ABSTRACT
Fish is an important food in many Iranian diets. This is a good source of protein. Fish is the main source of animal protein in Iran. The effects of three different traditional processing methods (freezing, brining and frying) on nutritive composition of halva sia fish stored under ambient room conditions were determined. Fresh halva sia fish were obtained from Behbahan fish market. Cooking and processing techniques were carried out on fish Halva sia Parastromateus niger. The proximate composition of raw Parastromateus niger was affected by cooking and processing techniques that were carried out by AOAC methods. Moisture contents decreased in fried and brined fillet while protein, fat and ash contents were significantly increased in fried fillet. The loss of moisture in fried and brined samples amounted to the highest levels; also the protein and fat values was proportionally high. The fish Parastromateus niger showed a decrease in their contents of moisture and fat as affected by frozen storage periods while ash and protein contents were increased after frozen storage periods. The nutritional value fish Parastromateus niger preserved until the end of the storage period.

Keywords: frying; brining; fish; Parastromateus niger; freezing; proximate composition

INTRODUCTION
Fish can be a source of protein for humans. In addition, with proper processing methods, it can also generate foreign exchange (Mazrouh, 2015). The nutrients composition of fish is essential in fish processing, as it affects both its quality and technological properties (Farid et al., 2014). In addition, conservation and processing can result in fish availability throughout the year (Ben Smida et al., 2014; Oparaku, and Nwaka, 2013). Different methods of processing fish have different effects on their properties physico-chemicals, organisms and nutrients. (Akinneye, Amoo, and Bakare, 2010). These effects can be caused by physicochemical changes, which affect digestion due to protein denaturation and reduced content of unsaturated fatty acids. The quality and shelf life of the fish varies with different methods and with acceptance by consumers (Mojisola, 2014). Freezing and thawing have many effects on the physicochemical properties of frozen fish fillets. Boonsumrej et al., (2007) found that rapid shrimp freezing in cryogenic freezers at temperatures of -120 °C, which has very good effects on nutrient composition. Several changes have occurred during fish processing. Depending on the amount of heat and temperature, protein denaturation may result in exposure to reactive groups. Most proteins are compounds that can change in the heat process in terms of quality and quantity. The decrease solubility of temperature-sensitive protein can be used as an indicator of the time and temperature used in the heating process of fish species and fish products (Akinneye, Amoo, and Bakare, 2010.; Mojisola, 2014; Boonsumrej et al., 2007; Alipour et al., 2010; Sarker et al., 2012).

El and Kavas (1996) has been reported that protein digestion to be reduced as a result of chemical reactions of the protein or protein with fat when boiling at high temperatures. Pourshamsian et al., (2012) reported that frying has the effects on the nutritional composition and properties of fish fatty acids and fish products. However, no basic information has been reported on the effects of processing methods on the nutritional and physical properties of fish processed in Eritrean fish processing plants. In general, different fish processing methods can include frostbite, freezing, salting, frying and boiling, and various combinations of this kind to give the fish a fresh and attractive form for the consumer and to provide long-term shelf life. These processing methods have many different applications and techniques and have a significant impact on the chemical, physical and nutritional composition of processed fish. This is because heating, freezing, and exposure to high salt concentrations lead to chemical and physical changes.
Finally, these methods can be of varying quality, so the subsequent effect on the shelf life of processed fish also varies (Magnussen, Hemmingsen, and Vidar Hardarsson 2008; Lourdes et al., 2007). The cooking processes are widely carried out to increase the quality of seafood and to extend the shelf life of the products (Talah, 2014). During the cooking process, some physical and chemical changes occur that decrease the nutritional value of the food. Thus, digestibility is increased due to protein denaturation in foods, while the content of thermo sensitive labile compounds, vitamins or unsaturated fatty acids is often reduced (Alizade et al., 2009). The aim of current study was to follow up the changes which occur in proximate composition of Parastromateus niger by frying, brining and freezing techniques.

The preservation and processing can assure availability of fish in all year round (Smida et al., 2014; Oparaku et al., 2013). The bio-chemical composition of fish is the vital aspect in fish processing, because which influences both the quality and technological properties of it (Farid et al., 2014). Different processing methods of fish have different effect on their physicichemical and nutritional compositions (Akinneye, et al., 2010).

Scientific hypothesis
The processing methods (freezing, brining and frying) have effects on nutritive composition and energetic values of fish Parastromateus niger.

MATERIAL AND METHODOLOGY
Sample collection and preparation
The fish samples with three replicates of Black pomfret (Parastromateus niger) (Figure 1) with an average weight of 1100-1700 g were procured from the Behbahan city local market, Iran. The fish were gutted and washed with the tap water. The sampled fish was cut down into sex parts; one as fresh sample was used and the three parts were used for freezing 7, 21 and 35 days and a part was used for frying in oil and last part was used for brining process. All the samples were used for proximate analysis in laboratory.

Proximate analysis
The moisture, protein, lipid and ash content of the fish samples were determined by the AOAC (2005).

Protein determination
Protein was determined using Kjeidahi method which involves digestion, distillation and titration as recommended by AOAC (2005). The percentage protein was obtained using the formula: 

\[ \text{% Protein} = \frac{N}{6.26} \]

Where \( N \) is nitrogen free extract.

Moisture determination
Moisture was determined using method as recommended by AOAC (2005). Percentage of moisture was calculated using the formula; 

\[ \text{% water} = \frac{W_i}{W_o} - 1 \times 100 \]

Where; \( W_o \) = initial weight, \( W_i \) = final weight.

Fat analysis
Fat was determined using soxhlet method as recommended by Association of official analytical (AOAC, 2005) the percentage fat will be obtained

\[ \text{% fat} = \frac{W_o - W_i}{W_o} \times 100 \]

Where:
\( W_o \) = Initial weight of fat,
\( W_i \) = final weight of fat.

Determination of pH
A 5 g sample of the fish sample was homogenized in 40 ml of distilled water and the mixture was filtered. The pH of the filtrate was measured using a pH meter (Mettler Toledo 320-s, Shanghi, China) (Vynke, 1981).

Statistical Analysis
Chemical composition data were analyzed statistically using SPSS 15.0. The least significant difference test (LSD) at \( p \leq 0.05 \) and Standard Error (Mean ± SE) were calculated.
RESULTS AND DISCUSSION

The effect of frozen storage on moisture, protein, fat, and ash contents of the fish were studied. The obtained results are tabulated in Table 1.

Table 1 showed the effects of storage at -18°C at different periods on the moisture contents of raw the fish. The initial moisture contents of raw, frozen 7 days, 21 days and 35 days fish samples were 84.72, 84.74, 74.65 and 74.18 %, respectively. The differences were due to a gradual decreasing in their contents of moisture as affected by frozen storage different periods. With increasing storage time, moisture content decreased significantly. The loss of moisture in frozen fish samples can be attributed to the sublimation of ice in frozen storage and the loss of drop during the thawing process (Abo Taleb, Sherif, and Ibrahim, 2011). Similar findings were reported for other species of fish such as Sea bass fillets (Benjakul et al., 2005), Carp fish cutlets (Surabhi and Das, 2007), Tilapia fillets (Ibrahim and El-Sherif, 2008), Labeo rohita (Gandotra et al., 2012) and Catla fish cutlet (Vanitha et al., 2013). The initial protein contents of raw, frozen 7 days, 21 days and 35 days fish samples were 7.67, 8.52, 16.64 and 20.89 %, respectively (Table 1). These differences were due to increase in their protein content, which is affected by the frozen storage period. As storage time increased, protein content increased significantly.

The decreasing in fat content of raw, frozen 7 days, 21 days and 35 days fish samples might be due to oxidation and hydrolysis of fats which result in the formation of some volatile chemicals as aldehydes and ketones (Gandotra et al., 2012). The some studies showed a decreasing in ash content in fish during frozen storage which was related to the drip loss during thawing process (Gandotra et al., 2012).

Table 2 showed that moisture content in fresh sample was affected brining process was decreased respectively (84.72% to 33.99%) with significant different (p <0.05), while protein, fat, ash and energy values was affected brining process were increased. The obtained results in this study were agreed with results Aberoumand and Ziaei-Nejad, (2015). The effects of frying cooking technique on the proximate composition (moisture, protein, lipid, ash and carbohydrates) of the studied fish are presented in Table 3. Moisture content of raw and fried fish was 84.72 %, and 21.10% respectively. There was significant loss in the moisture content of raw fish due to the cooking process by frying (p <0.05). This observation agreed with El Sherif, Ibrahim and Abou-Taleb, (2011) for fried Tilapia fish as well as for some fish species (Gokoglu, Yerliyaka and Cengiz, 2004). The protein content in raw the fish was significant increased (p <0.05) in the fried samples. Increasing protein content in the cooked fish samples (fried) due to the water loss during cooking. Protein contents were 7.67 % in raw and 14.16% fried, respectively. Similar data showed that deep-fried fish had the highest protein value comparing other cooking methods (Gokoglu, Yerliyaka and Cengiz, 2004; Kucukgulmez et al., 2006). Data given in Table 3 showed that total lipids in raw and fried samples were 6.52, and 62.76%, respectively. These values were differing significantly (p <0.05). The higher lipid content of fried the fish due to the absorption of oil and losing moisture during frying process (Saguy and Dana 2003). Ash contents were 0.99 and 1.97 in raw and fried fish, respectively (Table 3). The differences of ash content higher of fried is due to more loss of moisture took place during deep frying cooking method (Kucukgulmez et al., 2006). The changes found in the chemical composition of fish cooked by frying were similar to several studies carried out in other fish species included Sea bass (Gokoglu, Yerliyaka and Cengiz, 2004; Kucukgulmez et al., 2006; Marimuthu et al., 2012; Garcia Arias, Alvarez, and Garcia Linares, 2003).

Table 4 showed that pH was found 6.18 in fresh sample and increased significantly (p <0.05) to the value 6.50 in 7 days frozen fish. There was comparatively slow increase in pH between fresh fillets during freezing periods. It was increased from 6.18 to 6.50. There was significant differences (p <0.05) between fresh fish and frozen fish that was frozen for 7 and 21 days. No significant difference between groups of fresh fish that was exposed to the different freezing periods. These results are in accordance with Erkan and Ozden, (2008) who stated that the increase was due to an increase in volatile bases from the decomposition of nitrogenous compounds by endogenous or microbial enzymes. Obemeata, Nnenna and Christopher, (2011) observed that the increase in pH was higher in the 4 °C stored sample of Tilapia, indicating that biochemical and microbial changes are occurring faster in 4 °C stored fish. Pawar et al. (2013) showed slightly increased pH in Catla catla from 6.50 to 6.79 when stored at chilled temperature (-2 to -4 °C). The change in pH of fish sample is usually good index for quality assessment. The increase in pH is caused by the enzymatic degradation of fish muscle.

An increase in protein content in processing methods was due to aggregation of proteins after the removal of water molecules present between proteins (Ninawe and Ratnakumar, 2008). The increase in method time and loss of moisture leads to denaturation of the protein (Begum et al., 2013). The fat content increases in brining method with a decrease in water content as the lipid plus water content of fish flesh equal to 80% (Bligh et al., 1988). The higher ash content was due to the substantial loss of moisture (Mustapha et al., 2014). During brining, the mass transfer occurs basically between salt and water: the fish fillets takes up salt and loses water (Chaijan, 2011; Oliveira, et al. 2012). Nutritional composition, such as protein, lipid, and ash, were increased due to the loss of water in fish fillets in the brining process (Brás and Costa, 2010; Chaijan, 2011).

The increased protein degradation is occurred by major changes in the protein fraction of the salted fish and the increased NaCl concentration. Consequently, the decrease pH value is because of the increase of the ionic strength of the solution inside of the cells (Goulas and Kontominas, 2005; Leroi and Joffraud, 2000). The decrease in sample lipid content during freezing was associated to the fat hydrolysis and due to the oxidation rancidity. Similarly Siddique et al. (2011) found that total lipid content decreased during frozen storage of three species of Puntius. The decrease in ash content was associated to the drip loss during thawing process (Roopma et al., 2013).
Table 1 Proximate composition (g/100g) and caloric value of fresh and frozen fish (Parastromateus niger), on a dry basis.

<table>
<thead>
<tr>
<th>Parastromateus niger</th>
<th>Proximate composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>Protein</td>
</tr>
<tr>
<td>Fresh</td>
<td>84.72 ±0.27a</td>
</tr>
<tr>
<td>Frozen 7 days</td>
<td>84.74 ±0.7b</td>
</tr>
<tr>
<td>Frozen 21 days</td>
<td>74.65 ±0.3b</td>
</tr>
<tr>
<td>Frozen 35 days</td>
<td>74.18 ±0.4b</td>
</tr>
</tbody>
</table>

Note: Mean of samples analyzed in duplicate. The same letters in the column do not differ from each other at the 5% level of significance.

Table 2 Proximate composition (g/100g) and caloric value of fresh and brined fish (Parastromateus niger) on a dry basis.

<table>
<thead>
<tr>
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<th>Proximate composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>Protein</td>
</tr>
<tr>
<td>Fresh</td>
<td>84.72 ±0.27a</td>
</tr>
<tr>
<td>Brined</td>
<td>33.99b</td>
</tr>
</tbody>
</table>

Note: Mean of samples analyzed in duplicate. The same letters in the column do not differ from each other at the 5% level of significance.

Table 3 Proximate composition (g/100g) and caloric value of fresh and fried fish Parastromateus niger, on a dry basis.

<table>
<thead>
<tr>
<th>Parastromateus niger</th>
<th>Proximate composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>Protein</td>
</tr>
<tr>
<td>Fresh</td>
<td>84.72 ±0.27a</td>
</tr>
<tr>
<td>Fried</td>
<td>21.10b</td>
</tr>
</tbody>
</table>

Note: Mean of samples analyzed in duplicate. The same letters in the column do not differ from each other at the 5% level of significance.

Table 4 pH value of raw, brined and frozen 7 days, 21 days and 35 days fish samples Parastromateus niger.

<table>
<thead>
<tr>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
</tr>
<tr>
<td>Brined</td>
</tr>
<tr>
<td>Frozen 7 days</td>
</tr>
<tr>
<td>Frozen 21 days</td>
</tr>
<tr>
<td>Frozen 35 days</td>
</tr>
</tbody>
</table>

Note: Mean of samples analyzed in duplicate. The same letters in the row do not differ from each other at the 5% level of significance.

CONCLUSION
Proximate composition and energetic values of Parastromateus niger fish showed significantly (p ≤0.05) differences between brined, cooked and raw samples and during frozen storage. The moisture loss in the boiled and fried samples reached its highest level. Also, protein, fat and energy were relatively high. The nutritional value of fish Parastromateus niger retained until the end of the storage period. Therefore, it must be beyond the process of useful and optimized processes that can lead to the production of superior products with nutrients, beyond consumer satisfaction. To prevent the impact of processing on fish nutritional and physical and chemical constituents, the use of appropriate methods for fish processing and fish products was essential.

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