

Full Length Research Paper

Mineral content in French type bread with sodium replacement using fluorescence spectrometry X-rays by energy dispersive

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Received 18 August, 2015; Accepted 26 October, 2015

The present study aimed to determine the mineral composition of the French type bread with partial replacement of sodium chloride by potassium chloride using the technique of X-ray fluorescence energy dispersive. The excitation energy used was 50 keV and detector operation at -176°C . The detected variations were from 10.16 to 613.69 mg 100 g^{-1} for sodium and from 211.58 to 958.96 mg 100 g^{-1} for potassium. The concentrations of iron, magnesium, phosphorus and calcium ranged from 10.62 to 21.45, 16.59 to 30.78, 92.53 to 125.77 and from 16.54 to 100.88 mg 100 g^{-1} , respectively. The use of this simple technique proved to be reliable on detecting the variations imposed on the French type bread formulation. The results of this study indicate that, at the levels studied, the addition of potassium chloride assisted in getting French type bread with lower levels of sodium and proved the technological feasibility of producing French type bread with 43% salt reduction (1.0% in the commercial formulation) with 0.5% potassium chloride, which provide bread with the amount of sodium proposed to meet the set limits (174.09 mg 50 g^{-1}), related to the salt standard formulation of 1.88% (306.5 mg 50 g^{-1}).

Key words: French bread, replacement, sodium chloride, potassium chloride, food analysis, minerals, energy dispersive.

INTRODUCTION

The reduction of salt (sodium chloride) is a public health problem in many countries because it has been identified as the main cause of various diseases such as

hypertension, renal diseases, stomach cancer, osteoporosis, stroke and obesity (He and Macgregor, 2010). Most of the salt in human diets is found in

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Table 1. Ingredients of the formulations expressed in percentage (in flour basis) for French type bread formulations.

Ingredients (%)*	Formulations						
	FP	FP1	F1	F2	F3	F4	F5
Wheat flour	100	100	100	100	100	100	100
Water	40	40	40	40	40	40	40
Ice	12.5	12.5	12.5	12.5	12.5	12.5	12.5
Biological yeast	3	3	3	3	3	3	3
Margarine	1.25	1.25	1.25	1.25	1.25	1.25	1.25
Flour improver	1	1	1	1	1	1	1
NaCl	1.88	0	0.4	1.6	0.4	1.6	1
KCl	0	1.88	0.2	0.2	0.8	0.8	0.5

*Values are expressed as % of wheat flour.

processed foods. The majority of people have no idea about the salt content of food, nor the amount of salt they are eating. As a result, the intake of high sodium content occurs without the knowledge of the consumers (Dótsch et al., 2009).

A recent review of studies evaluating sodium intake in many countries has shown that in most populations, the mineral consumption is above 2,300 mg day⁻¹, and particularly in China and Japan, the average was above 4,600 mg day⁻¹ (Brown et al., 2009). In Brazil, it was observed that the consumption varied between 3,100 and 4,900 mg day⁻¹ (Sarno, 2010). The current recommendation of the World Health Organization for daily intake of sodium is 2,000 mg (WHO, 2007). Of all foodstuffs, French type bread was identified as a major contributor to the total daily intake of salt (Dewettinck et al., 2008).

A way of reducing the sodium is a partial replacement by another salt. The most used is potassium chloride (KCl), which has similar properties to NaCl, is regarded as safe and can be used without loss of technological property. However, addition of potassium chloride is restricted due to the bitter taste that it gives to the product when used in large quantities. In wheat bread, the replacement of 55.2% of potassium chloride, 69.0% magnesium chloride and 34.8% calcium chloride was possible (Charton et al., 2007).

Several methods can be used to determine the amount of sodium chloride on bread, based on the determination of sodium or chloride. In published studies on this subject, the official analytical methods more applied are atomic absorption spectrometry, sodium direct potentiometry and classical titration for chloride. Generally, these techniques require prior partial or total destruction of organic matter in the sample and require a long time for its analysis, as well as providing loss of volatile elements, which has led to the search for faster alternatives (Castanheira et al., 2009; Julshamn et al., 2005; Yperman et al., 1993).

The fluorescence spectrometry X-ray by energy dispersive (EDXRF) is a nondestructive technique that

can be applied directly to solid samples without requiring complex preparations. Although, it has the disadvantage of not achieving detection limits comparable to the techniques of atomic spectrometry, it has great advantages such as simplicity, safety, low cost, minimal use of glassware, generates little or no waste and eliminates the step of decomposition of the sample. Another advantage of EDXRF over other spectroscopic techniques is the absence of chemical interference, since it involves the participation of electron inner layer and it is therefore insensitive to the chemical form that the element lies (Oliveira et al., 2006).

This paper proposed a method for the determination of minerals in samples of French type bread with partial replacement of sodium chloride with potassium chloride, employing fluorescence spectrometry x-ray by energy dispersive.

MATERIALS AND METHODS

The raw materials used in the production of breads were: wheat Gold Medal (M. Dias Branco) flour; flour improver (Zeas; contained corn starch, stearyl lactylate, ascorbic acid and amylase); margarine (Primor); fresh yeast (Fleishman); sodium chloride (Cisne) and potassium chloride (Plury).

Production of breads

Breads were produced by employing a standard formulation with 1.88% sodium chloride (PF) and a formulation with 1.88% potassium chloride (FP1). Replacement levels of sodium chloride with potassium chloride in other formulations (F1, F2, F3, F4 and F5) were based on the positive results of previous studies on French bread type (Charlton et al., 2007; Ignacio et al., 2013). The formulations of the breads are presented in Table 1.

The production of breads was carried out by the straight dough process with batches of 4.0 kg of wheat flour. The ingredients were mixed in supreme spiral dough mixer (Model SR 15, São Paulo, Brazil). This step was performed in two phases: slow speed (90 rpm) for 5 min, and fast speed (180 rpm) for 5 min fixed for all breads. Water was used at a temperature of about 10°C to obtain the final dough temperature of about 28°C. After mixing, the dough was divided into pieces of 1.8 kg and divided into portions of 60 g,

Table 2. Mineral content of French bread with partial substitution of sodium chloride with potassium chloride.

Formulations	Levels of minerals (mg 100 g ⁻¹)**						
	Sodium	Potassium	Chloride	Iron	Phosphorus	Magnesium	Calcium
F1	110.78 ^e ±1.57	211.58 ^f ±0.58	172.22 ^f ±0.87	214.5 ^a ±1.42	125.77 ^a ±1.69	24.38 ^b ±0.73	100.98 ^a ±1.19
F2	490.91 ^b ±0.69	322.97 ^d ±1.44	590.87 ^d ±1.41	16.39 ^{bc} ±0.35	92.53 ^c ±0.83	16.59 ^e ±0.25	48.55 ^{cd} ±0.63
F3	144.38 ^d ±1.83	474.56 ^b ±0.36	412.09 ^e ±1.80	13.25 ^{cd} ±0.92	94.65 ^c ±1.01	22.41 ^c ±0.69	18.88 ^e ±0.10
F4	490.86 ^b ±1.10	481.65 ^b ±0.52	901.64 ^a ±1.76	18.39 ^{ab} ±0.60	96.78 ^{bc} ±0.21	30.72 ^a ±0.12	65.97 ^b ±0.67
F5	348.18 ^c ±0.98	367.11 ^c ±0.94	590.72 ^d ±1.35	10.62 ^d ±0.49	79.50 ^d ±1.59	18.40 ^d ±0.49	46.54 ^d ±0.39
FP	613.69 ^a ±0.85	247.77 ^e ±0.18	728.76 ^c ±1.10	14.40 ^c ±0.50	102.54 ^b ±0.45	30.78 ^a ±0.53	66.01 ^b ±0.09
FP1	10.16 ^f ±0.28	958.96 ^a ±1.01	747.46 ^b ±1.40	16.61 ^{bc} ±0.15	102.22 ^b ±0.29	29.70 ^a ±0.56	50.97 ^c ±0.56

**Values expressed as mean of three replicates ± standard deviation. Averages followed by the same letter in the same column do not differ statistically ($P > 0.05$) by Tukey's test.

left to rest for 20 min and molded in the shape of French type bread in shaping model HM2 0.5 Hp (Hypo, Ferraz de Vasconcelos, SP, Brazil), arranged on drilled trays and allowed to proof in the fermentation chamber with temperature around 32°C and relative humidity of 80% for a period of 8 h. After fermentation, the surface was cut and the baking process was performed in an electric oven with steam injection for 15 min at 220°C. The cooling of the loaves was performed in wire mesh at room temperature.

Determination of the content of mineral

The minerals were quantified by Energy Dispersive X-Ray Fluorescence (EDXRF) model EDX-720 (Shimadzu - Japan) from ashes of the breads. The total ash was measured according to AOAC Official Method 923.03 (AOAC, 1997). The samples were placed in a cuvette covered with a polypropylene film of 5 µm in thickness. The X-ray tube used was rhodium and the working atmosphere was nitrogen. The excitation energy used was 50 keV and detector operated at -176°C. Analyses were performed in triplicate.

Determination of specific volume

The specific volume of the breads was determined by method 10-05.01 of the AACC (2000) on the same day in which they were processed. These determinations were performed in decaplicate ($n = 10$).

Analysis of results

Data were statistically analyzed by analysis of variance (ANOVA) and Tukey's test was applied to check the significant differences between the averages with a significance level of 0.05, using the statistical package Statistica version 5.0 (Statsoft, 2004).

RESULTS AND DISCUSSION

In Table 2, there are concentrations of sodium, potassium, chloride, phosphorus, magnesium, iron and calcium in bread of different formulations. The variation was from 10.16 to 613.69 mg 100g⁻¹ for sodium and from 211.58 to 958.96 mg 100g⁻¹ for potassium. The sodium content decreased with the percentage of substitution of sodium

chloride by potassium chloride. F5 formulation (1.0% NaCl and 0.5% KCl) provided a 43% reduction in sodium from the standard formulation (FP) with 1.88%, which would mean that a 50 g bread would pass from 306.84 mg to 174.90 mg sodium.

Similar results were found by Ignatius et al. (2013). By replacing sodium chloride with potassium chloride in 30 and 50% on French bread, they found values ranging from 8.87 to 613.87 mg 100g⁻¹ for sodium and from 156.20 to 548.72 mg 100g⁻¹ for potassium.

According to the Best Practice Guidelines for Nutritional Bread French by ANVISA (Brazil, 2013), it was agreed that the addition of salt to the product be gradually reduced from 2 to 1.8% by the end of 2014, representing a reduction 10% of the amount of sodium in the product. Thus, a unit of French bread (50 g) currently that had an average 320 mg sodium, will have 288 mg in 2014.

The presence of sodium and potassium in the formulations FP1 and FP can be explained in part by the composition of minerals from wheat flour, which has sodium content close to 1 mg 100g⁻¹ and near 151 mg 100 g⁻¹ potassium (TACO, 2011).

A Canadian study of Na and K content of 154 foods consumed widely representative in this country, found values of sodium and potassium to bread: 601.2 and 121.4 mg 100 g⁻¹ respectively. These authors recommended decreasing sodium intake and increase potassium intake (Tanase et al., 2011).

The amount of chlorine ranged from 172.22 to 901.64 mg 100g⁻¹, a very high rate. This can be justified by the amount of chlorides (sodium chloride + potassium chloride) present in the sample in lesser and greater amounts.

The concentrations of iron, phosphorus, magnesium and calcium ranged from 10.62 to 21.45; 79.50 to 125.77; 16.59 to 30.78 and 18.88 to 100.88 mg 100g⁻¹, respectively. The presence of these minerals is justified by the use of wheat flour, which is the main raw material in the manufacture of bread and these elements are present in the same concentrations of 1.0 mg 100 g⁻¹ for iron, 115 mg 100 g⁻¹ for phosphorus, 31 mg 100 g⁻¹ for

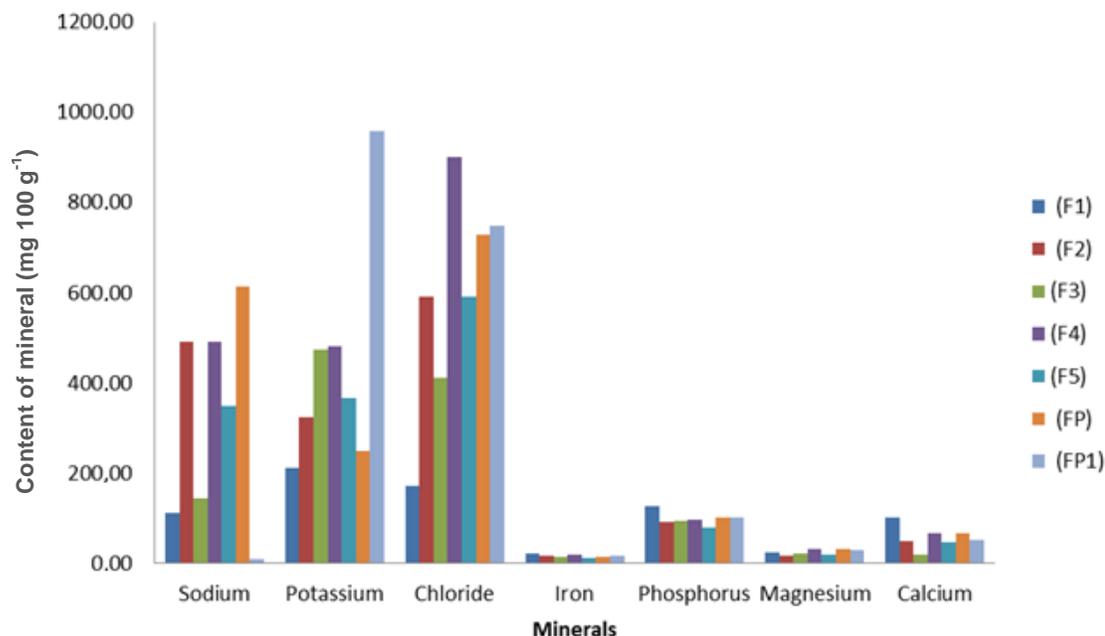


Figure 1. Mineral content of French type bread with partial substitution of sodium chloride by potassium chloride.

magnesium and 18 mg 100 g⁻¹ for calcium (TACO, 2011).

In a study conducted in France, were analyzed the contents Na, K, Mg and Ca by atomic emission spectrometry (AAS) in 1319 foods commonly consumed by the population. For the 14 bread samples analyzed, these authors found values of Na varying from 669.6 to 1001.00 mg 100 g⁻¹ with an average of 669.6 mg 100 g⁻¹. Mg values ranging from 27.7 to 70.3 mg 100 g⁻¹ were found to have an average of 40.6 mg 100 g⁻¹. For Ca, they found a variation from 18.4 to 130.0 mg 100 g⁻¹ with an average of 47.7 mg 100 g⁻¹. K values have a range of 154.0 to 362.0 mg 100 g⁻¹ with an average of 238.9 mg. The bread is included in the cereals group, which is responsible for the eighth position for the Ca intake, fourth to Mg intake, third for the intake of Na and has the first position of K intake (Chekri et al., 2012).

Due to the high rates of anemia and diseases caused by deficiency of folic acid in the Brazilian population, the Ministry of Health and ANVISA become compulsory in the fortification of flour and corn. With the publication of Resolution - RDC no. 344, of December 13, 2002, each 100 g of wheat and maize flour should contain 4.2 mg of iron and 150 mg folic acid. Thus, flours and products such as breads, pasta, cookies, cake mixes and snacks should contain higher amounts of iron and folic acid in the final formulation (Brazil, 2002).

A potentiometric study compared two methods with a reference method (atomic absorption spectrometry) to determine the level of salt (sodium chloride) into bread in various cities in the north of Portugal. Significant differences between the results of the two analysis

methods were proposed as the content of sodium chloride exceeded the legal limit methods when using potentiometric methods, but when using atomic absorption spectrometry method, they were not observed. The difference between the results of methods emphasizes that care must be taken when analyzing samples for lawful purposes. Therefore, it is advisable that the authorities provide additional information about the review process that must be followed (Plácido et al., 2012).

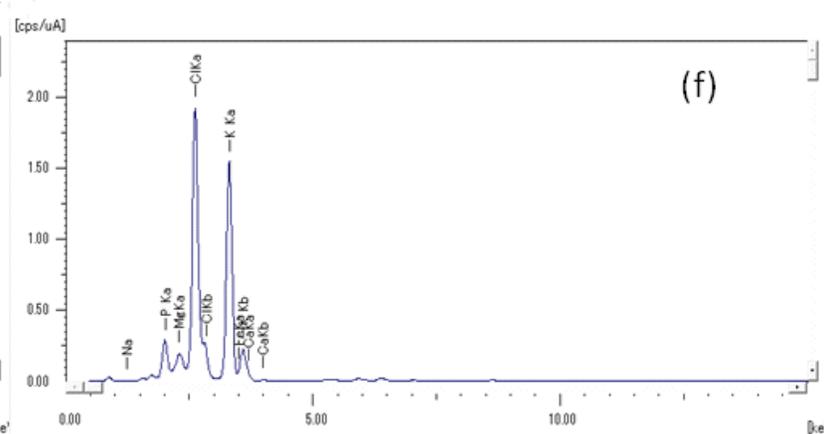
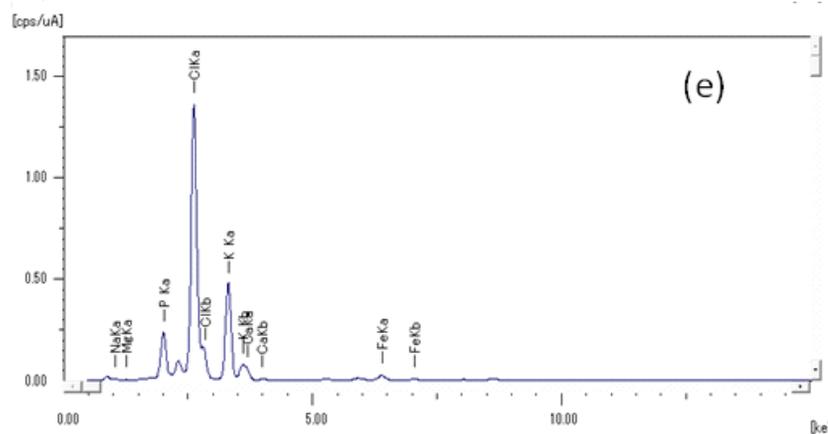
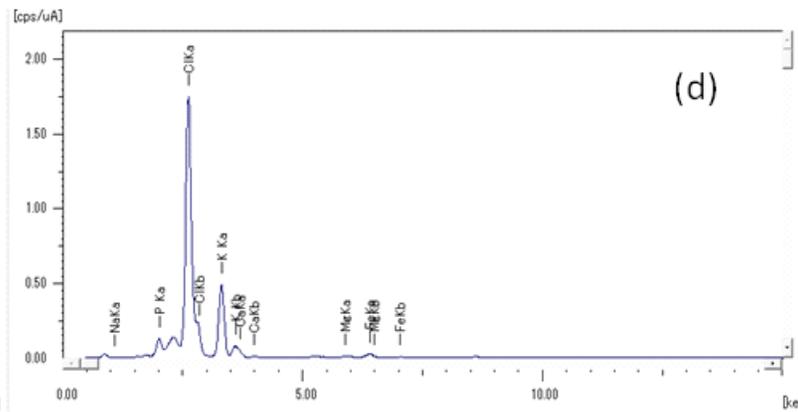
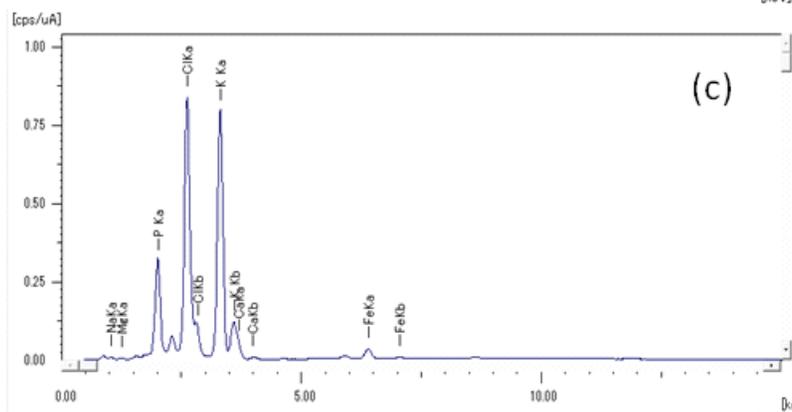
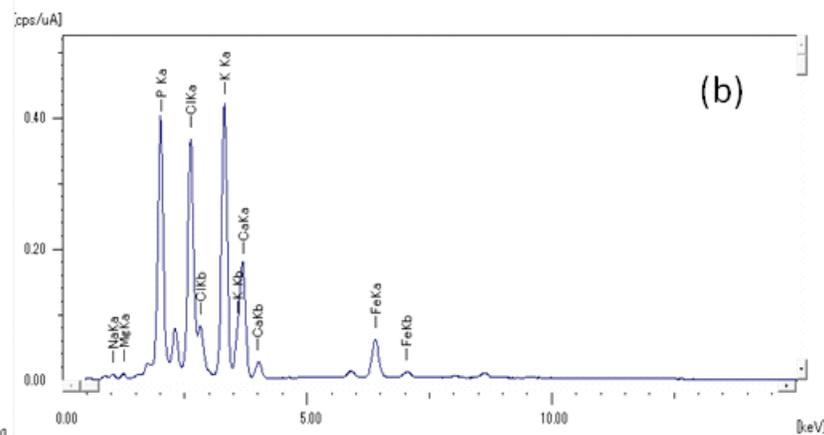
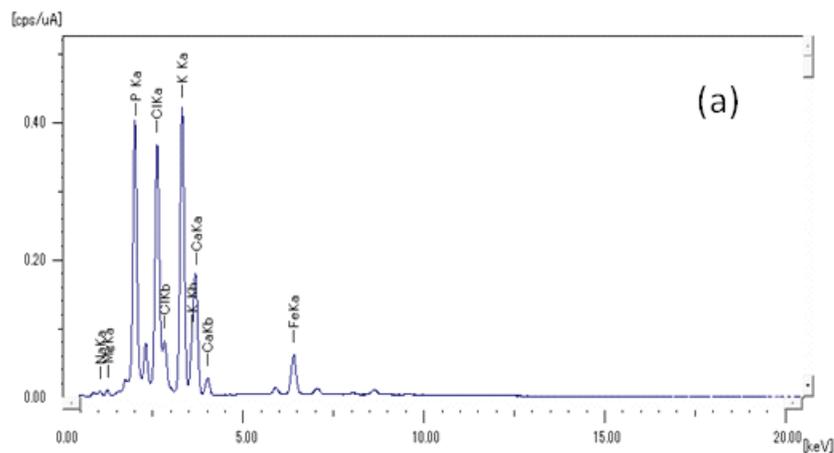
The replacement of sodium chloride by potassium chloride did not significantly alter their specific volumes. The average specific volume of samples FP, FP1, F1, F2, F3, F4 and F5 were 7.00, 5.82, 7.38, 6.07, 6.98, 6.50 and 6.95 cm³ g⁻¹, respectively. Yi and Kerr (2009), considered a satisfactory specific volume which are situated in the range of 5.0 and 8.0 cm³ g⁻¹.

It can be seen in Figure 1 that the minerals that are in larger quantities are potassium, chloride, sodium, phosphorus and calcium. The iron and magnesium are present in smaller quantities.

Figure 2 shows the spectra of X-ray fluorescence of the samples with the characteristic emission lines for each mineral. Each peak corresponds to the characteristic energy of each mineral present in the sample.

Conclusion

In the present work, French type bread formulation was successfully altered to lower sodium chloride content.



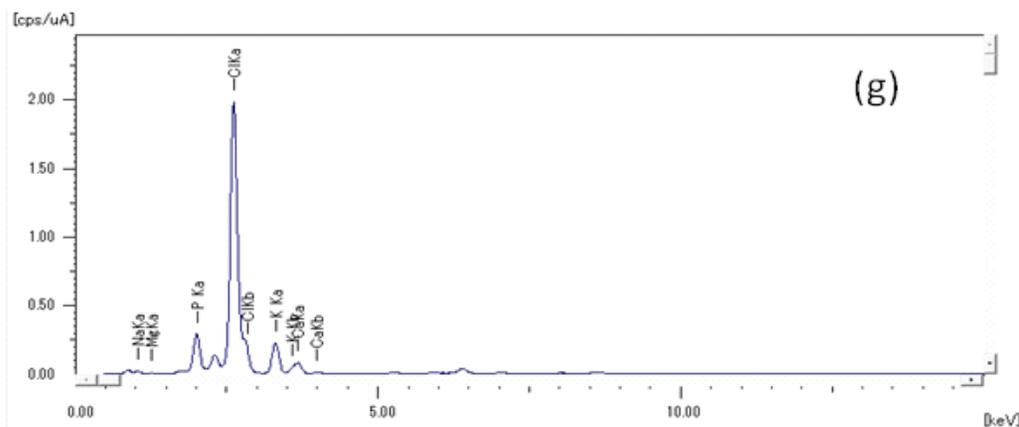


Figure 2. Fluorescence spectra of X-ray by energy dispersive samples of French bread. (a) F1; (b) F2; (c) F3; (d) F4; (e) F5; (f) FP1; (g) FP.

The variation of sodium in French bread type was 10.16 to 613.69 mg 100 g⁻¹ and 211.58 to 958.96 mg 100 g⁻¹ for potassium. Sodium content decreased with the increasing replacement percentage of potassium chloride. The amount of chloride ranged from 172.22 to 901.64 mg 100g⁻¹. Concentrations of iron, magnesium, phosphorus and calcium ranged from 10.62 to 21.45; 16.59 to 30.78; 92.53 to 125.77 and from 16.54 to 100.88 mg 100 g⁻¹, respectively. The presence of these minerals is justified by the use of wheat flour, which is the main raw material in the manufacturing of bread. The use of EDXRF, which is a simpler method, proved to be reliable on detecting the variations imposed on the French bread formulation and an alternative to determining the mineral content in the food.

Conflict of Interests

The authors have not declared any conflict of interests.

REFERENCES

- AACC (2000). Approved methods of the American Association of Cereal Chemists (10th ed.). St. Paul, MN: The Association.
- AOAC (Association of official analytical chemists) (1997) Official methods of analysis of AOAC International. Gaithersburg.
- Brazil, Agência Nacional de Vigilância Sanitária – ANVISA (2002) Guia de boas práticas nutricionais pão francês. Available from: <http://portal.anvisa.gov.br>. (accessed 02 July 2014).
- Brazil, Agência Nacional de Vigilância Sanitária – ANVISA (2013) Resolução RDC nº 344, de 13 de dezembro de 2002. Aprova o Regulamento Técnico para fortificação de farinhas. Available from: <http://www.anvisa.gov.br/alimentos/farinha.htm>. (accessed 14 October 2014).
- Brown IJ, Tzaulaki I, Candeias, V, Elliot P (2009) Salt intakes around the world: implications for public health. *Int. J. Epidemiol.* 38(3):791-813.
- Castanheira I, Figueredo C, André C, Coelho I, Silva TA, Santiago S, Fontes T, Mota C, Calhau AM (2009). Sampling of Bread for added sodium as determined by flame photometry. *Food Chem.* 113:621-628.
- Charton EK, Mac Gregor E, Vortes HN, Levitt SN, Stey K (2007). Partial replacement of NaCl can be achieved with potassium, magnesium and calcium salts in brown bread. *Int. J. Food Sci. Nutr.* 58(7):508-521.
- Chekri R, Noel L, Millour S, Vastel C, Kadar A, Sirot V, Leblanc JC, Guérin T (2012). Calcium, magnesium, sodium and potassium levels in foodstuffs from the second French Total Diet Study. *J. Food Compos. Anal.* 25:97-107.
- Dewettinck K, Van Bockstaele F, Kuhne B, Van De Walle D, Courtens TM, Gellynck X (2008). Nutritional value of bread: influence of processing, food interaction and consumer perception. *J. Cereal Sci.* 48(2):243-257.
- Dótsch M, Busch J, Batenburg M, Liem G, Tareilus E, Mueller R (2009) Strategies to reduce sodium consumption: a food industry perspective. *Crit. Rev. Food Sci.* 49(10):841-851.
- He FJ, Macgregor GA (2010). Reducing population salt intake worldwide: from evidence to implementation. *Prog. Cardiovasc. Dis.* 52(5):363-382.
- Ignácio AKF, Rodrigues JTD, Niizu PY, Chang YK (2013). Efeito da substituição de cloreto de sódio por cloreto de potássio em pão francês. *Braz. J. Food Technol.* 16(1):1-11.
- Julshamn K, Lea P, Norli HS (2005). Determination of sodium in foods by flame atomic absorption spectrometry after microwave digestion: NMKL interlaboratory study. *J. AOAC Int.* 88(4):1212-1216.
- Oliveira AL, Almeida E, Silva FBR, Nascimento VFF (2006). Elemental contents in exotic brazilian tropical fruits evaluated by energy dispersive x-ray fluorescence. *J. Agric. Sci.* 63(1):82-84.
- Plácido A, Kupers R, Paíga P, Magalhães J, Nouws HPA, Delerue-Matos C, Oliveira MBPP (2012). Salt content in bread and dough from northern Portugal: Method development and comparison. *J. Food. Compos. Anal.*

- 27(1):14-20.
- Sarno F (2010). Estimativas do consumo de sódio no Brasil, revisão dos benefícios relacionados à limitação do consumo deste nutriente na síndrome metabólica e a avaliação do impacto de intervenção no local de trabalho. PhD Thesis, School of Public Health, SP.
- Statsoft (2004) Statistica for Windows, Tulsa, USA.
- TACO (Tabela Brasileira de Composição de Alimentos) (2011). Available from: <http://www.unicamp.br/nepa/taco/tabela.php?ativo=tabela> (accessed 20 August 2014).
- Tanase CM, Griffin P, Koski KG, Cooper MJ, Cockell KA (2011). Sodium and potassium in composite food samples from the Canadian Total Diet Study. *J. Food Compos. Anal.* 24(2):237-243.
- WHO (World Health Organisation) (2007). Reducing salt intake in populations. Report of a WHO Forum and Technical Meeting. Geneva, Switzerland, WHO Document Production Services.
- Yi J, Kerr WL (2009) Combined effects of dough freezing and storage conditions on bread quality factors. *J. Food Eng.* 93:495-501.
- Yperman J, Carleer R, Reggers G, Mullens J, Van Poucke L (1993). Automation of potentiometric measurements – determination of water-extractable sodium in bread using a sodium-ion selective electrode with minimum sample preparation. *J. AOAC Int.* 76(5):1138-1148.