differential pulse polarograms of CN- in the cassava

Table 3.3.Concentrations of CN^- in the cassava

Cassava samples	C_{CN^-} (mg/l)	C_{CN^-} (mg/g)
High yield cassava (body)	0,2277	0,6072
High yield cassava (of head, tail)	0,6713	1,7902
Fresh normal cassava	0.215	0.5730
Dried normal cassava	0.105	0.2670
Boiled normal cassava	0.000	Undetectable

As shown in table 3.3, the highest CN^- content in the yield cassava (of head, tail) was 1,7902 mg/g , whereas the lowest CN^- content in boiled normal cassava was undetectable.So we recommend users should not eat high yield cassava and not boiled normal cassava.

3.4. Linear range, detection limit, reproducibility and precision

The linear range of cyanide determination was evaluated at the parameters in table 3.1. The peak current increased linearly with cyanide concentration over the range 0.05 -30.0 mg/l. The limit of detection and limit of quantification (3σ) of 0.017mg/l; 0.057mg/l cyanide were obtained, respectively. Repeated polarograms show that relative standard deviation for 0.5mg/l cyanide was 3%. Two artificial samples with 0.067 and 0.25mg/l CN^- were analyzed according to the above method. The analytical results of two artificial samples were 0.064; 0.248 mg/l, respectively. The difference of results in all samples not exceeding 5% is acceptable.

4. CONCLUSION

An optimal, simple procedure for differential pulse polarography analysis of cyanide was researched. That procedure was applied to determine cyanide contents in the cassava and bamboo shoot samples. Some recommendations were given to the user of these products. High accuracy of the analysis was evaluated by repeatability (RSD = 3%) and result of concentration of cyanide in the artificial samples. High sensitivity of the method was described by the limit of detection (LOD = 0.017mg/l).

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