



Comparative study to evaluate the effect of calcium carbide (CaC_2) as an artificial ripening agent on shelf life, physio-chemical properties, iron containment and quality of *prunus persica l. Batsch*

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Abstract:

The synthetic ripening of fruits harmfully affects the quality of fruit. In order to recognize the effects of calcium carbide (CaC_2) as an artificial ripening agent (ARA) on shelf life and health, related physical properties of peach fruit were evaluated. As revealed by the present research work, artificial ripped fruits (ARF's) have less aroma, are less attractive, less weight per fruit, mild pleasant taste than natural ripped fruits (NRF's), a less shelf life, total solids, un-dissolved solids, approximate equal value of dissolved solids and 0.64% less moisture. Total metal containment in ARF's was found to be 0.0183 to 0.0442 mmol/g whereas in NRF's it was found to be 0.0181 to 0.0493mmol/g. Qualitative analysis (based on K_{sp} values) of both types of fruits reveals the presence of copper, iron, chromium, zinc, calcium, magnesium, and manganese while aluminium was only detected in NRF's. By spectroscopy (UV-Visible), low amount of total iron analyzed in ARF's 7.6 ± 1.08 mg/100 g to 30.10 ± 1.34 mg/100g as compared to NRF's 10.63 ± 0.75 to 31.49 ± 0.79 mg/100g, Fe^{+2} were analyzed in ARF's in low concentration 1.87 ± 0.50 mg/100g to 24.24 ± 4.51 mg/100g as compared to NRF's 7.41 ± 0.30 to 25.84 ± 0.38 mg/100g, while Fe^{+3}

found to be high in ARF's 1.94±0.42 to 8.26±0.37mg/100 g than NRF's 1.43±0.2 to 4.08±0.52 mg/100g.

Key words: shelf life, Physio-chemical properties, spectroscopy, Iron, minerals

Introduction

Recently, the link between food intake and health has been proven important to a great extent in scientific exploration to identify the particular plant components that express health benefits (Carlos, Zavala, and Aguilar 2011). Throughout the last decades, the rising demand of food safety has inspired researchers about the risk related to the use of food contaminated by pesticides, heavy metals or toxins (D'Mello 2003). Fruits are the natural staple food of humans, contain considerable quantities of essential nutrients in a major proportion and prevent all diseases and keep a person energetic throughout his life (Zahir, Naqvi, and Uddin 2009). Fruit consumption decreases the risk of several diseases including atherosclerosis, heart and brain disorders, or different types of cancer (Block, Patterson, and Subar, 1992; Dauchet, and Dallongeville 2008). Quality of fruit includes nutritional properties (for example, vitamins, minerals, dietary fiber) and health benefits (for example, antioxidants) and these are attractive factors in consumer preferences (Lyne and Bassi 2008). Fruits and vegetables are wealthy sources of phytochemicals, which are known as potentially bioactive compounds (Carlos, Zavala, and Aguilar 2011). Research exposed that the health promoting factors of the fruits are due to the additive and synergistic combinations in a complex mixture of phytochemicals, a lot of them possessing strong antioxidant capacity including ascorbic acid, flavonoids, carotenoids, and others (Liu 2003).

Peaches are rich sources of carbohydrates, sugars (Fructose, Glucose, and Sucrose), vitamins (A, E, C, Thiamin, Riboflavin, Niacin, Pyridoxine, Folate), minerals (Fe, Ca, P, Mg, K, Na, Zn, Cu, Se), proteins, fats, Fiber (Hui et al. 2006).

Peaches have great antioxidant properties including chlorogenic acid and this fruit may be beneficial to the industry for health promotion for the consumers (Rossato et al. 2009). Mineral nutrition of plants is a complex process and plant uptake of minerals from the rhizosphere to all its parts (Miller, Pushnik, and Welkie, 1984). Mineral nutrition of plants is highly dependent on nutrients in the soil and the genetically determined characteristics of plant (Miller, Pushnik, and Welkie, 1984). The concentration levels of elements in plants and fruits are directly related to their interaction with all environmental, geological and biological systems (Braetter and Schramel 1980).

Ripening is a course of action in fruits that causes them to become edible and more delicious. The growth of fruit and ripening are unique to plants and corresponded to an important part of human and animal diets (Giovannoni 2004). All fruits have modes of ripening, different from one another. Fruit ripens when a change in composition occurs, the change is the conversion of starch into sugar. CaC₂ is used for ripening fruit artificially in various countries (Kader 2002). The use of CaC₂ as an artificial ripening agent for fruit ripening has been known for many years (Per et al. 2007). Ripening agents increase the rate of ripening procedure. In artificial ripening of fruits, CaC₂ is used as a source of acetylene (C₂H₂) gas which is an artificial ripening agent and similar to ethylene (C₂H₄) the natural ripening agent (Abeles and Gahagan 1986). CaC₂-laced fruits are unfit for human consumption and these can cause intoxication (Chace 1934). The fast ripened fruits contain harmful properties because CaC₂ contains traces of arsenic and phosphorous and the production of acetylene gas has a hazardous effect on humans - it may affect the neurological system by inducing prolonged hypoxia which causes headache, dizziness, mood disturbances, sleepiness, mental confusion, memory loss, cerebral edema and seizures (Per et al. 2007). CaC₂ is banned in many countries because it has carcinogenic properties and hazardous effects (Rahman, Chowdhury, and Alam 2008; Siddiqui and Dhua 2010). Mineral and antioxidant constituents are affected when fruits are picked up before maturation and complete ripeness. Mineral constituent and

antioxidant property of ARF's is lower than NRF's this is directly related to mineral oxidation process in fruit as oxidation of minerals are harmful for health and fruit quality. Fruits ripened with CaC₂ excessively soft and less tasty and have a shorter shelf-life. ARF's seem nice looking from outside while the fruit remains green and raw and unfit for health (Per et al. 2007; Siddiqui and Dhua 2010).

Iron is an essential micronutrient present in food, in both organic and inorganic (Fe⁺³/Fe⁺²) form, most important of them being heme. Iron is present in hemoglobin for the transportation of CO₂ and O₂ and also a component of various enzymes that are significant for energy production and necessary for appropriate immune system functioning (Carpenter and Mahoney 1992). Synthetic ripening affects the well absorbed form of iron. The majority of persons linked with fruit business are not well informed about the hazardous effect of CaC₂ application as an ARA; they even do not know that application of CaC₂ on fruits shortens their shelf life and minimizes the business related qualities of fruits.

The use of ARF's in industry for anti-oxidant extraction, supplements, and cosmetics products gives a poor yield. Having less quality, therefore for this purpose the use of NRF's is mandatory.

Material and Methods

Sample Collection: Samples of Peach fruit (*Prunus Persica* (L.) Batsch) were randomly selected and purchased from the open market. Two types were purchased - first one is naturally ripped (NRF's) while the other one is artificially ripped (ARF's).

Sample Labeling: Samples were prepared in different mediums and labeled according to medium as (Table 1).

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| Label | Medium | Type of sample | | |
|-------|--------------------------------|----------------|--------|-------|
| | | Digested | Soaked | |
| | | | 2 Hr. | 4 Hr. |
| X1 | - | - | - | - |
| X2 | Distilled Water | - | √ | - |
| X2' | Distilled Water | - | - | √ |
| X3 | HCl | - | √ | - |
| X3' | HCl | - | - | √ |
| X4 | HNO ₃ | - | √ | - |
| X4' | HNO ₃ | - | - | √ |
| X5 | H ₂ SO ₄ | - | √ | - |
| X5' | H ₂ SO ₄ | - | - | √ |
| X1D | Simple | √ | - | - |
| X3D | HCl | √ | - | - |
| X4D | HNO ₃ | √ | - | - |
| X5D | H ₂ SO ₄ | √ | - | - |

Table 1. Sample labeling for *Prunus Persica (L.) Batsch*

Pre-treatment of samples: The skin (body) of selective Fruits was washed gently with distilled water then cleaned properly with cotton cloth to remove dust, adhered particles and agricultural chemicals then stored in a cool and dry place.

Soaking of samples: Accurately weighed and cleaned, chopped fruit (chopped flesh form) were soaked in 60mL of distilled water, similarly 0.1M HCl, 0.1M H₂SO₄ and 0.1M HNO₃ were used for different time intervals (2 and 4 Hrs.) at room temperature 32±2 °C. After different time intervals the sample was filtered in a 100mL volumetric flask and then made up the volume with their respective solutions. These samples were labeled (Table 1) and stored in cool and dry place; these samples were used for different techniques such as Visible Spectrophotometry, and Complexometry.

Digestion of samples: On complete ignition of organic matter, metal oxides were obtained as ashes. In a neat and clean weight china dish, 5g fruit's flesh was taken and then 30mL of concentrated acid (HCl/H₂SO₄/HNO₃) was poured and then heated on a hot plate until complete dryness. This material was transferred in weighed crucible and heated in furnace first at 550 °C and then at 900 °C. This ash was transferred in 100mL flask and then made up with 0.1M respective acid (HCl/HNO₃/H₂SO₄).

Another ash was prepared just by heating weighed amount of fruit's flesh at hot plate (without adding any acid) at 550 °C and at 900 °C, this sample was given the name “Simple Ash” (Table 1).

Determination Methods

Total metal content by Na₂-EDTA titration: Total metal content of different soaked and digested samples of *Prunus Persica (L.) Batsch* were determined by a well-known volumetric method called complexometry. In this method sample solution (5mL soaked or 1mL digested sample) was titrated against Na₂-EDTA.H₂O at pH10 and Erichrome Black T was used as an indicator, the color change was green. Total metal content was determined after obtaining concordant reading. The same process was repeated with respective solvents and different time intervals i.e. 2 and 4 Hrs.

Determination of Total iron: The determination method for total iron (Fe⁺³, Fe⁺²) was 1,10-phenanthroline method. Only Fe⁺² ions could be analyzed at 509nm, there was no any interfering effect of making the exact determination of Fe⁺² in the complex environment of the fruit. Sodium acetate was used to adjust pH, and to convert ferric into ferrous hydroxylamine hydrochloride was used. For this purpose 10mL of sample + 2mL hydroxyl amine hydrochloride + saturated solution of sodium acetates to maintain pH 3.5 + 2mL of OPT was taken in 50mL volumetric flask and solution was made up with distilled water. The absorbance was measured at 509nm. Similarly blank solution was prepared except adding sample.

Care was taken to scan the sample under maximum 45min. Otherwise the coloration would be changed and leads to erroneous result.

Determination of Fe⁺³: When the determination of Fe⁺³ by complexation with KSCN was quantitatively applied, ferric ions present in the sample did not give red color of [Fe(SCN)₆]³⁻. Removal of ferric ions with ammonium hydroxide was done to form ferric hydroxide and then complexes with KSCN, results

in the formation of desired blood red complex. Here ferrous ions could be determined by using this method even in the presence of large quantities of interfering substances, but the complex was not very stable it was recommended that the absorption of this complex is recorded as soon as possible. For this purpose in the 20mL of sample solution (or 10mL digested sample) drop by drop ammonia solution was added to obtain ppt. These ppt. Were dissolved in dilute HCl (1:10) then transferred in 25mL volumetric flask + 2mL of KSCN and made up the solution with distilled water and then the observance of this red complex was recorded at 480 nm.

Results and Discussion

Soil type, the root stock used for fruit trees, mulching, irrigation, fertilization and other cultural practices influence the water and nutrient supply to the plants, that can affect the composition and quality attributes (appearance, texture, taste and aroma) of the harvested plant parts (Goldman, Kader, and Heintz 1999). When these studies were initiated, they were designed to assess the effect of CaC₂ on physio-chemical properties. Iron (Fe⁺²/Fe⁺³) containment, and antioxidant conclusion indirectly by Fe⁺² containment. The present work is focused on comparing between peach fruits ripped by different (natural and artificial) methods different types of fruit samples were analyzed in order to find differences.

Business based inquiry analysis

Available in an open market: As revealed by verbal discussion and interrogative inquiry as to the availability of ripped fruit, it is noted that all the 25 sellers did not know about the harmful effects of CaC₂ type in open market; for the 25 sellers of fruit questioned and interrogated whether the fruit they are selling are artificially ripped or naturally ripped, there are only 2 sellers aware of the natural application as a fruit ripening agent, the ratio of availability being 1:11.5 (Fig.1).

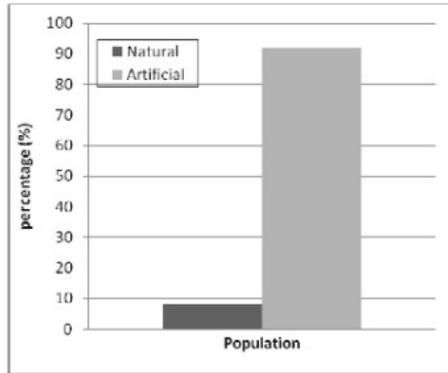


Fig. 1. Comparison between NRF’s and ARF’s availability in open market

Shelf life test: Application of CaC₂ as a ripening agent affects hardly on the shelf life of fruits. According to observation the ARF’s shelf life is approximate equal to 12 or less than 16 days while NRF’s has between the 12 and 16 days. It showed that NRF’s has high shelf life and by this it has also less economical loss and has maximum time to reach to sellers on time (Fig. 2). It was noted that all the 25 sellers don’t know about the harmful effects of CaC₂ (as a fruit ripening agent), the ratio of availability was 1:11.5.

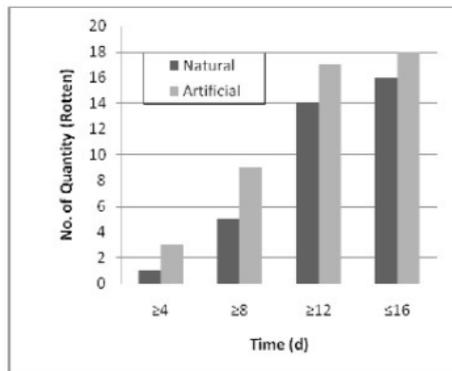


Fig. 2. Comparison shelf life between NRF’s and ARF’s

Quality of fruit from the business’s point of view: Quality of fruit is mildly affected by application of CaC₂; the ARF’s has the fair weight per fruit, texture is not very attractive, aroma is

mildly good, fair firmness and in taste it is sour from in core and mildly pleasant, while NRF's has a good weight per fruit, texture is attractive, aroma is good, and also have fair firmness, sweet and pleasant taste (Table 2).

| Business Based Qualities | Type of fruits | |
|--------------------------|-------------------------------|-----------------|
| | Artificial (CaC2) | Natural |
| Weight per fruit | fair | good |
| Texture | not very attractive | attractive |
| Aroma | mildly good | good |
| Firmness | fair | fair |
| Taste | In-core sour, mildly pleasant | sweet, pleasant |

Business dependent qualities: data were based on verbal inquiry.

Table 2. Business based physical differences

Physiochemical analysis

Moisture and Dry matter test: Water in any form is necessary for human life. As revealed by analytical test, the moisture content of ARF's is about 0.64% less than NRF's. Here we can calculate that 100mg NRF's provides 2.43% of the daily requirement, while ARF's provides 2.39% of daily intake 0.04% less than NRF's. Analytical data also show that ARF's possesses 1.47% more dry matter than NRF's. This is directly related to moisture content as NRF's contains high moisture value (Fig. 3).

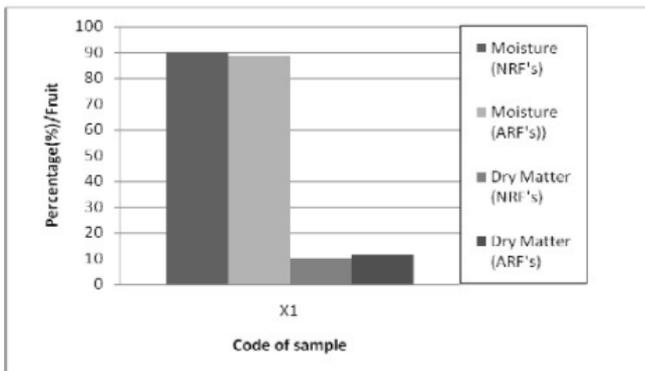


Fig. 3. Comparison between moisture and dry matter content of fraction X1 and also between NRF's and ARF's.

Total solids (TD), dissolved solids (DS) and Un-dissolved solids (UDS): TS, DS and UDS tests were carried out in different solvents (distilled water and HCl). Analytical testing revealed that ARF's have low values of TS and UDS but having an approximate equal value of TDS in contrast to NRF's. Therefore we can conclude that by taking NRF's in appetite is better than ARF's. Also when TDS is compared in acid extract and water extract, it was also observed that water extract has however dissolved solid in higher amounts than acidic extract. It means fruit has substances which are highly water soluble (Fig. 4).

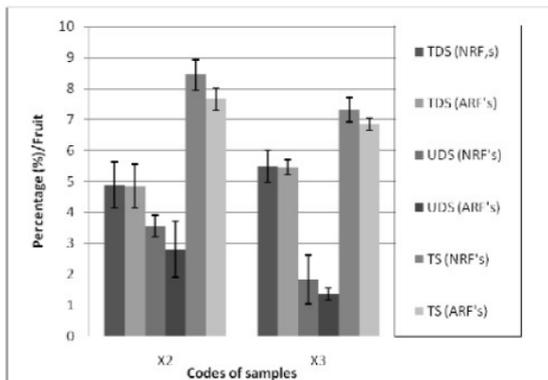


Fig. 4. Comparison between NRF's and ARF's against their TDS, UDS and TS for sample fraction X2 and X3.

Ashes test

On complete ignition of organic substances, metal oxides were obtained as ash. Samples were analyzed in different mediums and at different temperatures (that is 500 °C and 900 °C). Analytical test results showed that ARF's possess less ash than NRF's. It is also observed that complete oxidation takes place in the presence of H_2SO_4 which shows that a high amount of ash was found. In HNO_3 medium least amount of ash was found which shows that HNO_3 activity inhibits due to the presence of antioxidants in fruit, which may produce less ash (Fig. 5).

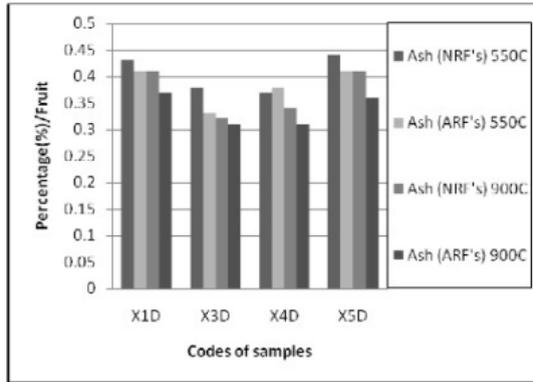


Fig. 5. Comparison between NRF's and ARF's against their ashes for sample fraction X1D, X3D, X4D and X5D respectively at 550°C ignited and 900°C ignited.

Edible part: As revealed by weight testing ARF's have a lower % of edible parts than NRF's. NRF's have a high amount of edible part. ARF's have approximately 0.82% less edible part than NRF's (Fig. 6).

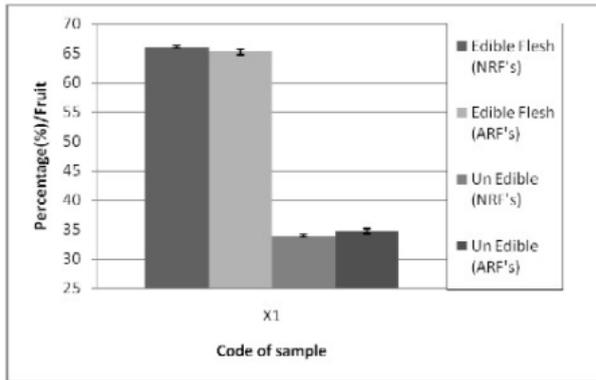


Fig. 6. Comparison (by weight) for both flesh and un-edible part against NRF's and ARF's

Detection of metals by complexometry: It was revealed from analysis of samples that ARF's have less metal content than NRF's. It showed that NRF's provide mineral in more quantity which are necessary for certain physiological and psychological processes. The result also proved that HNO₃ showed high metal content than other soaked samples and HCl extract has least

metal content; hence it is shown that HNO₃ is the best medium for analyses of metals from fruits. When the ashes were examined for metal content, the result shows that simple ash has a high metal content than other digested samples while it is at least in an amount in HCl medium. It is shown that ARF's provides minerals in less quantity which are necessary for certain physiological and psychological processes (Fig. 7).

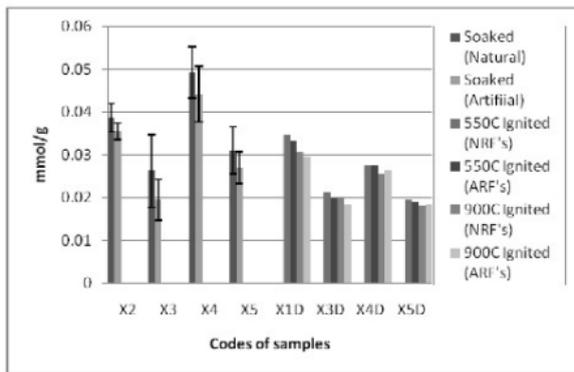


Fig. 7. Total metal content as a function of labeled samples against 550 °C and 900 °C

Qualitative analysis: On qualitative analysis of fruit the following metals were present in both type copper, iron, chromium, zinc, calcium, magnesium, and manganese while aluminium was only detected in NRF's based on K_{sp} value.

Iron Analysis

Detection of total iron and Fe^{+2} : Iron is a vital mineral that is essential for human life. Iron proteins are found in all living forms of life. As revealed by analytical results low amount of total iron were analyzed in ARF's as compared to NRF's in all mediums. It is shown that ARF's nutritional value is less than NRF's; it is also shown that in soaked samples iron concentration increases in time. The maximum amount of iron was analyzed in 4Hrs, in soaked sample of distilled water, while the minimum obtained in the HNO₃ soaked sample. It was expected that HNO₃ gives the highest value of iron because

it can oxidize more iron but less amount shows that there may be antioxidant present, which affects the efficiency of HNO₃. There was a low amount of total iron found in ARF's as compared to NRF's. The well absorbable form (Fe⁺²) was founded in ARF's in low concentration as compared to NRF's. Tolerance limit is 40 to 45 mg/day, so its use is safe and it provides the huge amount of iron for daily requirement (Fig. 8-A and 9).

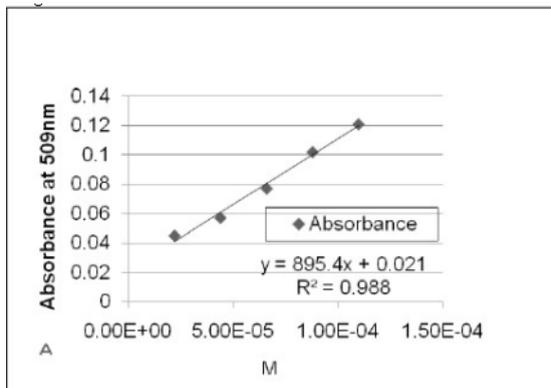


Fig. 8 A - Calibration curve for [Fe(OPT)₃]²⁺

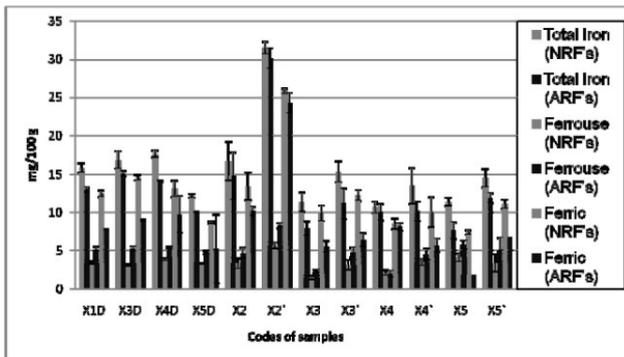


Fig. 9. Comparison of Conc. of total iron, ferrous and ferric (mg/100g) against labeled sample fraction for both NRF's and ARF's

Detection of Fe⁺³: Ash samples were analyzed for Fe⁺³, as it was expected that in ashes all iron was converted into Fe⁺³, but the presence of Fe⁺² in ashes may be due to presence of the

antioxidant power of the complex environment of the fruit. This suppresses that oxidizing power of acids especially in case of HNO_3 , which shows that antioxidants present in the fruits compete the action of HNO_3 and this effect dominates, therefore the iron remaining in the reduced form similarly in soaked samples of water and iron. The concentration of Fe^{+2} is increasing with time and as well as in the case of Fe^{+3} that may be due to increase of stability of iron complex present in the complex environment of fruit. The presence of Fe^{+3} and Fe^{+2} confirms the antioxidant activity of fruit which is high in the case of distilled water. It was also analyzed that ARF's possess high amount of Fe^{+3} but lesser amount of Fe^{+2} . NRF's possess high amount of Fe^{+2} while the less amount of Fe^{+3} may be due to the ARF's having less amount of antioxidants than NRF's (Fig. 8-B and 9).

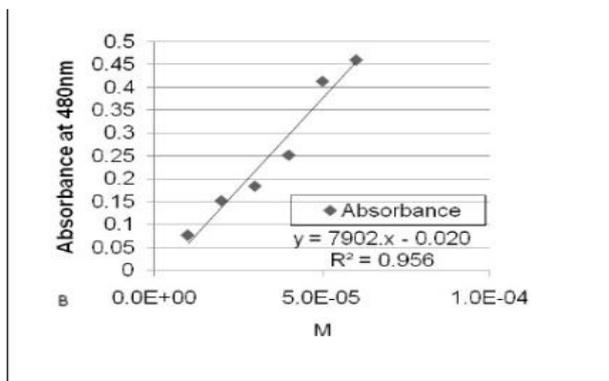


Fig. 8 B - Calibration curve for $[\text{Fe}(\text{SCN})_6]^{2+}$

Conclusion

On the basis of all results it can be concluded that application of CaC_2 as ARF not only harms the business based qualities of fruits but also greatly affects the physiochemical, nutritional and antioxidant property of fruits so the use of ARF's gives the least amount of antioxidants, nutrients and less amount of digestible iron. Furthermore it was also reported that use of ARF's is harmful for human health while NRF's are good dietary sources of the reduced form of iron thus having

been proved to possess a high antioxidant activity. The use of ARF's is not only fatal for human consumption but also unfavorable from a business point of view.

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