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Levels of phosphorus in citrus fruits

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Abstract Phosphates are inorganic compounds, based on the element phosphorus, combined with oxygen to form phosphates, the form in which phosphorus is present in nature. Phosphates are essential for plant growth, crops, and human health. Phosphates have been used in processing and preservation of fruits and to protect the color of fresh vegetables and fruits destined for direct consumption. The researchers have found that a high intake of phosphates in human organism, which are increasingly used as food additives, appear to activate a metabolic pathway that stimulates the growth of the lung tumors. The purpose of this paper is to characterize freshly squeezed citrus fruits juices (pH, density and total acidity) and to determine the total phosphorus level (as phosphates) from different parts (peel, film and pulp) of citrus fruits (lemon, grapefruit and orange). Phosphates have been analyzed using molybdenum blue method with $SnCl_2$ as reducing agent at CAMSPEC M 330 spectrometer, after the method performances' verification. Limit of detection (LOD) and quantification (LOQ) were 0.0074 respectively 0.0393 mg/L. The obtained concentrations of phosphorus were between 1.1 and 18.6 mg/100g fruit material.

Keywords: phosphorus, molecular absorption spectrometry, citrus fruits

1. Introduction

Citrus fruits are classified as acid fruits, since their soluble solids are composed mainly of organic acids and sugars, which are used as the main index of maturity and one of the major analytical measures of flavor quality. The main acids of citrus fruits are citric and malic acids [1].

Phosphorus is a nutrient vital to human, animal, and plant life. It is one of the most common substances in our environment, naturally occurring in our food, our water, and our bodies, as well as. In our body, phosphorus is present in our genes, our teeth, and our bones even our muscles. Polyphosphates are based on the element Phosphorus, which is essential for all living organisms, plants, animals and man. Phosphates are present in sewage from both detergents and (the main source) from human foods, transferred into human wastes; and also in animal manures, food industry wastes. Phosphates can be recovered from these sources and recycled back into industry, into fertilisers or into detergents [2].

Phosphorus (P) is macro nutrient for plant. The amount of P needed by plant is second highest after Nitrogen. P nutrient have a role in carbohydrate, fat and protein metabolism. Phosphorus act as intermedier, to keep and supply energy for metabolism process like respiration and fermentation. P also arranges enzimatic process, closely related to compilation of crop essential part like nucleic acid at cell core, increases resilience to disease and increases crop quality.

Sufficient amount of available P can increase root development, assist forming of flower initiation and other reproductive organ and quickens ripening process of fruit [3].

The past and present use of P in relation to a crop's uptake, the soil-surface balance of P, is a key factor controlling P transport from agricultural fields into the environment [4, 5].

In recent years, many rapid and simple methods are used for the determination of phosphorus as phosphate in different samples.

Spectrophotometric methods are based on the formation of yellow molybdophosphoric acid and its

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reduction to a blue hetero poly compound, phosphomolybdenum blue [6, 7].

There have been many reports on various modifications of these methods in order to make the sensitivity and stability high, such as the malachite green method [8], rhodamine B method [9], thiamin method [10] and luminol method [11].

The purpose of this paper is to characterize freshly squeezed citrus fruits juice and to determine the phosphorus level from different parts (peel, film and pulp) of citrus fruits (lemon, grapefruit and orange) after the phosphates determination method performances' verification.

2. Experimental

All used reagents were of analytical reagent grade and were purchased from Merck.

Sampling

The studies were performed on peel, film and pulp of citrus fruits (lemon, grapefruit and orange) purchased from local supermarkets.

Sample analysis

pH, density and total acidity were measured to characterize freshly squeezed citrus fruits juices. pH was measured using a pH-meter IQ 125 Mini Lab and for the determination of density was used a picnometer. Total acidity was measured by direct titration of a 10 mL sample with 0.1 N NaOH and the results were expressed as citric acid.

For quantitative determination of total phosphorus in the phosphate form the CAMSPEC M 330 spectrometer of molecular absorption was used. The phosphates were determined using molybdenum blue spectrometric method with $SnCl_2$ as reducing agent.

The phosphate reacts with ammonium molybdate forming ammonium phophomolybdate, a yellow precipitate. This is reduced to a compound of unknown structure called molybdenum blue which gives a blue color to the solution.

10 grams of sample was processed in an electric furnace at a temperature of 600-700^{0}C for six hours to obtain a white residue that was left to cool in a exicator and finally weighed. The obtained ash was treated with HCl and brought to 50 mL with distilled water in calibrated flask. In order to measure the phosphate concentration in analyzed samples a calibration curve was obtained.

2 mL of sample with unknown concentration of phosphate, 1 mL of ammonium molybdate (50 g/L) solution and 1 mL of $SnCl_2$ (5g/L) were added in a 50 mL calibrated flask. After 10 minutes (time to stabilize the color) it was fill up with distilled water to the mark and homogenized. The absorbance was read at 715 nm (Fig 1).

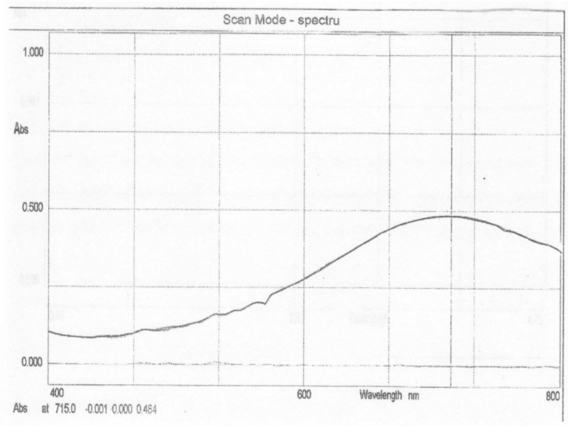

Fig 1. The spectrum of molybdenum blue (maximum absorbance at 715 nm)

Linearity of the method was established for the concentration range 0.04-0.24 mg/L (6 solutions) of K_2HPO4, phosphate certified solution, MERCK. Each concentration level was determined in five repetitions.

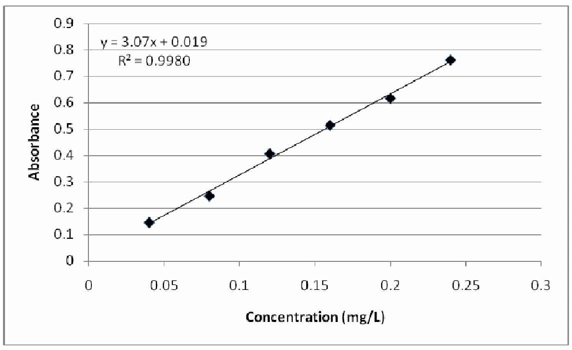

Fig 2. The calibration curve for phosphate determination

The corresponding calibration equation, limit of detection (LOD), of quantification (LOQ) and other statistical parameters are listed in Table 1. LOD and LOQ were calculated as $(3 \cdot S_a\text{-}a)/b$ respectively $(10 \cdot S_a\text{-}a)/b$.

Table 1. Regression and statistical parameters for the determination of phosphates

LOD	LOQ	R^2	a	S_a	b	S_b
0.0074	0.0393	0.9980	0.019	0.014	3.07	0.095

where: LOD - limit of detection; LOQ - limit of quantification; R^2 - correlation coefficient; a - intercept; Sa - standard deviation of intercept; b - slope. Sb - standard deviation of slope.

3. Results and Discussions

In table 2 the values of pH, density and total acidity that characterize freshly squeezed citrus fruits juices are presented.

Table 2. Characteristics of freshly squeezed citrus fruits juices

Citrus juice	pH	Density	Total acidity (citric acid g/L)
Orange	4.4	2.2202	13.36
Lemon	2.7	2.2213	58.72
Grapefruit	3.6	2.2224	20.59

pH is a function of the log of the citric acid concentration and can be used to express acidity of juice. Hydrogen ion is believed to be the chemical agent responsible for the sensation of tartness, although other factors are involved in the psychological reaction. In general, tartness is inversely proportional to the pH [12].

This demonstrates that in our case the most acidulous juice is lemon juice because pH has the smalest value (2.7).

Baldwin [13] also reported that tangerines and oranges have the lowest acidity, while lemons, limes and sour oranges have the highest acidity among citrus fruits. In our case also lemon has the highest acidity (58.72 citric acid g/L).

In Fig. 3, 4, and 5 are presented the measured concentrations expressed as mgP/100g fruit using the molecular absorption spectrometry.

Fig. 3. Phosphorus concentrations levels in different parts of orange

Fig. 4. Phosphorus concentrations levels in different parts of lemon

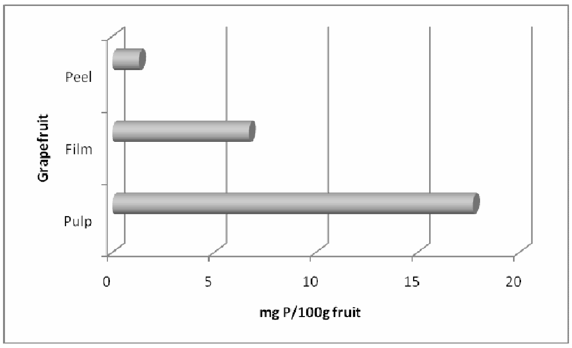

Fig. 5. Phosphorus concentrations levels in different parts of grapefruit

It can be noticed that the highest value for phosphorus was found in citrus's pulp except orange where phosphorus was found in higher quantity in citrus's film. In fruit's peel was found a small quantity of phosphorus.

Normal level of phosphorus in orange is 12mg/100g fruit, in grapefruit 8mg/100 g fruit and 16.2mg/100 g fruit in lemon [14].

This suggests that phosphates used in processing and preservation of studied citrus fruits to protect the color of fresh fruits destined for direct consumption, are not over the permitted limit.

Trace elements, whether essential or non-essential, above threshold concentration levels, can cause morphological abnormalities, reduce growth and increase mortality and mutagenic effects in humans [15]. The average intakes are 1000, 2, 18, 400, 2, 1000, 15, 4000 and 2400 mg per day for Ca, Cu, Fe, Mg, Mn, K, Zn, P and Na, respectively. This daily nutrient intake is likely to pose no risk of adverse effects [16].

4. Conclusions

The tartness juice is lemon's juice and the highest acidity (58.72 citric acid g/L) was obtained for lemon.

The levels of phosphorus found in citrus fruits suggest that phosphates used in processing and preservation of these citrus fruits to protect the color of fresh fruits destined for direct consumption, are not over the permitted limit.

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