#### **RESEARCH ARTICLE**

#### OPEN ACCESS

# Analysis of Phosphorus as an Impurity from The Use of Calcium Carbide as an Artificial Ripening Agent in Banana (*Musa acuminate*)

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#### Abstract

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In order to achieve early ripening of fruits, chemicals and ripening agents are used by retailers and farmers. Artificial fruit ripening is illegal but also practiced regularly and most of them are banned. These agents or chemicals create health problems. These chemicals exhibit several adverse effects on human health hence precaution or control should be put in place. The aim of this research was to identify the trace elements of calcium carbide present in the banana samples and determine the level of these trace elements present in the banana samples on both Ghanaian and Chinese market as well as ascertain its severity and toxicity content.

Using Vanado-molybdate method, the ash banana samples were boiled with 10mLof 5 g/mL HCl and the solution was then washed into a 100 mL volumetric flask using water, and then filtered. The solution was then neutralized by drop wise addition of 0.88 g/mL ammonia (the volume at this stage was 55 mL) and then a standard solution was prepared. This was done by just adding the HCl to the dilute nitric acid, then 25ml of the Vanado-molybdate reagent was added and diluted to the mark.

The optical density was then measured. Phosphorus was present in all the six samples. There was a significant difference in the amount of phosphorus present in the banana samples from both the Ghanaian market and Chinese Market. From the experiment conducted, if a person is to consume 100g of banana (powdered) from Ghana, he/she will be taking in as much as 2020.66mg of phosphorus, a figure almost three times the highest tolerable amount in humans per day. If this same person is to consume 100g of banana (powdered) from China, he/she will be taking in as much as 2001.66mg of phosphorus, another figure almost three times the highest tolerable amount in humans per day. **Keywords**: calcium carbide, ethephon, banana, pesticides, artificial ripening, phosphorus.

#### **INTRODUCTION**

The effect of artificial ripening has become questionable because of various health related issues. There are direct and indirect health hazards associated with artificial ripening agents and their impurities which require qualitative and quantitative analysis of chemical toxicity and their impact on fruit quality. To understand the possible health hazards, it is important to analyze chemicals present within artificiallyripened fruits, and to analyze any change in food value.

Nowadays, several artificial ripeners are available and are used. Examples include calcium carbide, acetylene gas, carbon monoxide, potassium sulfate, ethephon, potassium dihydrogen arthophosphate, putrisein, oxytocin and photoporphyrinogen. They are used during pre-harvest, post-harvest, transportation, capping and storage (1, 2). However there are about fifteen artificial ripeners. They accelerate fruits ripening and induce color changes. Although the market quality of such artificially ripened fruits are found to improve. Less is thought about its adverse effects on humans and its toxicity profile. Artificial ripening agents are used in parts of Africa including Ghana and parts of Asia including China as well as all over the world (3-5).

Artificial ripeners have several effects on humans including memory loss, cerebral edema, colonic, prostates and lung cancer, quick-buck syndrome, DNA, RNA and hematological changes. Artificially ripened fruits lead to quick production of bacteria, fungus and viruses which can cause diarrhea, peptic ulcer and other disease. No steps have been taken so far to keep a check on it as farmers in Ghana and China continuously used these ripening agents (5-8).

Calcium carbide  $(CaC_2)$  is a chemical compound used in the production of acetylene and calcium cyanamide(9, 10).

Acetylene is believed to affect the nervous system by reducing oxygen supply to the brain. The pure  $CaC_2$  is colorless but technical-grade  $CaC_2$  are grey or brown and consist only 80-85% of  $CaC_2$  (the rest is CaO (calcium oxide). It is used in carbide lamps. However, carbide lamps are still used extensively in slate, copper and tin mines. It is still used for mining in some countries. Carbide lamps were also used as headlights in early automobiles, motorcycles and bicycles. In the ripening process of fruit,  $CaC_2$  is sometimes used as source of acetylene gas(11-13).

 $CaC_2$  is also used for ripening of fruit. It reacts with water to produce acetylene, which acts as an artificial ripening agent.  $CaC_2$  may contain traces of arsenic and phosphorus which is the major concerned to human health. A deadly chemical, calcium carbide is used widely across the country to artificially ripen fruit. This is risky to the health of consumers. Some fruits such as Mangos, Bananas, Papayas and Cashew are found to have been treated with calcium carbide. This hazardous and carcinogenic chemical creates short-term and long-term health problems. Early symptoms of arsenic or phosphorus exposure include diarrhea, thirst and irritation in the eyes, mouth, nose and throat. Chronic exposure to the chemical could lead to peptic ulcers(14, 15).

Calcium carbide has carcinogenic and neurological disorders properties. It can result in tingling sensation, numbness and peripheral neuropathy. If pregnant women consume fruit ripened with carbide, the children born could develop abnormalities(16, 17). The use of calcium carbide is not only toxic to consumers, but it is also harmful to those who handle it. It affects the neurological system, resulting in headache, dizziness, mood disturbances, sleepiness, mental confusion and seizures on a short-term basis, while in the long-term it can cause memory loss and cerebral edema. CaC2 decreased hemoglobin (Hb), Red blood cell, White blood cell and some blood indices. They also alter DNA, RNA and protein constituents in humans. A study revealed that calcium carbide alters blood indices in exposed rabbit as compared to control (18-21). The reaction of calcium carbide with water, producing acetylene and calcium hydroxide, was discovered by Friedrich Wöhler in 1862(22).

 $CaC_2 + 2 H_2O \rightarrow C_2H_2 + Ca(OH)_2$ 

This reaction was the basis of the industrial manufacture of acetylene and is the major industrial use of calcium carbide. Acetylene is mainly manufactured by the partial combustion of methane or appears as a side product in the ethylene stream from cracking of hydrocarbons. Calcium carbide reacts with nitrogen at high temperature to form calcium cyanamide:

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

Carbide lamps are still used for mining in some fewer wealthy countries, for example in the silver mines near Potosí, Bolivia. Carbide lamps are also still used by some cavers exploring caves and other underground areas, although they are increasingly being replaced in this use by LED lights. Carbide lamps were also used extensively as headlights in early automobiles, motorcycles and bicycles, but have been replaced entirely by electric lamps (23, 24).

Table 1. Nutritional value per 100 g of banana powder (3.5oz) (25)

Energy	371kj
Carbohydrates	22.84g
Sugars	12.23g
Dietary fiber	2.6g
Fat	0.33g
Protein	1.09g
Thiamine (B1)	0.031mg
Riboflavin (B2)	0.073mg
Niacin (B3)	0.665mg
Pantothenic acid (B5)	0.334mg
Vitamin (B6)	0.4mg
Folate (B9)	20µg
Choline	9.8mg
Vitamin C	8.7mg
Iron	0.26mg
Magnesium	27mg
Manganese	0.27mg
Phosphorus (element of interest)	22mg
Potassium	358mg
Sodium	1mg
Zinc	0.15mg
Fluoride	2.2µg

Phosphorus is an essential macro mineral, meaning to be healthy you must include this nutrient in your diet. Dietary sources include almost all foods. Phosphorus is the second most abundant mineral nutrient in the body, after calcium. This mineral is part of all cells, especially cell membranes, and is essential to bone strength, because it's the main structural component of bones and teeth, as calcium phosphate(26). Phosphorus is also an important element in energy production. . Your main energy-storage molecule, adenosine triphosphate (ATP) contains phosphorus. Helps synthesize protein and is part of phospholipids (fat molecules), such as lecithin, which cells use to make membranes. Almost all foods contain phosphorus, but the amounts of phosphorus are greater in animal products and high-protein foods like meats, fowl, fish, eggs, and dairy. Nuts, seeds, and many vegetables are rich in phosphorus as well. Phosphorus is a required mineral. Adults need a maximum of 750 mg daily. Sodas and other drinks containing phosphoric acid may cause excessive amounts of phosphorus intake, which can interfere with proper calcium metabolism. The optimum calcium to phosphorus ratio is approximately 1:1, but in the average American diet, that ratio commonly varies between 1:2 and 1:4. Phosphorus deficiency and toxicity are not very predominant; excesses of phosphorus may alter calcium balance, and phosphorus deficiency may lead to energy and metabolic problems(26).

The fast ripening of fruits means they may contain various harmful properties. A commonly used agent in the ripening process is calcium carbide, a material most commonly used for welding purposes. Calcium carbide treatment of food is extremely hazardous because it contains traces of heavy metal arsenic and phosphorous. The calcium carbide produces acetylene gas when react with water. Acetylene gas may affect the neurological system by inducing prolonged hypoxia. Calcium carbide causes various health hazards like, headache, dizziness, mood disturbances, sleepiness, mental confusion, memory loss, cerebral edema and seizures. These results indicate that fruit treatment with calcium salts not only affects the ripening process but also influences the aroma of the fruits. The commonly used ripening agents other than calcium carbide are acetylene, ethylene, propylene, ethrel (2chloroethyl phosphonic acid), glycol, ethanol and some other agents. The calcium carbide is one of the most commonly used ripening agent for fruits while other calcium salts like calcium ammonium nitrate, calcium chloride and calcium sulphate are used to delay fruit ripening agents for local fruit industries.

The aim of this research was to identify the trace elements of calcium carbide present in the banana fruit of *Musa acuminate* from Ghana and China and determine the level of these trace elements present in the banana samples on both Ghanaian and Chinese market as well as ascertain its severity and toxicity content.

#### MATERIALS AND METHODS

#### Materials

Banana (*Musa acuminate*) was obtained from Chinese market in Nanjing and Ghanaian Market in Accra. Calcium carbide was obtained from Aladdin Industrial Corporation, Shanghai (China). Ammonium molybdate was supplied by Muby Chemicals (Gujarat India). Ammonium vanadate was obtained from Jay Dinesh Chemicals (Gujarat, India). All other chemicals used in the study were of analytical grade.

#### Methods

A survey was done at the Madina (Ghana) and Nanjing (China) market. The survey was conducted to know the time **DRY ASHING (SAMPLE PREPARATION)** 

3g of the dried, ground banana samples were placed in a porcelain crucible. This was then placed in a cool muffle furnace and ash at 500<sup>o</sup>C overnight. The ash obtained was the cooled and dissolved in 5 Ml of 20 % HCl, warming the solution to dissolve the residue. The solution was the filtered through an acid washed filter paper into a 50 mL volumetric flask. The filter paper was then washed and the solution was diluted to volume with deionized water and mix well(27).

#### **DETERMINATION OF PHOSPHATE Preparation of Standard Graph**

To a series of 100ml volumetric flasks 0, 2, 4 and 8 mL of the standard phosphate solution (equivalent to 0-10 mg pentaphosphate) was put in the volumetric flask and each was diluted with water to the 50 mL mark. Few drops of ammonia solution (0.88) was then added and few drops of nitric acid was then added in the 1:2. 25 mL of vanadate- molybdate reagent

the banana (*Musa acuminate*) were obtained from the various farms and the time interval it is takes to ripen and made available for human consumption. The survey involved five market women from both countries and the observation made was recorded.

#### **Sample preparation**

Two fingers each of ripened and unripened banana were obtained from these five market women. The unripened banana were then kept at room temperature to ripe. The already ripened banana was then sliced and kept in an oven at a temperature of  $65^{\circ}$ C for 7 days. The sample was placed on an aluminium foil spread on a tray. The unripened banana which was allowed to ripen was then sliced, placed on an aluminium foil and spread on a tray then kept in an oven for 7 days at a temperature of  $65^{\circ}$ C. The dried samples were then collected and grounded to powder and made ready for analysis.

Calcium carbide was obtained from the market. New set of unripened banana were obtained from the market women. The calcium carbide was reacted with water to produce acetylene gas which caused the ripening the banana. This reaction was done under a hood and a nose mask was used worn as the gas produced is toxic. The now ripened samples were then sliced and placed on an aluminium foil spread on a tray, kept in an oven at a temperature of  $65^{\circ}$ C for 7 days. The dried samples were then collected and grounded to powder using a mortar and pestle and made ready for analyse.

was then added and diluted to the mark with water and swirled. The solution was then allowed to stand for 10 minutes and the optical density was measured in a 2.5 cm cell at a wavelength of 480 nm(28).

#### **Preparation of test samples**

Using the vanado-molybdate method, the ashed banana samples were boiled with 10ml of 5N HCl and the solution was then washed into 100 mL volumetric flask using water, and then filtered. The solution was then neutralized by drop wise addition of 0.88 ammonia (the volume at this stage was 55 mL) and then a standard solution was prepared which is stated above. This was done by just adding the HCl to the dilute nitric acid, then 25 mL of the vanado-molybdate reagent was added and diluted to the mark. The optical density was then measured after allowing the solution to stand for 10mins (29).

#### RESULTS



FIG 1. A. Banana (China sample) reacted with carbide and allowed to ripen then kept at in an oven for 7 days at 65°C Grounded and ready to be sieved, B. Banana (China sample) after being kept in an oven for 7 days at 65°C, C. Dried Banana (Ghana sample) kept on an aluminium foil at 65°C. Ready to be grounded, D. Banana (Ghana sample) reacted with carbide and allowed to ripen then kept in an oven for 7days at  $65^{\circ}$ C, grounded and ready to be sieved, E. Banana (China sample) and Banana (Ghana sample) grounded and ready to be sieved, F. Banana (Ghana sample) after being kept in an oven for 7 days at  $65^{\circ}$ C

# STATISTICAL ANALYSIS OF THE AMOUNT OF PHOSPHORUS PRESENT IN THE THREE DIFFERENT BANANA SAMPLES (Naturally ripened served as the control).



#### One way ANOVA followed by a Dunnett's Multiple Comparison test

P<0.001. (There was a significant difference in the amount of phosphorus present in the control (The natural banana sample) and the two test samples.

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#### DISCUSSION

From the results obtained, several inference can be made. From literature or collected works, the amount of phosphorus present in 100 g of banana powder is 22 mg(30). As a result, 3g of banana sample that was weighed in the laboratory is expected to contain 0.66mg of phosphorus. From the study, 3g of banana sample weighed in the laboratory contains a phosphorus range of (53.24-68) mg. The already ripened banana contained 54.76mg of phosphorus, the banana ripened with carbide contained 62.05mg of phosphorus and the unripened banana left to ripen contained 69.99mg of phosphorus. The Naturally ripened banana was used as the control. If 100g of the banana sample was weighed, it is will contain 2020.66mg of phosphorus. This was in relation to the Banana collected from Ghana. Considering the Chinese Banana sample, from collected works, Amount of phosphorus in 100g of the banana sample is 34mg(30). As such 3g of banana weighed in the laboratory for the experiment is expected to contain 1.02mg of phosphorus. From the study, just 3g of banana sample weighed contains a phosphorus range of (49.78-70.32). The banana ripened with carbide contained

70.32 mg of phosphorus, the banana bought unripened and left to ripen contained 49.78 mg of phosphorus and the already ripened banana contained 64mg of phosphorus. Hence 100g of the banana sample will contain 2001.66 mg. The naturally ripened banana was used as a control. From the analysis performed using the One way ANOVA followed by a Dunnett's Multiple Comparison test, there was a significant difference between the control sample and the two test samples for the banana, and a p-value which shows the level of significance was obtained as P<0.001. The smaller the pvalue, the more significant the comparison is. This can be observed in fig 8 and 9 for the Chinese sample and Ghanaian respectively. Now, it can be inferred from the amount of phosphorus present in the naturally ripened banana sample that it was chemically treated on the market or in the farms. 3 g of the powdered samples of the banana used in the experiment contained an amount of phosphorus higher than what is expected to be present in 100 g of the banana powder from literature, which is very alarming and dangerous. It must also be noted aside the use of calcium carbide which produces phosphorus an impurity, farmers use fertilizers. These

fertilizers contain nitrogen, phosphorus and potassium and the phosphorus present can add up to the high level of phosphorus seen in the samples. For an adult, the predominant adverse reaction to orally administered phosphorus (as various phosphate salts) in human supplementation studies is osmotic diarrhea, which has been reported at intakes of 750 mg/day and above. From the experiment conducted, if a person is to consume 100g of banana (powdered) from Ghana, he/she will be taking in as much as 2020.66mg of phosphorus, a figure almost three times the highest tolerable amount in humans per day. If this same person is to consume 100g of banana (powdered) from China, he/she will be taking in as much as 2001.66mg of phosphorus, another figure almost three times the highest tolerable amount in humans per day.

#### **CONCLUSION AND FUTURE PERSPECTIVES**

Phosphorus was present in all the six samples. The amount of phosphorus varied with respect to each sample. Averagely there was phosphorus present in the banana samples obtained in Ghana than the banana samples obtained in China. There was a significant difference in the amount of phosphorus present in the Chinese and Ghanaian samples. Banana on the market can pose health risk to people who consume it both in China and Ghana.

Further studies should be done to know the arsenic content present in banana on the market. Further studies should be done to ascertain the nutritional values after ripening with calcium carbide. The nutritional values should be compared to a standard to know if they are in their right proportions. Routine checks should also be done on the various farms by the Food and Drugs Authority and the fruits produced should be checked for the presence of toxic chemicals. Farmers should be informed about these findings thus the toxic effects of calcium carbide.

**Conflict of Interest:** The authors declare no conflict of interest.

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#### Abbreviations Used: None

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SUPPLEMENTARY FIGURES AND TABLES



Fig. 1. Banana (China sample) after being kept in an oven for 7 days at  $65^{0}$ C



Fig. 2. Banana (Ghana sample) after being kept in an oven for 7 days at  $65^{0}$ C



Fig. 3. Banana (China sample) and Banana (Ghana sample) grounded and ready to be sieved.



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Fig. 4. Banana (China sample) reacted with carbide and allowed to ripen then kept at in an oven for 7 days at  $65^{\circ}$ C. Grounded and ready to be sieved.



Fig. 5. Banana (Ghana sample) reacted with carbide and allowed to ripen then kept in an oven for 7days at  $65^{\circ}$ C, grounded and ready to be sieved.



6. Dried Banana (Ghana sample) kept on an aluminium foil at 65°C. Ready to be grounded



Fig. 7. Dried Banana (China sample) on an aluminium foil ready to be grounded.

Material	absorbance	absorbance	absorbance	AVERAGE	WEIGHT	AMOUNT	AMOUNT
					IN MG	OF	OF P(mg)
						P2O5(%)	
Banana ripened (market	0.057	0.059	0.06	0.059	3.0104	0.2509	54.76
sample). (Ghana)							
Banana unripened (market	0.077	0.075	0.079	0.077	3.0734	0.32079	69.99
sample). (Ghana)							
Banana ripened with	0.068	0.066	0.068	0.067	3.0169	0.2844	62.05
calcium carbide. (Ghana)							
Banana ripened (market	0.068	0.069	0.069	0.069	3.0157	0.293	64
sample). (China)							
Banana unripened (market	0.055	0.053	0.053	0.054	3.0311	0.228	49.78
sample). (China)							
Banana ripened with	0.082	0.077	0.079	0.079	3.1388	0.322	70.32
calcium carbide. (China)							

### Table 3. SHOWING THE ABSORBANCE OBTAINED FOR THE VARIOUS SAMPLES

Material	absorbance	absorbance	absorbance	AVERAGE
Banana ripened (market sample).	0.057	0.059	0.06	0.059
(Ghana)				
Banana unripened (market sample)	0.077	0.075	0.079	0.077
naturally ripened. (Ghana)				
Banana ripened with calcium carbide.	0.068	0.066	0.068	0.067
(Ghana)				
Banana ripened (market sample).	0.068	0.069	0.069	0.069
(China)				
Banana unripened (market sample)	0.055	0.053	0.053	0.054
naturally ripened. (China)				
Banana ripened with calcium carbide.	0.082	0.077	0.079	0.079
(China)				

### Table 4. INDICATING THE AMOUNT OF PHOSPHORUS PRESENT IN THE SAMPLES.

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