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Determination Of Cyanide In Peruvian Cassava By Chemical Technique

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The concentration of free cyanide in Peruvian Cassava was determined by volumetric titration techniques, steam distillation and using a cyanide ion selective electrode. This was done in order to investigate whether the Peruvian Cassava studied was a sweet or bitter variety. The bitter variety is not commonly edible, but is used as a source of cyanide for use in artisanal mining.

Index Terms— Cyanide, Distillation, Peruvian Cassava, Selective Electrode, Titration.

I. INTRODUCTION

AGM (Artisanal Gold Mining) refers to miners who use rudimentary techniques for the process of mining gold minerals, regardless of the size of the operation. Mercury has commonly been used to extract gold by forming an amalgam of it, which is extremely toxic to both humans and the environment [1]. Therefore, other lixiviants that are more friendly to nature are being evaluated. One of them is free cyanide from plants such as cassava, which is produced thanks to the fact that they have cyanogenic glycosides that when hydrolyzed give a HCN product. That is why it is relevant to find in our country, Peru, the way to cultivate this variety of cassava, with the aim of benefiting artisanal mining and reducing environmental pollution [2].

II. PROCEDURE

A. Extraction, storage and treatment of cassava leaf, peel and pulp extract

To extract cyanide from cassava pulp, all cassava intended for extraction is first weighed. Then, the cassava is peeled, removing the shell, then it is passed through the extractor. In this case, the bagasse was passed through the extractor twice to recover all the liquid, obtaining 3,500 mL. Then, it is stored in labeled glass containers; likewise, 10 mL of NaOH at a concentration of 10M is added to stabilize the pH. With respect to the cassava peel, it

is weighed, then it is passed through the extractor, because it has a fairly dense consistency, 200 mL of water is added, obtaining a volume of 520 mL. It is also stored in a glass container, adding 5 mL of NaOH at a concentration of 10M. The cassava leaves are also weighed and passed through the extractor. Additionally, these leaves are squeezed with a cloth to obtain more liquid. In the extractor, they are mixed with 500 mL of water to obtain a more liquid texture, obtaining a volume of 750 mL. Likewise, 5 mL of 10M NaOH is added and the mixture is stored.

These volumes extracted and diluted with water, are referred to as extracts, containing the concentrate of each material.

Table 1. Weight of samples

Sample	Weight (grams)
Leaf	273.7
Pulp	1329
Peal	5314.72

B. Determination of Cyanide by Titration

Analysis of the liquid extracted from the pulp and Rhodamine as an indicator.
The burette is filled to the mark with the previously standardized $AgNO_3$ solution. In an Erlenmeyer flask, 25 mL of the Cassava sample is placed and titrated, subsequently adding 5 drops of rhodamine as an indicator, which produces an intense yellow color. Next, the flask is placed on a magnetic stirrer and the titration is started with the $AgNO_3$ solution from the burette, stirring constantly until a color change to pink is seen, which indicates the end point of the free cyanide determination. The volume of $AgNO_3$ used is noted to be able to determine the cyanide concentration in the sample. The same procedure is repeated in triplicate to obtain more precise results [3].

C. Determination of Cyanide by Distillation

First, the standard sample of Manipueira (Cassava liquid extract) was prepared; then, 10 mL of the sodium hydroxide solution (1M), prepared previously, was added to the distillation flask and distilled water was added until the tube was covered at the 50 mL mark; this hydroxide solution should have a relatively high pH (pH = 12.8) to avoid the formation of hydrocyanic acid in the recovery [4].

Fig. 1. Laboratory mounted distiller.

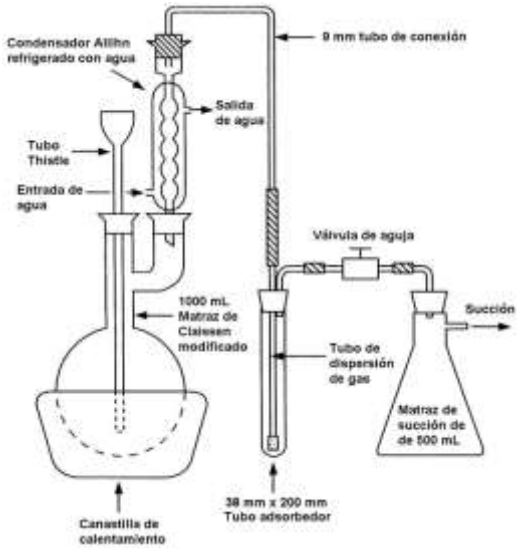

Fig. 2. Cyanide distillation apparatus.

D. Cyanide Determination with the Electrode (EIS)

With an electrode previously calibrated with 5 concentrations of CN^- (10, 20, 50 and 100) the slope of the calibration curve was found, which was in the range of 57+3 mV [5]. This relationship complies with the Nernst equation:

(1)

$$E = E_a + 2.3\frac{RT}{nF}\log(A_{ion}) \qquad (1)$$

Fig. 3. Mounting the cyanide electrode

III. RESULTS AND DISCUSSIONS

1) Obtaining results by degree

The data in the table 1 reflect the concentration of CN present in the cassava pulp sample without previous dilutions. The experiment was carried out in triplicate to obtain more accurate and reliable results, but in the case of the second sample, where a value far from the concentration is observed, this may be due to problems in the measurement or the oxidation of $AgNO_3$ so it loses sensitivity.

Table 2. Concentration of cyanide in cassava pulp by titration.

Sample	Concentration (mg/L)	Concentration (mg/kg)
1	144.44	105.17
2	115.55	84.14
3	144.44	105.17

2) Obtaining the following results by distillation

First, a standard sample of known inorganic cyanide was prepared to determine the parameters that influence recovery, such as time, sulfuric acid concentration, and temperature.

10 mL of the sodium hydroxide solution (1M), prepared previously, was added to the distillation flask and distilled water was added until the tube was covered at the 50 mL mark; this hydroxide solution must have a relatively high pH (pH = 12.8) to avoid the formation of hydrocyanic acid in the recovery. Sulfuric acid was prepared at two different concentrations (10% and 15%) which will serve to increase the efficiency of the distiller.

Using a water bath, it was regulated to the desired distillation temperature. In the experiments that were done, a heating range of 30 to 35 °C was used because it does not require high temperatures. The water tap is opened to supply the condenser inlet and outlet and the pump is turned on to generate air suction.

When the desired temperature is reached, add the problem solution and wait for it to reach thermal stability. Add the sulfuric acid (15 mL) and allow the solution to distill at different times.

Finally, turn off the heating equipment, suction motor and condenser, wait for the equipment to stabilize.

Measure the volume of the distillate and the solution that was distilled. Their volumes should also be noted. Each distillate is titrated to know the concentration recovered [6, 7].

Table 3. Results of the first experiment with 10% sulfuric acid.

Test	Original concentration (mg/L)	Time (min)	Concentration (mg/L)	%Recovery
1	190	10	135.30	71.21%
2	190	15	136.34	71.76%
3	190	20	139.47	73.40%
4	190	30	183.14	95.86%

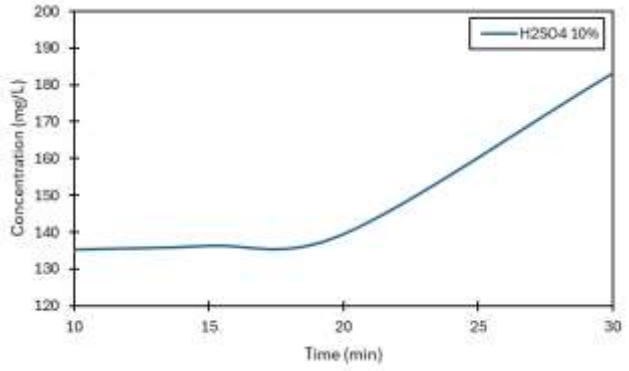

Fig. 4. Distillation curve at 10% vs time (min)

Table 4. Results of the second experiment with 15% sulfuric acid.

Test	Original concentration (mg/L)	Time (min)	Concentration (mg/L)	%Recovery
1	190	10	153.00	80.53%
2	190	15	161.32	84.91%
3	190	20	171.73	90.39%
4	190	30	181.10	95.32%
5	190	40	179.02	94.22%

6	190	60	183.18	96.41%

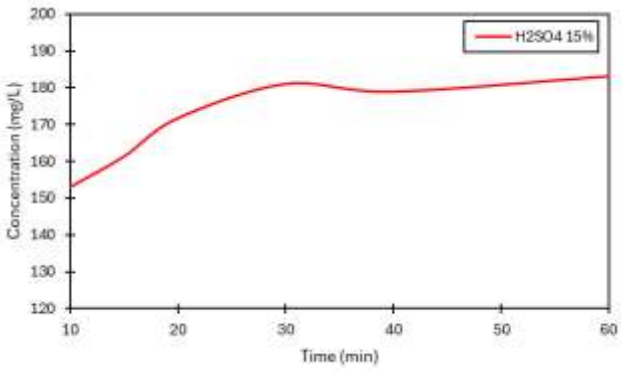

Fig. 5. Distillation curve at 15% vs time (min)

Table 4 presents the results of the second experiment, in which a concentration of 15% sulfuric acid was used. The data reveal a significant recovery rate. As shown in Figure 5, after 10 minutes, the recovery rate surpasses that obtained with a 10% sulfuric acid concentration. At 30 minutes of distillation, an efficiency of 95.32% is achieved, comparable to that obtained with 10% sulfuric acid. This indicates that increasing the sulfuric acid concentration not only improves recovery efficiency but also significantly reduces the time required to obtain a high-purity distillate. Therefore, a higher percentage of sulfuric acid is preferable for the distillation process of bitter cassava [8].

3) Distillation of cassava leaf, peel and pulp

Following the same methodology, before distilling each sample, it is titrated with $AgNO_3$ 0.01M to have a reference of the cyanide content in each one and compare the recovery obtained, with a distillation time of 30 min. In order to correctly observe the color change of each sample when titration, 50 mL of each extract sample will be dissolved by adding 50 mL of distilled water to a volumetric flask, thus obtaining 50 mL for distillation and 50 mL for titration.

Table 5. Results of the distillation of 50 mL samples of cassava leaf, peel and pulp diluted with 50 mL of water.

Test	Extract concentration to the holder (mg/L)	Concentration (mg/L)	Recovery
Leaf	26.02	20.82	80.00%
Pulp	108.24	98.88	91.35%
Peal	66.61	62.45	93.75%

Table 6. Cyanide concentration in cassava pulp, leaf and peal by distillation.

Sample	Concentration (mg/kg)

Leaf	114.08
Pulp	104.18
Peal	48.87

4) Obtaining results with the Cyanide Electrode

By carrying out measurements with the electrode system (EIS and reference) and using a potentiostat, the following was found:

Table 7. Cyanide concentration results with electrode.

Sample	Extract concentration (mg/L)	Concentration (mg/L)	Concentration (mg/kg)
Leaf	41.721	125.16	114.32
Pulp	203.594	203.59	107.26
Peal	112.506	182.82	44.02

CONCLUSIONS

Electrode calibration is an essential process in electrochemical measurement techniques, as it ensures the accuracy and reliability of voltage readings. The slope value calculated during calibration confirms that we are working within the appropriate range, which is vital for obtaining accurate measurements. Proper calibration helps reduce errors and increase the reproducibility of results, thus ensuring that measurements correctly represent the concentrations of the substances analyzed in the samples [5 and 9].

The analysis of bitter cassava samples using the technique used has proven to be effective for the determination of cyanide. This process is of great importance, as it allows for the precise quantification of cyanide concentrations in different parts of the sample.

To perform the titration of the cassava pulp, previously standardized $AgNO_3$ of 0.01 M concentration was used. Initially, NaCN titrations were performed to select the most suitable indicator, looking for one with high sensitivity and the ability to clearly identify the equivalence point. During the titration of cassava pulp, a pretreatment was performed to extract the liquid from the pulp. In addition, 1 mL of NaOH was added to stabilize the pH in an alkaline medium of pH 12 [3].

The pulp extract had a milky white color, which interfered with the effect of rhodamine as an indicator. Therefore, it was decided to make dilutions of the extract to improve the visibility of the color change during the titration. This procedure ensured greater precision in determining the cyanide concentration in cassava pulp. The titration was performed in triplicate for each concentration, guaranteeing the reliability of the results. The validation of the cyanide ion electrode showed a slope of -57.256 mV, within the acceptable range indicated in the manual (57 + 3 mV), confirming that the electrode is working correctly for the detection of cyanide. In addition to the slope, the electrode was calibrated according to the instructions in the manual with different concentration points, ensuring the accuracy and reliability of the measurements since the slope is still within the range [9]. It is concluded that the equipment is ready to proceed with the analysis of cyanide in the leaves, peels and pulp of cassava, guaranteeing optimal conditions to obtain accurate and reproducible data.

For the distillation process, after evaluating the parameters and selecting the appropriate concentration of H_2SO_4, the NaOH used must also have a pH between 12 and 13 to maintain the necessary alkaline medium. The distillation process takes approximately 30 minutes. Once completed, the liquid is removed from the cylinder and the titration is carried out to determine the concentration of CN. The results obtained indicated the presence of cyanide in the leaves, pulp and peal, with concentrations of 114.08 mg of CN/kg, 104.18 mg of CN/kg and 48.87 mg of CN/kg, respectively. This analysis shows that all parts of cassava contain cyanide, with the leaves having the highest concentration.

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