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# Application of Inductively Coupled Plasma-Mass Spectrometer in the Measurement of the Elemental Constituents of the Peels, Seeds and Pulps of Nigerian Ripe Grape Fruits

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***Abstract:***
*There is increase in the use of grape fruits for juice production in Nigeria, without the corresponding assessment of the nutritional constituents of the ripe grape fruit. Arising from this background, this paper was set to examine the elemental compositions of the peels, seeds and pulps of the grape fruits grown in Nigeria and to generate data on this fruit. The inductively coupled plasma-Mass Spectrometer (ICP-MS) was used in measuring the elemental constituents of the peels, seeds and pulps of the grape fruits. The elements determined were Zn, Ca, Na, K, Mg, Mn, Fe, Cu, N, and P. The results indicate that the elements were in varied concentrations in each of the segments (Peel, seed and pulp) analysed. Additionally, variations in the concentrations of a particular type of element were also observed when the segments were compared. When the results were subjected to statistical analysis significance differences were observed between some of the elements within the same segment, P<0.05%. Overall, the elements detected in all the grape fruits are known to play significant metabolic roles in humans. The consumption of grape fruits from the results obtained would contribute to the daily elemental requirements.*

**Keywords:** *Grape fruits, Elements, Inductively coupled plasma, spectrometer*

## 1. Introduction

Inductively coupled plasma spectroscopy (ICP-MS) is an advanced tool for metal speciation, quantification of proteins, biomolecules and elemental analysis. It can measure most elements except C, H, O, N and the halogens. Samples in the solid forms are dissolved or digested in liquid medium (acidic aqueous solution) before the sample is sprayed into the core of the inductively coupled argon plasma at high temperature of about 8000 degrees centigrade. At high temperature the elements are atomized, ionized and thermally excited. With the aid of the attached Mass spectrophotometer (MS), the ionized analyte is detected and quantified. Thus, the ions created in the plasma are separated by their mass to charge ratios, enabling the identification and quantification of unknown material [1]. The ICP-MS has low detection limits for a wide range of elements.

Grapefruit is a subtropical tree grown for fruit which was originally named the "forbidden fruit of Barbados [2]. Like other citrus, grape fruit grows on flowering ever green trees but they are distinguishable by the way in which they grow in clusters like grapes on trees. They are one of the largest citrus species with size ranging from 10cm - 15cm in diameter and when ripe, it is larger than the largest orange and they are oblate in shape. Botanists believe grapefruit was an accidental hybrid of two primal citrus species Citrus *maxima* and Citrus *sinensis* (Pummelo and sweet Orange). Grape fruit got its scientific name Citrus X *paradisi* in the 1800s [3]. James Macfayden a botanist published his book "Flora of Jamaica in 1837 in which he suggested that the grape fruit was a spontaneous genetic, variation or mutation.

Grapefruits are consumed fresh or utilized for processed citrus product and citrus-by-products. Approximately one third of the fruits produced are utilized for processing. In addition, these fruits utilization also apply to their juice used as flavoring in beverages [4]. In addition, citrus fruits can be processed to obtain other food products such as dehydrated citrus products or marmalades and jam (Ferguson, 1990). They also possess essential oil as by-product and there is volatile oil obtained from their peels sacks. They are used by the food industry to give flavor to drinks and foods. They also serve as components for the pharmaceutical industry in the preparation of drugs, soaps, perfumes and other cosmetics as well as for home cleaning products [5, 4]. Grapefruits are an excellent source of vitamin C. Vitamin C is a water soluble essential nutrient which act as an antioxidant and is involved in iron metabolism, the biosynthesis and carnitine, neurotransmitters, collagen and in the cross-linking of these fibres in bones and is a cofactor in various enzymatic and hormonal processes. In view of the increased use 0f grape for fruit juice processing and the scarce literature on the elemental constituents of the Nigerian grape fruits grown in Nigeria, this paper was set to examine the elemental compositions of the peels, seeds and pulps of the fruit as a guide towards its consumption

## 2. Materials and Methods

### *2.1. Collection and Preparation of Samples*

Sixteen fresh ripe grapefruits were purchased from four major markets (Oba, New Benin, Oliha and Evbotubu) in Benin City metropolis. The above markets are centers where citrus fruits are received from farmers and sold. Random selection was adopted during their purchase in the month of August, 2013. Thereafter, they were conveyed to the laboratory where they were washed and dried in the open air. The 16 grapefruits were peeled off with a knife. The juice of the above fruits was squeezed out and the seeds were filtered off by using a filter and the pulp were collected. The seeds and pulps from the fruits were kept on different foil paper and labeled accordingly. Thereafter, the seeds, peels and pulps were dried in an oven at a temperature of 600C for several days. The dried samples were crushed with mortar and pestle, before grinding into fine powder with an electric blender. The ground powders of the peels, seeds and pulps were put in dried plastic cans previously washed and rinsed with deionized water and labelled.

### *2.2. Experimental*

The ground samples of the seeds, peels and pulps of the grape fruits were analysed with the inductive Mass Spectrophotometer as described by [6].

### *2. 3. Statistical Analysis*

The results obtained were statistically analysed with ANOVA and all results are expressed as mean ± SEM of duplicate determinations.

## 3. Results

The results obtained are presented in Tables 1-3

The peels, seeds and pulps of the grape fruits had all the minerals measured but phosphorus was not detectable in the peels, seeds and pulps. The other elements detected were present in varied concentrations. The concentrations of Na, Fe, Cu, and Zn were very low relative to their counterparts. The statistical analysis conducted on the results of the peels, seeds and pulps along the same column of each element shows that significant differences exists at $P < 0.05\%$ between some the elements.

| Samples | Ca | Na | K | N | P | Mg | Mn | Fe | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $0.72^{e}$ ± 0.04 | $0.11^{a,b}$ ± 0.02 | $0.88^{a}$ ± 0.06 | $1.00^{b}$ ± 0.01 | ND | $0.09^{b}$ ± 0.002 | $0.0006^{a}$ ± 0.00 | $0.0024^{b}$ ± 0.0001 | $0.0003^{a}$ ± 0.0001 | $0.0003^{a,b}$ ± 0.00 |
| 2 | $0.32^{a}$ ± 0.02 | $0.12^{a,b}$ ± 0.01 | $8.55^{a}$ ± 0.12 | $2.36^{e}$ ± 0.06 | ND | $0.08^{b}$ ± 0.001 | $0.0004^{a}$ ± 0.0001 | $0.0025^{b}$ ± 0.0002 | $0.0001^{a}$ ± 0.0001 | $0.0002^{a}$ ± 0.0001 |
| 3 | $0.87^{f}$ ± 0.02 | $0.09^{a,b}$ ± 0.01 | $0.87^{a}$ ± 0.12 | $4.00^{d}$ ± 0.01 | ND | $0.16^{d,e}$ ± 0.005 | $0.0007^{a}$ ± 0.0001 | $0.0010^{a}$ ± 0.0001 | $0.0004^{a}$ ± 0.0002 | $0.0004^{a,b,c}$ ± 0.0002 |
| 4 | $1.19^{g}$ ± 0.02 | $0.10^{a,b}$ ± 0.00 | $1.72^{a}$ ± 0.02 | $1.36^{c}$ ± 0.01 | ND | $0.19^{f}$ ± 0.001 | $0.0006^{a}$ ± 0.0002 | $0.0031^{b}$ ± 0.0001 | $0.0003^{a}$ ± 0.0000 | $0.0002^{a}$ ± 0.0001 |
| 5 | $0.68^{d}$ ± 0.02 | $0.13^{a,b}$ ± 0.06 | $1.22^{b}$ ± 0.01 | $2.10^{d}$ ± 0.07 | ND | $0.85^{a,b}$ ± 0.002 | $0.0008^{a}$ ± 0.0001 | $0.0008^{a}$ ± 0.0001 | $0.0003^{a}$ ± 0.0001 | $0.0002^{a}$ ± 0.0000 |
| 6 | $0.48^{b}$ ± 0.02 | $0.14^{b}$ ± 0.00 | $1.07^{a,b}$ ± 0.01 | $4.00^{f}$ ± 0.12 | ND | $0.11^{c}$ ± 0.006 | $0.0009^{a}$ ± 0.0001 | $0.0006^{a}$ ± 0.0001 | $0.0004^{a}$ ± 0.0001 | $0.0003^{a,b}$ ± 0.0001 |
| 7 | $1.57^{h}$ ± 0.02 | $0.08^{a,b}$ ± 0.01 | $1.47^{c}$ ± 0.02 | $2.10^{d}$ ± 0.01 | ND | $0.17^{e}$ ± 0.001 | $0.0013^{a}$ ± 0.0001 | $0.0025^{b}$ ± 0.0001 | $0.0003^{a}$ ± 0.0001 | $0.0006^{c}$ ± 0.0001 |
| 8 | $0.48^{b}$ ± 0.03 | $0.06^{a}$ ± 0.01 | $1.45^{c}$ ± 0.04 | $1.28^{c}$ ± 0.07 | ND | $0.08^{a,b}$ ± 0.001 | $0.0005^{a}$ ± 0.0002 | $0.0007^{a}$ ± 0.0001 | $0.0003^{a}$ ± 0.0001 | $0.0002^{a}$ ± 0.0001 |
| 9 | $0.61^{c}$ ± 0.01 | $0.09^{a,b}$ ± 0.03 | $1.99^{a}$ ± 0.12 | $1.44^{c}$ ± 0.01 | ND | $0.17^{e}$ ± 0.005 | $0.0023^{a}$ ± 0.0001 | $0.0013^{a}$ ± 0.0001 | $0.0002^{a}$ ± 0.0001 | $0.0005^{b,c}$ ± 0.0001 |
| 10 | $0.87^{f}$ ± 0.02 | $0.10^{a,b}$ ± 0.02 | $1.00^{a}$ ± 0.12 | $0^{a}$ | ND | $0.15^{d}$ ± 0.12 | $0.0008^{a}$ ± 0.0018 | $0.0023^{b}$ ± 0.0001 | $0.0003^{a}$ ± 0.0001 | $0.0006^{c}$ ± 0.0001 |

*Table 1: Mineral contents of the peels of 10 ripe grape fruits(mg/kg)*

*Mean Value (± SEM) with different superscript alphabets along the same column are significantly different from each*

| Samples | Ca | Na | K | N | P | Mg | Mn | Fe | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.52$^{g}$ ± 0.01 | 0.09$^{b,c}$ ± 0.02 | 0.82$^{a}$ ± 0.01 | 2.43$^{b}$ ± 0.05 | ND | 0.045$^{d}$ ± 0.001 | 0.0002$^{a}$ ± 0.0001 | 0.0052$^{e}$ ± 0.0001 | 0.0004$^{b}$ ± 0.0000 | 0.0002$^{a}$ ± 0.0001 |
| 2 | 0.18$^{a}$ ± 0.01 | 0.13$^{d}$ ± 0.02 | 7.95$^{a}$ ± 0.10 | 5.43$^{g}$ ± 0.01 | ND | 0.020$^{b,c}$ ± 0.001 | 0.0001$^{a}$ ± 0.000 | 0.0031$^{c}$ ± 0.0001 | 0.0002$^{a,b}$ ± 0.0001 | 0.0001$^{a}$ ± 0.0001 |
| 3 | 0.71$^{i}$ ± 0.01 | 0.05$^{a}$ ± 0.01 | 0.76$^{a}$ ± 0.02 | 6.40$^{i}$ ± 0.01 | ND | 0.084$^{e}$ ± 0.001 | 0.0001$^{a}$ ± 0.0001 | 0.0026$^{ab}$ ± 0.0002 | 0.0007$^{c}$ ± 0.000 | 0.0003$^{a,b}$ ± 0.0001 |
| 4 | 0.43$^{f}$ ± 0.0 | 0.05$^{a}$ ± 0.01 | 1.71$^{f}$ ± 0.01 | 5.64$^{h}$ ± 0.01 | ND | 0.101$^{f}$ ± 0.001 | 0.0005$^{a}$ ± 0.0001 | 0.0044$^{d}$ ± 0.0002 | 0.0001$^{a}$ ± 0.0001 | 0.0002$^{a}$ ± 0.0001 |
| 5 | 0.41$^{e,f}$ ± 0.01 | 0.12$^{c,d}$ ± 0.01 | 1.21$^{c}$ ± 0.05 | 4.36$^{d}$ ± 0.01 | ND | 0.022$^{c}$ ± 0.001 | 0.0002$^{a}$ ± 0.0001 | 0.0016$^{ab}$ ± 0.0001 | 0.0001$^{a}$ ± 0.0001 | 0.0002$^{a}$ ± 0.0001 |
| 6 | 0.23$^{b}$ ± 0.01 | 0.11$^{c,d}$ ± 0.01 | 1.03$^{b}$ ± 0.01 | 5.21$^{f}$ ± 0.02 | ND | 0.088$^{e}$ ± 0.001 | 0.0003$^{a}$ ± 0.0001 | 0.0018$^{b}$ ± 0.0001 | 0.0007$^{c}$ ± 0.0005 | 0.0002$^{a}$ ± 0.0001 |
| 7 | 0.68$^{h}$ ± 0.01 | 0.11$^{c,d}$ ± 0.01 | 1.39$^{d}$ ± 0.02 | 4.57$^{e}$ ± 0.05 | ND | 0.090$^{e}$ ± 0.001 | 0.0008$^{a}$ ± 0.0001 | 0.0028$^{c}$ ± 0.0002 | 0.0003$^{a,b}$ ± 0.0000 | 0.0005$^{b}$ ± 0.0001 |
| 8 | 0.35$^{d}$ ± 0.01 | 0.06$^{a,b}$ ± 0.01 | 1.04$^{b}$ ± 0.01 | 3.42$^{c}$ ± 0.01 | ND | 0.024$^{c}$ ± 0.001 | 0.0001$^{a}$ ± 0.0002 | 0.0012$^{a}$ ± 0.0000 | 0.0001$^{a}$ ± 0.0001 | 0.0001$^{a}$ ± 0.0001 |
| 9 | 0.32$^{c}$ ± 0.01 | 0.12$^{c,d}$ ± 0.01 | 1.32$^{c,d}$ ± 0.02 | 3.50$^{c}$ ± 0.01 | ND | 0.015$^{b}$ ± 0.001 | 0.140$^{b}$ ± 0.0023 | 0.0020$^{b}$ ± 0.0001 | 0.0003$^{a,b}$ ± 0.0001 | 0.0005$^{b}$ ± 0.0001 |
| 10 | 0.39$^{e}$ ± 0.01 | 0.10$^{c,d}$ ± 0.01 | 1.57$^{e}$ ± 0.02 | 2.14$^{a}$ ± 0.05 | ND | 0.0001$^{a}$ ± 0.0001 | 0.0008$^{a}$ ± 0.0001 | 0.0083ot$^{f}$ ± 0.0001 | 0.0001$^{a}$ ± 0.000 | 0.0008$^{c}$ ± 0.0001 |

*Table2: Mineral contents of the pulps of 10 ripe grape fruits (mg/kg)*

*Mean Value (± SEM) with different superscript alphabets along the same column are significantly different from each other (P < 0.05%)*

| Samples | Ca | Na | K | N | P | Mg | Mn | Fe | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.31$^{d}$ ± 0.02 | 0.21$^{d}$ ± 0.01 | 0.22$^{a}$ ± 0.004 | 4.14$^{a}$ ± 0.01 | ND | 0.850$^{b}$ ± 0.004 | 0.0005$^{a,b}$ ± 0.0001 | 0.0012$^{c}$ ± 0.0001 | 0.0002$^{a}$ ± 0.0001 | 0.0001$^{a}$ ± 0.0000 |
| 2 | 0.14$^{a}$ ± 0.02 | 0.13$^{c}$ ± 0.001 | 0.32$^{b}$ ± 0.00 | 14.64$^{f}$ ± 0.10 | ND | 0.065$^{a}$ ± 0.001 | 0.0003$^{a,b}$ ± 0.0001 | 0.0022$^{e}$ ± 0.0001 | 0.0001$^{a}$ ± 0.0001 | 0.0001$^{a}$ ± 0.0001 |
| 3 | 0.54$^{g}$ ± 0.01 | 0.08$^{a,b}$ ± 0.002 | 0.21$^{a}$ ± 0.01 | 15.29$^{g}$ ± 0.01 | ND | 0.113$^{c,d}$ ± 0.001 | 0.0003$^{a,b}$ ± 0.0000 | 0.0007$^{b}$ ± 0.0001 | 0.0003$^{a}$ ± 0.0001 | 0.0002$^{a}$ ± 0.0001 |
| 4 | 0.38$^{e}$ ± 0.01 | 0.09$^{a,b}$ ± 0.01 | 0.58$^{d}$ ± 0.01 | 12.21$^{e}$ ± 0.02 | ND | 0.150$^{e}$ ± 0.012 | 0.0006$^{b}$ ± 0.0001 | 0.0018$^{d}$ ± 0.0001 | 0.0003$^{a}$ ± 0.0001 | 0.0001$^{a}$ ± 0.0001 |
| 5 | 0.22$^{b}$ ± 0.01 | 0.09$^{a,b}$ ± 0.01 | 0.25$^{a}$ ± 0.01 | 10.43$^{d}$ ± 0.01 | ND | 0.051$^{a}$ ± 0.005 | 0.0004$^{a,b}$ ± 0.0001 | 0.0004$^{ab}$ ± 0.0001 | 0.0002$^{a}$ ± 0.0001 | 0.0001$^{a}$ ± 0.0001 |
| 6 | 0.12$^{a}$ ± 0.01 | 0.07$^{a,b}$ ± 0.001 | 0.32$^{b}$ ± 0.01 | 17.2$^{h}$ ± 0.01 | ND | 0.102$^{b,c}$ ± 0.006 | 0.0005$^{a,b}$ ± 0.0001 | 0.0003$^{a}$ ± 0.0001 | 0.0003$^{a}$ ± 0.0001 | 0.0003$^{a}$ ± 0.0001 |
| 7 | 0.47$^{f}$ ± 0.01 | 0.08$^{a,b}$ ± 0.01 | 0.77$^{e}$ ± 0.01 | 12.36$^{e}$ ± 0.01 | ND | 0.199$^{f}$ ± 0.007 | 0.0006$^{b}$ ± 0.0001 | 0.0024$^{e}$ ± 0.0002 | 0.0003$^{a}$ ± 0.0001 | 0.0001$^{a}$ ± 0.0001 |
| 8 | 0.24$^{b,c}$ ± 0.02 | 0.06$^{a}$ ± 0.01 | 0.33$^{b}$ ± 0.01 | 8.21$^{c}$ ± 0.12 | ND | 0.056$^{a}$ ± 0.001 | 0.0002 ± 0.0001 | 0.0003$^{a}$ ± 0.0000 | 0.0002$^{a}$ ± 0.0000 | 0.0001$^{a}$ ± 0.000 |
| 9 | 0.29$^{d}$ ± 0.01 | 0.16$^{d}$ ± 0.01 | 0.44$^{c}$ ± 0.02 | 8.21$^{c}$ ± 0.01 | 0.42$^{b}$ ± 0.01 | 0.125$^{d}$ ± 0.010 | 0.0028$^{c}$ ± 0.0002 | 0.0006$^{a,b}$ ± 0.0001 | 0.0002$^{a}$ ± 0.0001 | 0.0003$^{a}$ ± 0.000 |
| 10 | 0.27$^{c,d}$ ± 0.02 | 0.10$^{b}$ ± 0.02 | 0.34$^{b}$ ± 0.03 | 7.07$^{b}$ ± 0.02 | ND | 0.104$^{b,c,d}$± 0.046 | 0.0005$^{a,b}$± 0.0001 | 0.0012$^{d}$ ± 0.0002 | 0.0002$^{a}$ ± 0.0000 | 0.0002$^{a}$ ± 0.0001 |

*Table 3: Mineral contents of the seeds of 10 ripe grape fruits (mg/kg)*

*Mean Value (± SEM) with different superscript alphabets along the same column are significantly different from each other P < .05%*

*ND= Not detectable*

**4. Discussion**

The Potassium concentrations of the peels, seeds and pulps were high and this could be attributed to the bioavailability of these minerals in the plants. Additionally, minerals nutrition by plants have shown that Potassium is always demanded in higher concentrations than nitrogen because it is needed for photosynthesis, carbohydrate transport and water regulation. Potassium is an important element due to its diuretic nature [7]. It regulates body fluid balance and needed for nerve transmission of impulses and contraction of muscles and proper metabolism (Griff [8].

The high concentrations of nitrogen in the pulps of the fruits relative to the peels and seeds could be as a result of the high crude protein concentration that may be present in the pulps, nitrogen element being one of the building blocks of this organic compound. The peels and seeds of the grape fruits could be dried, ground or milled and added to animal feed (livestock). It could serve as additives in human food preparations. Nitrogen like potassium is abundant in plants and needed in high amounts. The complete absence of phosphorus as an element in the peels, seeds and pulps of the fruits could be attributed to various factors which include the bioavailability of the element in the soil and the conversion of phosphorus by plants to phytates, which is a form of phosphorus in plants. The RDA of phosphorus is between 800 and 1500mg/day. It is also needed for the utilization of protein, fats and carbohydrates [9].

The calcium concentration is third in abundance relative to the other elements in the grape fruits. Calcium was higher in the peels and pulps of grape fruits compared to the other parts of the fruits. As a consequence, the pulp of the fruits could serve as a useful source of this mineral when consumed. The peels and seeds could be used in the formulation of drugs, and livestock feeds. Calcium function as a constituent of bones and teeth, plays vital roles in metabolic processes, and also function in nerve/muscle contractions and blood clotting. Calcium also plays vital roles in the function of the heart and synthesis of blood cells. The RDA of calcium is 800 – 1200mg/day [10].

The sodium concentrations in the parts of the fruits analysed agree with previous work done by [11], but disagrees with the results of [7]. Fruits are known to be low in natural sodium. The differences in the concentrations of sodium in the pulps, peels and seeds of the grape fruits are not very much. Sodium is the principal cation in extracellular fluid which regulates plasma volume and acid-base balance involved in the maintenance of osmotic pressure of body fluid. Its RDA according to [12] is 1500mg. The cumulative intake of the pulps of the grape could supplement the RDA requirement in humans.

Magnesium like sodium also function in the maintenance of osmotic equilibrium, required in many enzyme catalyzed reactions. About 15 – 20% of the plant Mg is contained in chlorophyll which help these plants to capture sun energy. Magnesium is an essential activator for the phosphate-transferring enzymes myokinase, diphosphopyridine nucleotide kinase and creatin kinase. It also activates pyruvic acid oxidase and the condensing enzymes for the reaction in the citric acid cycle [13]. Poor growth in chicks results from magnesium-deficient diet. To meet this lapse, the peels, pulps and seeds of grape fruits could be processed and incorporated into feeds of chickens to promote good growth and feathering. Magnesium is needed for healthy bones and blood vessels, muscles function, nerves transmission and energy formation. [12]. The pulp could also be useful as additive in food preparations and drugs.

The low concentration of copper detected in the peels, pulps and seeds of the grape fruits agree with the earlier finding of [14] that plants only take copper in small quantities and that its uptake is metabolically controlled. In man, copper acts as a constituent of enzymes such as cytochrome oxidase, amine oxidase, ascorbic acid oxidase etc. Copper is an essential micro nutrient necessary for hematologic and neurologic system.

Studies have shown that plant absorbs and translocate low quantities of zinc [7]. Physiologically, zinc functions as a co-factor and as a constituent of many enzymes like superoxide dismutase, DNA and RNA polymerase etc. Zinc is required for normal testicular development and for the function of taste buds. It is needed for tissue repair, wound healing, in protein synthesis, digestion and it is necessary for optimum insulin.

The low concentrations Iron in the peels, pulps and seeds of the grape fruits could be as result of the fact that most plants absorb small quantities of iron and thereafter translocate to other parts of the plants. Iron functions as haemoglobin in the transport of Oxygen.

**5. Conclusion**

This research has revealed that the peels, seeds and pulps of the Nigerian grape fruits consists of vital minerals which could contribute to the RDA in man. Additionally, the minerals detected c0uld assists in metabolism, where they function as cofactors in enzyme-catalysed reactions, forms synergy with other minerals in bone formation and as constituents of body fluids and organs. Conclusively, the consumption of the Nigerian grape fruits used in fruit juice preparation is of immense health benefits to the consumer.

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