Determination of Sodium, Potassium, Magnesium, and Calcium Minerals Level in Fresh and Boiled Broccoli and Cauliflower by Atomic Absorption Spectrometry

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Abstract Vegetables from the cabbage family vegetables consumed by many people, which is known healthful, by eaten raw, boiled, or cooked (stir fry or soup). Vegetables like broccoli and cauliflower contain vitamins, minerals, and fiber. This study aims to determine the decrease percentage of sodium, potassium, magnesium, and calcium minerals level caused by boiled broccoli and cauliflower by atomic absorption spectrometry. Boiled broccoli and cauliflower prepared by given boiled treatment in boiling water for 3 minutes. Fresh and boiled broccoli and cauliflower carried out dry destruction, followed by quantitative analysis of sodium, potassium, magnesium, and calcium minerals respectively at a wavelength of 589.0 nm; 766.5 nm; 285.2 nm; and 422.7 nm, using atomic absorption spectrometry methods. After the determination of the sodium, potassium, magnesium, and calcium minerals level followed by validation of analytical methods with accuracy, precision, linearity, range, limit of detection (LOD), and limit of quantitation (LOQ) parameters. Research results showed a decrease in the sodium, potassium, magnesium, and calcium minerals level in boiled broccoli and cauliflower compared with fresh broccoli and cauliflower. Validation of analytical methods gives results that spectrometry methods used for determining sodium, potassium, magnesium, and calcium minerals level are valid. It concluded that the boiled gives the effect of decreasing the minerals level significantly in broccoli and cauliflower.

1. Introduction

Vegetables like broccoli and cauliflower are different plants with the same species name, Brassica oleracea L. with abundant minerals and phytochemical contents [1]. Minerals content contained in broccoli and cauliflower are sodium, potassium, magnesium, calcium, iron, and zinc [2,3]. Based on its needs, minerals are divided into two classes, namely macro minerals (the body needs in large quantities) and micro minerals (the body needs in small quantities). Minerals included in the macro minerals are sodium, potassium, magnesium, and calcium. Minerals included in the micro minerals are iron and zinc [4]. Figure 1 showed broccoli plants and Figure 2 showed cauliflower plants.

Sodium is the most important cation in extracellular fluid by contributing to the regulation of acid base balance, regulation of membrane potential and osmotic pressure of body fluids, activation of nerve and muscle impulses, regulation the absorption process of monosaccharide, amino acids and bile
sodium. Potassium is the most important cation in intracellular fluid by contributing to the regulation of acid base balance, regulation of membrane potential and osmotic pressure of body fluids, delivery of nerve and muscle impulses, regulation of glycogenesis processes. Magnesium serves as an active component of several enzyme systems with thiamin pyrophosphate as cofactors, an important component of several enzyme activators, bone and tooth structure, and enzyme compositions. Calcium serves as a major component of bone and tooth structure, nerve regulation and muscle function, blood coagulation, and enzyme activation [5].

Vegetables like broccoli and cauliflower are often consumed by the public, whether eaten raw, boiled, or cooked (stir fry or soup). Processes experienced by vegetables such as boiling may allow a decrease in the minerals content and phytochemicals in the vegetables to be consumed [6]. So, it becomes important to know the decrease percentage of the minerals content contained in boiled broccoli and cauliflower compared to fresh broccoli and cauliflower. This study aims to determine the decrease percentage of sodium, potassium, magnesium, and calcium minerals level caused by boiled broccoli and cauliflower by atomic absorption spectrometry.

2. Methods
This research is an experimental research. This study aims to determine the decrease percentage of sodium, potassium, magnesium, and calcium minerals level caused by boiled broccoli and cauliflower by atomic absorption spectrometry. The sample used in this study is broccoli and cauliflower growth in Gundaling, Berastagi, Karo, Sumatera Utara, 22152, Indonesia.

2.1. Materials
Materials used in this research are a standard solution of sodium, potassium, magnesium, calcium, concentrated nitric acid (Merck), and demineralized water (Brataco).

2.2. Tools
Tools used in this research are the atomic absorption spectrometer (Shimadzu) connected to the computer (Toshiba) with air acetylene flame complete with hollow cathode lamp for sodium, potassium, magnesium, and calcium, hotplate (Boeco), filter paper (Whatman), glassware (Iwaki).

2.3. Materials preparation
Two hundred grams of broccoli and cauliflower was cleaned by washing using flowing water, cut into small sections and drained it until dry. One hundred grams of fresh broccoli and cauliflower ready to be used as sample. Remainder broccoli and cauliflower were given boiled treatment subsequent boiled in about 100 mL of boiling water for 3 minutes, drained it until dry. One hundred grams of boiled broccoli and cauliflower ready to be used as sample.

2.4. Samples destruction
Samples were crushed and weighed in a crucible porcelain in an amount of 10 grams, dried in an oven for 5 hours, charred on a hot plate, and ashed in a furnace for 3 hours at an initial temperature of 100°C automatically rise to the final temperature of 500°C. Destruction results allowed to cooled in the desiccator, spilled a few drops of demineralized water through the wall of the crucible porcelain until wet, dissolved in 5 mL of nitric acid 5 N, putted in a 100-mL volumetric flask, rinsed crucible porcelain 3 times each flushing with 10 mL demineralized water, putted in the same volumetric flask, diluted with demineralized water until the marking line, and shook until until homogenous. The mixture was filtered with filter paper, discarded the first 10 mL filtrate, accommodated the subsequently filtrate in amber glass bottles, stored, and used for quantitative analysis [7].

2.5. Determination of linearity, limit of detection and limit of quantitation
- Sodium: sodium standard solution was diluted to obtained a series solution of standard sodium with concentration 0.1 μg/mL, 0.2 μg/mL, 0.3 μg/mL, 0.4 μg/mL, and 0.5 μg/mL.
- Potassium: potassium standard solution was diluted to obtained a series solution of standard potassium with concentration 0.5 μg/mL, 1.0 μg/mL, 1.5 μg/mL, 2.0 μg/mL, and 2.5 μg/mL.
- Magnesium: magnesium standard solution was diluted to obtained a series solution of standard magnesium with concentration 0.1 μg/mL, 0.2 μg/mL, 0.3 μg/mL, 0.4 μg/mL, and 0.5 μg/mL.
- Calcium: calcium standard solution was diluted to obtained a series solution of standard calcium with concentration 1.0 μg/mL, 2.0 μg/mL, 3.0 μg/mL, 4.0 μg/mL, and 5.0 μg/mL.

All the standard solution was further measured by atomic absorption spectrometer using sodium, potassium, magnesium, and calcium hollow cathode lamp at a wavelength respectively 589.0 nm, 766.5 nm, 285.2 nm, 422.7 nm using air acetylene flame [8]. Calculated the coefficient of correlation (r), coefficient of determination (r²), regression line equation, limit of detection (LOD), and limit of quantitation (LOQ) [9].

2.6. Determination of calcium, potassium, and magnesium levels in the sample
- Sodium: The sample solution was pipetted 1.0 mL, diluted in a 50-mL volumetric flask with demineralized water. Subsequently the solution was pipetted 2.0 mL, diluted in a 10-mL volumetric flask with demineralized water.
- Potassium: The sample solution was pipetted 1.0 mL, diluted in a 50-mL volumetric flask with demineralized water. Subsequently the solution was pipetted 1.5 mL, diluted in a 10-mL volumetric flask with demineralized water.
- Magnesium: The sample solution was pipetted 1.0 mL, diluted in a 100-mL volumetric flask with demineralized water. Subsequently the solution was pipetted 0.5 mL, diluted in a 10-mL volumetric flask with demineralized water.
- Calcium: The sample solution was pipetted of 4.0 mL, diluted in a 10-mL volumetric flask with demineralized water.

All the standard solution was further measured by atomic absorption spectrometer using sodium, potassium, magnesium, and calcium hollow cathode lamp at a wavelength respectively 589.0 nm, 766.5 nm, 285.2 nm, 422.7 nm using air acetylene flame, and the measurement results must be within the concentration range of the series solution of standard sodium, potassium, magnesium, and calcium. The treatment for each sample was repeated six times [8].

2.7. Determination of accuracy and precision

Test of accuracy was done by the standard addition method. Each of the sample matrices (fresh and boiled broccoli and cauliflower) was carefully weighed 10 grams of sample in a crucible porcelain, added 10% of the sodium, potassium, magnesium and calcium minerals level contained in each sample matrix, followed by a dry destruction procedure, dilution procedure as has been done in the assay procedure. Determination of the accuracy of the analysis method is determined by calculation of Recovery Percentage (% Recovery) [10]. Precision test is done by calculating the Relative Standard Deviation (RSD) of the percentage of the Recovery Percentage (% Recovery) that has been obtained from the accuracy test [11,12].

3. Results and discussion

3.1. Determination of linearity, limit of detection and limit of quantitation

Determination of linearity of the each series solution of standard sodium, potassium, magnesium, and calcium was obtained by measuring the absorbance of each concentration of standard solutions at their each wavelength. Furthermore, is the calculation of regression equation, coefficient of determination, and correlation coefficient. Linearity data of the series solution of standard sodium, potassium, magnesium, and calcium can be seen in Table 1, Table 2, Table 3, and Table 4.
After measuring absorbance of each series solution of standard sodium, potassium, magnesium, and calcium at each standard wavelength, then plotting the concentration and absorbance to obtain linearity curves that describes the relationship between concentration and absorbance, and the calculation of the regression line equation, coefficients of correlation and coefficient of determination. Linearity curves of series solution of standard sodium can be seen in Figure 3, linearity curves of series solution of standard potassium can be seen in Figure 4, linearity curves of series solution of standard magnesium can be seen in Figure 5, and linearity curves of series solution of standard calcium can be seen in Figure 6.
Figure 4. Linearity Curves of Potassium

Figure 5. Linearity Curves of Magnesium

Figure 6. Linearity Curves of Sodium
Linearity data of series solution of standard sodium, potassium, magnesium, and calcium followed by calculation of the regression line equation which then obtained regression line is \( Y = 0.18188 \times X - 0.00009 \) for sodium, \( Y = 0.05237 \times X - 0.00027 \) for potassium, \( Y = 0.61116 \times X - 0.00027 \) for magnesium and \( Y = 0.03536 \times X - 0.00017 \) for calcium. The value of the coefficient of correlation \((r)\) calculated for sodium, potassium, magnesium, and calcium respectively is 0.99998, 0.99998, 0.99998, and 0.99997. The value of coefficient of determination \((r^2)\) calculated for sodium, potassium, magnesium, and calcium respectively is 0.99997, 0.99996, 0.99996, and 0.99995. Correlation coefficient and determination coefficient of more than 0.995 indicate a linear correlation and linear determination between \(X\) (concentration) and \(Y\) (absorbance) [13].

### 3.2. Determination of sodium, potassium, magnesium, and calcium levels in the sample

Absorbance measured on an atomic absorption spectrometry according to the wavelength of each mineral. The concentration of the sodium, potassium, magnesium, and calcium minerals in the sample was determined by regression line equation obtained from the determination of the linearity standard solution of each mineral. Results of determination of the sodium, potassium, magnesium, and calcium minerals level in the fresh and boiled broccoli and cauliflower sample can be seen in Table 5.

| Minerals  | Fresh (mg/100g) | Boiled (mg/100g) | Decrease Percentage (%) | Fresh (mg/100g) | Boiled (mg/100g) | Decrease Percentage (%) |
|-----------|-----------------|------------------|-------------------------|-----------------|------------------|-------------------------|
| Sodium (Na) | 118.213± 0.557 | 57.464± 0.275 | 51.39% | 101.213± 0.542 | 51.233± 0.251 | 49.38% |
| Potassium (K) | 727.156± 3.318 | 325.154± 1.637 | 55.28% | 705.540± 3.157 | 300.232± 1.591 | 57.45% |
| Magnesium (Mg) | 8.903± 0.041 | 5.912± 0.029 | 26.95% | 5.004± 0.024 | 3.819± 0.018 | 23.68% |
| Calcium (Ca) | 10.131± 0.054 | 8.751± 0.033 | 13.62% | 6.327± 0.032 | 5.515± 0.021 | 12.83% |

Levels of sodium, potassium, magnesium, and calcium minerals in fresh broccoli and cauliflower differ from literature. The content of phytochemicals and minerals contained in plants is influenced by many factors including seasonal factors, location factors, soil factors, cultivation factors, and varietal factors [14,15].

The data show that after boiled occurs the effect of significantly decreasing levels of minerals in the sample broccoli and cauliflower. The highest to the lowest decreased level of minerals in the sample broccoli and cauliflower are potassium, sodium, magnesium, and calcium. This can be due to oxalate ions which are found mainly in plants through the incomplete oxidation process of carbohydrates. Oxalate ions contained in the plants will form salts with alkali metals and alkaline earth metals. Based on the solubility of the oxalate salt, the potassium oxalate has the highest solubility, followed by sodium oxalate, magnesium oxalate and calcium oxalate have the lowest solubility. Thus, the order of the decrease percentage in sodium, potassium, magnesium, and calcium minerals in broccoli and cauliflower that has been boiled from the highest to the lowest are in line with the solubility of the oxalate salt minerals are potassium, sodium, magnesium, and calcium [6,16].

### 3.3. Determination of accuracy and precision

Test of accuracy was done by standard addition method. Table 6 showed the accuracy test and precision test result data on atomic absorption spectrometry method for determination of sodium, potassium, magnesium, and calcium minerals in each sample with standard addition method.
Table 6. Accuracy Test and Precision Test Result Data for Minerals Determination

| Sample           | Recovery Percentage & Relative Standard Deviation |
|------------------|--------------------------------------------------|
|                  | Sodium   | Potassium | Magnesium | Calcium   |
| Fresh Broccoli   | 98.82%   | 100.75%   | 101.18%   | 99.80%    |
|                  | 0.83%    | 0.65%     | 0.55%     | 0.51%     |
| Fresh Cauliflower| 98.21%   | 101.37%   | 99.18%    | 98.10%    |
|                  | 0.88%    | 0.81%     | 0.64%     | 0.72%     |
| Boiled Broccoli  | 98.99%   | 101.22%   | 100.57%   | 99.31%    |
|                  | 0.54%    | 0.74%     | 0.42%     | 0.67%     |
| Boiled Cauliflower| 98.09%  | 101.75%   | 98.33%    | 100.82%   |
|                  | 0.94%    | 0.88%     | 0.59%     | 0.69%     |

Accuracy test result with Recovery Percentage (% Recovery) parameter and precision test result with Relative Standard Deviation (RSD) parameter in atomic absorption spectrometry method for determination of sodium, potassium, magnesium, and calcium minerals in fresh and boiled broccoli and cauliflower obtained Recovery Percentage (% Recovery) and Relative Standard Deviation (RSD) meets the accuracy and precision requirements, where the value of the Recovery Percentage (% Recovery) is permitted between 98.0% to 102.0% and the value of Relative Standard Deviation (RSD) is permitted not more than 2% [8]. The concentration range obtained for method validation close to the concentration range for linearity determination of sodium, potassium, magnesium, and calcium minerals, 0.10 μg/mL to 0.50 μg/mL for sodium, 0.50 μg/mL to 2.50 μg/mL for potassium, 0.10 μg/mL to 0.50 μg/mL for magnesium, and 1.00 μg/mL to 5.00 μg/mL for calcium.

4. Conclusion

The results showed that boiled broccoli and cauliflower had lower sodium, potassium, magnesium, and calcium minerals compared to fresh broccoli and cauliflower. The highest to lowest minerals decrease percentage are potassium, sodium, magnesium, and calcium. The results of the analysis method validation test of atomic absorption spectrometry with accuracy, precision, linearity, range, limit of detection (LOD), and limit of quantitation (LOQ) parameters meet the requirements.

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