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Macro elemental analysis of food samples by nuclear analytical technique

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Abstract. Energy-dispersive X-ray fluorescence (EDXRF) spectrometry is a non-destructive, rapid, multi elemental, accurate, and environment friendly analysis compared with other detection methods. Thus, EDXRF spectrometry is applicable for food inspection. The macro elements calcium and potassium constitute important nutrients required by the human body for optimal physiological functions. Therefore, the determination of Ca and K content in various foods needs to be done. The aim of this work is to demonstrate the applicability of EDXRF for food analysis. The analytical performance of non-destructive EDXRF was compared with other analytical techniques; neutron activation analysis and atomic absorption spectrometry. Comparison of methods performed as cross checking results of the analysis and to overcome the limitations of the three methods. Analysis results showed that Ca found in food using EDXRF and AAS were not significantly different with p-value 0.9687, whereas p-value of K between EDXRF and NAA is 0.6575. The correlation between those results was also examined. The Pearson correlations for Ca and K were 0.9871 and 0.9558, respectively. Method validation using SRM NIST 1548a Typical Diet was also applied. The results showed good agreement between methods; therefore EDXRF method can be used as an alternative method for the determination of Ca and K in food samples.

1. Introduction

Many studies have demonstrated that the consumption of foods, such as fruits and vegetables is associated with human health improvement. Thus, individuals who eat five or more daily servings of fruits and vegetables have decreased risk of a wide variety development of cancer types, particularly those of the gastrointestinal tract. Other studies have shown that fruits and vegetables alleviate the effects of Alzheimer's disease, diabetes, obesity and metabolic, due to the bioactive components in these foods [1]. Fruits and vegetables are valuable sources of these minerals. Micronutrients in human diet are essential nutrition required by the human body in a small amount. They are needed in maintaining normal physiological function and involved in many metabolism processes [2,3]. An adequate intake of these minerals is essential to prevent deficiency-related diseases. The risk of nutritional deficiency, and of associated pathologic conditions, depends on a wide range of factors, including the magnitude of dietary intake, processing practices, the presence of substances that could reduce or increase mineral bioavailability and the physiologic and health condition of the individual [4,5].

Micronutrients consist of vitamin and mineral. Minerals play an important role in chemical, biological, biochemical, metabolic, catabolic and enzymatic reactions and involved in many metabolism processes in the living cells of plants, animals and human beings and they have great



significance due to their tendency to accumulate in the vital human organs over prolonged periods of time [6,2,3]. A mineral is an element which is needed in an amount of more than 100 mg per day like calcium (Ca) and potassium (K) and they are referred as macro minerals. Calcium is very important in human nutrition due to its direct relationship with bone mass and teeth, it plays a major regulatory role in numerous biochemical and physiological processes, while adequate of both K and Na intake are related to the development of hypertension and potassium is the principle cation in the extra and intracellular fluid [4,7]. They regulate nerves and muscle function. If these essential elements removed from diet, consistent and reproducible impairment of physiological function will occur. The deficiency of these elements results from a combination of poor availability and low intake. All the nutrient elements primarily supplied through diet. For the entire elements essential for metabolism, each of them has a range of intake over which their supply is adequate for the body. However, beyond this range, deficiency and toxic effects are observed [8,9].

Multi elemental methods for food analysis are increasingly attractive and often necessary due to increasing needs for information that is more detailed and for simpler, lower cost analytical methods that are reliable. For this purpose, a wide range of diverse instrumental techniques are available. Atomic Absorption Spectrometry (AAS) is a technique for measuring quantities of chemical elements present by measuring the absorbed radiation by the chemical element of interest. This is done by reading the spectra produced when the sample is excited by radiation [10]. Atomic absorption spectrophotometric technique has specificity, sensitivity, precision, simplicity and relatively low cost per analysis [11]. However, this technique implies a prior total destruction of the matrix by mineral acids, which may lead to problems of contamination by the reactants employed or disturbances of the measured concentration by element losses due to incomplete solubilisation and evaporation; and sample matrix effects must be carefully avoided for certain elements. Moreover, the methods of matrix destruction strongly depend on the chemical composition of the sample and on the element to be determined [12].

Instrument neutron activation analysis (INAA) is a non-destructive, versatile, sensitive, multi-element analytical technique with a very low detection limits that can be used for the investigation of samples [13]. Therefore, INAA is a very useful technique for performing both qualitative and quantitative multi-element analysis of major, minor and trace elements in samples from various fields of scientific or technical interest [14]. It is also having easier samples preparation, no need to dissolve the samples, and less matrices effects. However, NAA is high cost and requires access to a nuclear reactor [15,16] and relatively spent more time to analysis some elements with medium-long lived half time. These made the NAA were not quite suitable to be used for routine analysis. Due to the easier samples preparation, multi-elements and relatively fast analysis time, EDXRF is a potential nuclear analytical technique in the determination of elemental contents in food.

The application of X-Ray Fluorescence spectrometry in the determination of the mineral profile of foods has been reviewed with regard to the tremendous possibilities of these methodologies to provide fast, environmentally friendly alternative methods for evaluating the presence of essential and toxic elements or, at least, to provide screening of the mineral composition of foods and their safety for human nutrition [17]. The use of Energy Dispersive X-Ray Fluorescence spectrometry (EDXRF) for direct and multi-elemental analysis has increased over the last few years. For example; the application of XRF for food analysis such as Mg, P, S, Cl, K, Ca, Mn, Fe, Cu, and Zn in fruits, vegetables, grain products and trace elemental characterization of some food crustacean tissue samples have been carried out [15,18].

This paper described the use of EDXRF method for food analysis and the aim of this work was to demonstrate the applicability of EDXRF for food analysis especially its macro elemental contents. The analytical performance of non-destructive EDXRF was compared with other analytical techniques; neutron activation analysis and atomic absorption spectrometry. This paper reported the concentrations of Ca and K in fruits and vegetables. In addition, the quality control procedures were applied to ensure the precision and accuracy of EDXRF, NAA and AAS methods in food analyses by analyse standard reference materials from the U.S. National Institute of Standards and Technology (NIST).

2. Material and Method

2.1. Chemical and reagent

Stock solutions (Ca and K) of certified atomic absorption references (4000 mg/L) and HNO₃ for trace element analysis, Inductively Coupled Plasma (ICP) standard, standard reference materials, SRM NIST 1548a Typical Diet, deionized water made by filtration through a Millipore-Q system.

2.2. Sample preparation

Each type of food was weighed individually (only edible portion), and then mashed using Titanium blade-blender. Collected food samples were spinach, beans, papaya, star fruit, guava, mango, mangosteen, banana, salak (Indonesian fruit) and watermelon. Food samples that have been smoothed and homogenized were weighted and placed into a small tube, then stored in the freezer until frozen. The tubes filled with frozen samples were then attached to the freeze dryer. Freeze drying process was carried out at -85°C under vacuum for 2x24 hours until the samples dried and had constant weight. Dried samples then refined into fine powder using a Teflon mortar and pestle, and then placed into polyethylene container.

2.3. Analytical procedure for AAS

A 0.5 g powder food sample was dissolved by adding 2.5 mL deionized water, 7.5 mL concentrated HNO₃ and digested using microwave digestion for 20 minutes at 160°C and power 1000 W. The same steps were also applied to SRM NIST 1548a Typical Diet. Measurement of samples was done by flame atomic absorption spectrometer GBC Avanta P. The wavelength observed was 422.70 nm for Ca. The dissolved sample then diluted with deionized water into 25 mL flask and transferred to polyethylene container. The calibration optimum working range for Ca is 0.01-4 mg/L.

2.4. Analytical procedure for NAA

As much as 40-50 mg dried samples powder were placed into 0.3 mL polyethylene vial and then sealed by heating. Samples were then irradiated along with Standard Reference Material (SRM) NIST 1568a Typical Diet and standard 21 µg of K for 15 minute at thermal neutron flux of 10¹³ n.cm⁻².s⁻¹ in rabbit system facilities of multipurpose reactor the G.A. Siwabessy, Serpong. Samples were let to decay for 1 day then measured for 1000 s using a gamma spectrometer with high resolution of HPGe detector. The spectrum was observed using Genie 2000 software [19].

2.5. Analytical procedure for EDXRF

One gram of food samples and reference materials SRM NIST 1648a Typical diet was placed in a disposable plastic cup with 26 mm diameter which was assembled with Mylar; then pressed until the surface was homogeneous. No binder material was applied. The samples were placed in sample holders and loaded into the MiniPal 4 EDXRF spectrometer with two replicates (n=2). Sample were irradiated by X-ray generated from Rh tube (maximum power 9 W, window 75µm Be, maximum high voltage 30 kV, maximum current 300 µA, cooling medium air). Filters was not used in this application because Ca and K were considered as light elements. Matrix effects were corrected by using standards that have similar/approach to the sample matrices. Corrected were also done by applying correction factor from the results of the SRM. Optimum measurement parameters of elements were obtained in the previous study, presented in Table 1 [20].

Table 1. Optimum measurement parameters for the measurement of macro elements in food by Minipal 4 spectrometer [20].

Parameter	Information
Voltage (kV)	14
Current (μ A)	220
Medium or atmosphere	Air
Filter Material	None
Measurement time (s)	900

2.5.1. Lower limit detection (LLD) EDXRF. Lower Limit Detection of X-ray fluorescence method is particularly applicable to the quantitative and qualitative analysis of low concentrations of elements in a wide range of samples as well as allowing the analysis of elements at higher concentrations in limited quantities of materials. LLD of EDXRF was also measured in this study. The LLD was calculated using the following formula

$$LLD = \frac{3}{m} \left(\frac{R_b}{t_b} \right)^{1/2}$$

Where t_b is the time spent counting on the background, R_b is count of background and m is sensitivity [21].

2.6. Quality control

The standard reference material (SRM) was used as quality control assessment of data accuracy and precision. The results of SRM analysis were compared with its certificate value and evaluated its accuracy and precision by % recovery and % Coefficient of Variation (CV) calculation.

3. Result and Discussion

The quality control of analytical results of food samples using AAS, NAA and EDXRF was evaluated by analyzing SRM NIST 1548a Typical Diet. The comparison of measured values with the certified values as well as the accuracy and precision of each method that was describe as % recovery and %CV, were provided in Table 2.

Table 2. Quality control assessment using SRM NIST 1548a Typical Diet.

Reference	Methods	Elements	Result mg/kg	Certified Value (mg/kg)	% Recovery	% CV
Typical Diet (SRM 1548a)	AAS	Ca	1929 \pm 127	1967 \pm 113	98	6.6
		K	6983 \pm 156	6970 \pm 125	100	2.2
	NAA	Ca	1967 \pm 145	1967 \pm 113	100	7.4
		K	6754 \pm 155	6970 \pm 125	97	2.3
	EDXRF	Ca	1820 \pm 90	1967 \pm 113	93	4.9
		K	6375 \pm 192	6970 \pm 125	91	3.0

Table 2 showed that the results obtained were in good agreement with the certified values. The accuracies of the analysis were in the range of 91-100%; while the analytical precisions, described as %CV were in the range of 2.2 to 7.4%. Both analytical accuracy and precision were can be accepted

according to AOAC international guidelines, 90-108%. The measured value for K is out of certified value. However, this result was still in a good agreement with laboratory quality policy that referred to the AOAC guidelines, which requires the results of recoveries on verification methods for the concentration range of 0.1% was 90-108%. While analytical precision, described as % CV were in the range 2.2-7.4% which are fit in its acceptance level of $RSD \leq 15\%$ [22,23,24]. Therefore, it can be concluded that the three methods used for food samples analysis were reliable and accurate.

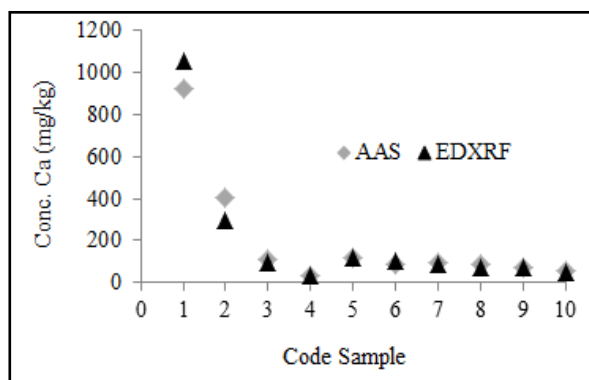


Figure 1. The results of Ca content (wet wt basis) in vegetables and fruits by AAS and EDXRF.

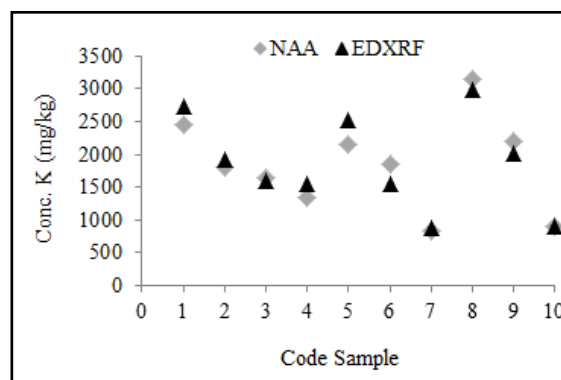


Figure 2. The results of K content (wet wt basis) in vegetables and fruits by NAA and EDXRF.

Table 3. Ca and K content in this study, Spain fruits, marketed internationally and USA.

Elements	Fruits/	Mineral Content mg/kg (wet wt basis)				
	Vegetable	This Study	LLD	Spain [1]	Markets International [1]	USA [9]
Ca	Papaya	97.8-108.0	0.11	190±90	243±50	-
	Starfruit	34.9-36.0	0.08	20±2	26±5	-
	Mango	89.7-103.0	0.19	90±25	64±1	-
	Spinach	927-1059.0	0.17	-	-	1800±420
K	Papaya	1600-1644	0.44	2840±38	1840±130	-
	Starfruit	1343-1541	0.42	1410±150	1450±240	-
	Mango	1551-1848	0.78	1380±210	1670±130	-
	Spinach	2446-2728	0.34	-	-	3600±570

Figure 1 and Figure 2 showed that the content of Ca and K respectively from vegetables (spinach and beans) and fruits samples (papaya, starfruit, guava, mango, mangosteen, banana, salak (Indonesian fruit) and watermelon). The results of EDXRF were close to the results obtained by NAA as well as AAS. The Ca concentrations ranged between 36.0-927mg/kg by AAS, while EDXRF got range between 34.9-1059 mg/kg. The K content of the NAA and EDXRF methods were in the range of 834-3152 mg/kg and 869-2993 mg/kg, respectively.

Concentrations of Ca and K in fruits in this study and results from other countries are summarized in Table 3. Generally, the Ca and K content in fruits and vegetables from this study were in the same range of other countries results. The Ca and K concentrations in the vegetable foodstuffs in our study were less than the values recorded in earlier study from USA. This can be due to the mineral and trace element contents of plants were known to be affected by the cultivar of plant, soil conditions and

weather conditions during the growing, the use of fertilizers and the ripeness of the plants at harvest time [25].

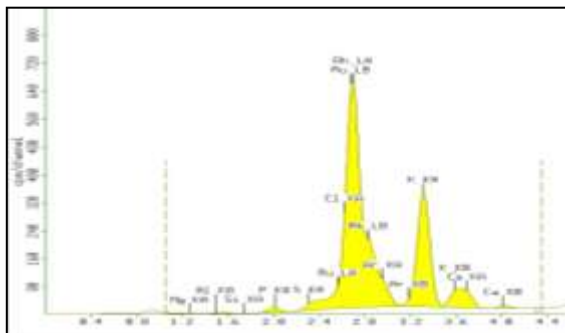


Figure 3. The spectrum of mango sample by EDXRF.

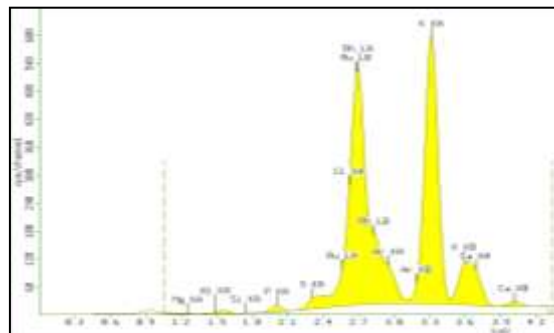


Figure 4. The spectrum of papaya sample by EDXRF.

Figure 3-4 showed EDXRF spectrum of the two samples; dried fruits mango and papaya. Mango and papaya have water content 80.51 and 88.88%, respectively. The analytical results of non-destructive EDXRF were compared with the results obtained by other analytical techniques; neutron activation analysis and atomic absorption spectrometry for analysis of Ca and K content in food samples. Comparison of methods were performed to ensure the analytical results of EDXRF and to overcome the limitations of the three methods. Statistical results of t-test and Pearson correlation of Ca and K in food using EDXRF-AAS and EDXRF-NAA were shown in Table 4 .

Table 4. Results of t-test, content elements Ca and K using EDXRF, NAA and AAS.

Elements	p-value (accept 0.05)	Pearson correlation
Ca	0.9887	0.9871
K	0.6575	0.9558

Table 4 shown that the p-value for both Ca and K are more than 0.05, which means that the results of Ca measurements for fruits and vegetables using EDXRF and AAS were not significantly different. Pearson correlation results for Ca and K were 0.9871 and 0.9558, which showed that there were good correlations between EDXRF and AAS results of Ca content as well as EDXRF and NAA results of K content in food samples. In general, the comparison showed a good agreement between methods; therefore, the EDXRF method can be used as an alternative method for the determination of Ca and K in food samples and can be as complementary method with NAA and AAS methods. However, EDXRF method has advantages over the AAS method for elemental analysis in food samples that EDXRF method does not involve the complex preparation stage such as in NAA and AAS methods. It has good accuracy up to the levels of trace elements. It is also simultaneous or multiple elements analysis, fast and cost-effective. Furthermore, it provides a fairly uniform detection limit across a large portion of the periodic table and is applicable to a wide range of concentrations from a 100% to few parts per million (ppm). Detection limits for Ca and K used EDXRF Minipal 4 were 0.08-0.19 and 0.34-0.78 mg/kg, respectively. Its main disadvantage is that analyses are generally restricted to elements heavier than fluorine [14].

The XRF method used in these analyses exhibited consistent accuracy, with well-defined precisions that were proportional to element concentrations. The consistency was promoted by automated analysis of samples and data, which avoided operator judgements, adjustments, and other interactions beyond sample preparation. Potential contamination and recovery problems related to

chemical dissolution were avoided by direct analysis of the solid, lyophilized sample pellets. By reanalysing samples non-destructively, actual analytical precisions were measured separately from homogeneity-related variations among replicate sample aliquots. The resulting analyses suggested that most of the fruit and vegetable materials were sufficiently homogeneous to be well represented by the measured mean mineral concentrations.

4. Conclusion

The EDXRF spectrometry was used for the determination of Ca and K contents in fruits and vegetables and evaluated its accuracy, precision and its conformity with other analytical techniques; NAA and AAS. The EDXRF method was quite accurate and precise to determine Ca and K content in fruits and vegetables. Prior notification should be taken to the limit of quantification of each XRF spectrometer to be used. Good comparability with NAA and AAS showed by statistical results (p-value) confirming no significant difference between EDXRF and both NAA/AAS methods. Therefore, and with its advantages of easier sample preparation and relatively fast analysis made the EDXRF potential to be used as an alternative and complementary analytical method to determine Ca and K in food matrix samples.

References

- [1] Alvarez M B, Andrade C D, Haro A, Olalla M, Seiquer I and Henare J A 2016 *Journal of Food Composition and Analysis* **48** 34-40
- [2] Pascal L, Andre B, Fernando E and Angela ML 2006 *Food Chemistry* **95** 644-652
- [3] Endah D, Widya A, Muhayatun S, Syukria K and Woro YNS 2011 *J.Atom Indonesia* **37** 62-70
- [4] Montserrat B A, Cristina D A, Ana H, Manuel O, Isabel S and Jose A R H 2016 *J. Of Food Composition and Analysis* **48** 34-40
- [5] Vrhovnik P, Dolenc M, Serafimovski T, Tasev G and Arrebola J P 2016 *Science of the Total Environment* **559** 204-211
- [6] Vishal M and Vishwa 2012 *APCBEE Procedia* **2** 135-140
- [7] Mofida WAE and Khairia MAAA 2005 *JKAU: Sci.* **17** 117-129
- [8] Edet OA 2006 *Journal of Nutrition* **5** 198-202
- [9] Alplasan A, Osman S, Birol E and Mehmet E 2008 *Spectroscopy* **22** 57-62
- [10] Rocío G and Armando AB 2012 *Atomic Absorption Spectrometry* (Intech) p 258
- [11] Sadia A, Feroza H W, Mahmood A, Muhammad H S W, Syed A T and Abdul W 2015 *Alexandria Journal of Medicine* **51** 19-23
- [12] Marijan N, Peter K, Janez S, Radojko J and et al 2008 *Spectrochimica Acta Part B.* **63** 1240-47
- [13] Supalak K, Wanne S, Phachirarat S and Arporn B 2016 *Energy Procedia* **89** 361-365
- [14] Hayder S N, Pegah M K and Eid M E 2013 *J. Chem.Chem. Eng* **7** 803-807
- [15] Kirk K N, Arthur W M, Lisa S W and Vern C R 1991 *Journal of Food Composition and Analysis.* **4** 39-51
- [16] Ravisankar R, Naseeruthen A, Chandrasekaran A, Satya N B, Kanagasabapthy K V, Prasad Mvr and Satpathy K K 2014 *Journal of Radiation Research and Applied Sciences.* **7** 44-54
- [17] Miguel D L G and Salvador G 2015 *Handbook of Mineral Elements in Food*, First Edition (Spain: John Wiley & Sons. Ltd) p 285
- [18] Anil M, T R Rautray, V Vijayan, Rajeeb K M and S K Dey 2007 *Aquaculture* **270** 552-558
- [19] Endah D, Widya D A, Muhayatun S, Syukria K and Woro YNS 2011 *Atom Indonesia* **37** 62-70
- [20] Woro Y N S, Endah D, Syukria K and Diah D L 2015 *Proc.of National Conference on Science and Nuclear Technology* (Bandung: Batan) pp 323-329
- [21] Selma MHAIJ 2009 *Journal of Kirkuk University Scientific Studies* **4** 12-19
- [22] Anonymous 2002 *Guidelines For Single Laboratory Validation* (AOAC International)
- [23] Anonymous 2011 *Guideline on Bioanalytical Method Validation* (United Kingdom: European Medicines Agency) p 8
- [24] Gustavo G and Angeles HM 2007 *Trends in Analytical Chemistry.* **26** 227-238

- [25] Ekholm P, Reinivuo H, Mattila P, Pakkala H and Koponen J 2007 *Journal of Food Composition and Analysis* **20** 487-495

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