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Determination the levels of potassium bromate beside some heavy metals (Fe, Ni and Cu) in Tost and bread samples collected from some local markets in Al –Beida City by using spectrophotometer

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ABSTRACT

The presence high levels of potassium bromate in bread is very undesirable considering its deleterious effects and heavy metals also are implicated in carcinogenesis, mutagenesis and teratogens . In our study standard curve of potassium bromate and heavy metals (nickel , iron and copper) the strategy showed good linearity regression ($R^2 = 0.99$).

linearity of the strategy was performed during a range 1- 5 ppm of KBO_3 and therefore the method showed good linearity regression ($R^2 = 0.97$) with y=0.157x , 10 – 50 ppm of Cu ($R^2 = 0.99$), with y = 0.001 x , 1- 5 ppm of Ni, with y = 0.018 x and ($R^2 = 0.99$) , 1-5 ppm of Fe with y= 0 . 59 x and ($R^2 = 0.99$) and Which is showing good linearity, precision, accuracy and sensitivity, which might be used for determination heavy metals .

The quantity of potassium bromate bread samples ranged from 0.38 to 13.72 ppm and therefore the amount of Ni in bread ranged from 0.66 to 2. 7 ppm the quantity of Cu ranged from 5 to 41 ppm and the quantity of Fe 0.003 ppm to 0.03 ppm

Introduction

Few foods evoke a picture of wholesomeness like fresh-baked bread. But the flour utilized in many commercial food may include an additive that's been linked to cancer, the additive is named potassium bromate, which is added to flour to strengthen the dough, allow it to rise higher and provides the finished bread an appealing white color (Kujore et al.,2010)., EWG's Food Scores, a web tool to assist consumers eat healthier, lists potassium bromate as an ingredient in a minimum of 86 food and other food products found on supermarket shelves, including well-known brands and products like Hormel Foods breakfast sandwiches, Weis Kaiser rolls and French toast , and Goya turnover pastry .
Bread Industry Bread is an important cereal product in human nutrition providing the maximum amount as 50-90% of total caloric and protein intakes. Daily consumption of bread in Addis Ababa rated to 37.4 g per capita (Khaniki et al.,2005). Bread is formed from wheat through variety of processes including milling, mixing, fermenting, molding and baking (Central Statistical Agency of Ethiopia) . Bakeries use potassium bromate, strong oxidant , for bread improving effects like preserve flavor or improve the taste and appearance (Emeje et al.,2010). When potassium bromate is added to freshly milled flour, it'll increase the time period of the flour (VanStaden et al.,2010).. But, beyond all the advantages , potassium bromate is toxic above certain level i.e. 0.02 ppm. It affects the nutritional quality of bread by degrading essential vitamins and fatty acids .

Bread, a baked staple food made from wheat flour, is widely consumed in all parts of world among all socioeconomic groups. Potassium bromate ($KBrO_3$) is a colourless, odourless and tasteless white crystal/powder that is used as a commonly used flour enhancing agent in world (Gandikota, et al.,2005), because of its efficient oxidizing properties. It acts as a maturing agent and dough conditioner by oxidizing the sulfhydryl groups of the gluten protein in flour into disulphide bridges making it less extensible and more elastic, this will make the dough viscoelastic such that it can retain the carbon dioxide gas produced by the yeast. The overall effect is to make bread rise in the oven, increase loaf volume and texture (Nakamura, et al.,2006).
Potassium bromate Toxicity Potassium bromate has many adverse effects on the nutritional quality of bread

and therefore the health of consumers of bread made with bromated (Ginocchio et al., 1979; Fujii, et al., 1984) .It degrades essential vitamins in bread (14) and has been classified by the International Agency for Research on Cancer (IARC) as a possible human carcinogen supported sufficient evidence that $KBrO_3$ is carcinogenic and mutagenic in experimental animals (IARC, 1986).

The Biochemistry of the baking of recent bread from flour is fundamentally a temperature-dependent two step progression, consisting of fermentation, during which CO_2 production linked with yeast activity is manifested in porous dough structure with the development of dough volume during baking where yeast activity is ended and therefore the bread structure is finalized (Gandikota, et al.,2012). During leavening, the metabolism of yeasts chemically transforms assailable carbohydrates into CO_2 and ethyl alcohol because the principal finished products. As a related amount of alcohol forms, which is water-miscible, it influences the colloidal nature of the wheat proteins and changes the interfacial surface tension within the dough. additionally , CO_2 , which partly dissolves within the aqueous phase of the dough, migrates toward the initial nuclei of the air bubbles formed during kneading causing their increase (Ahmad, et al.,2015).

Regulators within the us and abroad have reached troubling conclusions about the risks of potassium bromate that you simply probably don't realize , but should. In 1999 the International Agency for Research on Cancer determined that potassium bromate may be a possible human carcinogen. it's not allowed to be used or is banned as a artificial additive during a number of nations , including the uk , Canada, Brazil and therefore the European Union .The state of California requires food with potassium bromate to hold a warning label(IARC1999) .

In tests on lab animals, exposure to potassium bromate increased the incidence of both benign and malignant tumors within the thyroid and peritoneum – the membrane that lines the abdomen (Kurokawa, et al.,1986). Later research confirmed and expanded these findings, concluding that ingesting potassium bromate resulted in significant increases in cancer of the animals' kidneys, thyroid and other organs (DeAngelo, et al.,1998) .

Potassium bromate also has the potential to disrupt the genetic material within cells (US Environmental Protection Agency)Upon entering the body, potassium bromate will be transformed into molecules called oxides and radicals . These highly reactive molecules can damage DNA and will play a task within the development of cancer. Scientists have observed such damage in human liver and intestine cells, where exposure to potassium bromate resulted in breaks in DNA strands and chromosomal damage(Zhang, et al.,2011) .

Researchers also saw significant damage to the cell membranes of lysosomes – the tiny intracellular bodies liable for important cell functions like cellular digestion – ironically, the method by which food is broken down into components useful to our cells. Models of the connection between DNA damage and potassium bromate show a consistent low-dose linear response, which suggests that the quantity of DNA damage observed is proportional to the quantity of potassium bromate consumed (Spassova, et al.,2013) .

Analyzed bromate in bread by gas chromatography (GC) based on the formation of a volatile derivative of bromate and obtained a limit of 12 μg kg^{-1}. (Atkins et al., 1993; Dennis, et al., 1994) used inductively coupled plasma –mass spectrometry and obtained a higher C.V of 18% compared to 12% when G.C was used, while it was reported a kinetic study of Bordeaux oxidation and reported that the rate of reaction was dependent on Bordeaux concentration (Fuller, et al.,1970) .

The overall aim of the this project was to determine the levels of potassium bromate in bread, which are very important with regard to human health as well as the food quality control perspective, beside determination of some heavy metals (Fe, Ni and Cu).

Experimental

Sampling :

Table(1):Ten different samples of bread and its derivatives were collected from local markets at Al –Beida City,

Sample No	Sample Name/ Type
1	Abou-Hmadien Baruish
2	Abou-Hmadien Tost
3	Baruish - Libyan
4	Brauish – Lebanon
5	Birgger Bread – Al-Bared
6	Ehfatier –Tost
7	Local Bread – Al –Bayda Barkey
8	Baruish – Italian
9	Al –Garida Bread
10	Bab- Al Madiena –bread

preparation of standard Solution of $KBrO_3$

Exactly 1.57g of potassium bromate crystal of analytical grade was weighed and dissolved in 1000 ml of distilled water during a 1000 ml capacity conical flask to organize the quality solution of $KBrO_3$.

200 ml of water was measured into volumetric flask and 5 ml of Conc. HCl was added to make an acidified water, after which 10 g of potassium iodide crystal of analytical grade was weighed accurately using

the balance and was added to the acidified water and mixed to form 10 % KI solution. Aliquots of 0.1 ml, 0.2 ml, 0.3 ml, 0.4 ml and 0.5 ml of $KBrO_3$ were measure form the first standard solution of $KBrO_3$ prepared into five test tubes labeled 1-5. An Aliquot of 2 ml of the 10 % KI was added to every tub **(** Emejeet, et al., 2009). .

preparation of Standard solutions Nickel , iron and Copper

The standard stock solution 1000 ppm was prepared of (Nickel , iron and Copper) , then working diluted standard solutions was made 1,2,3,4,5 ppm Nickel , iron 10,20,,30,40 .50 ppm of Copper .

Reagents which we used with metals Dimethylglyoxime ,potassium thiocyanate and ammonia solution for Nickel ,

iron and Copper respectively ,the concentration of reagents 2M for each reagent .

Samples preparation :

The samples were prepared before the analysis by designed method . Aliquot 0.5 gram of each sample was designed with 5 ml of concentrated nitric acid until full evaporation , than about 20 ml of distilled water was added , the samples were heated then filtered , the volume then completed in measuring flask to 100 ml.

Instruments :

UV/ VIS – spectrophotometer was used.

Statistic calculation :

Statistic calculation was employed by using **Excel** and **IBM SPSS** software.

Table (2) : Wavelengths and Reagents used in this study

Ions	Rreagent	pH medium	Wave length
Fe	KSCN	Acidic	**464 nm**
Cu	NH_3	acidic	**745 nm**
Ni	dimethyglyoxinme	Basic	**550 nm**
Potassium bromate	KI	Acidic	**620 nm**

Results and discussion

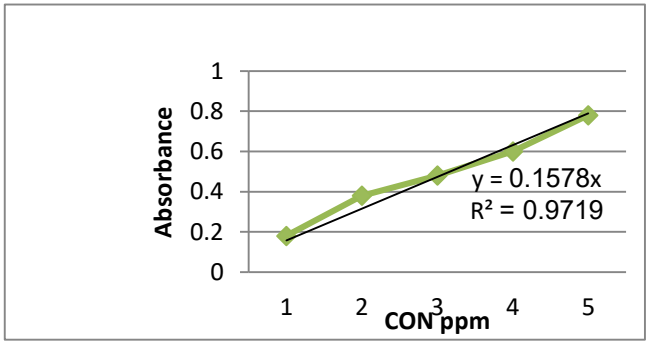

Fig 1: .Calibration curve of potassium bromate

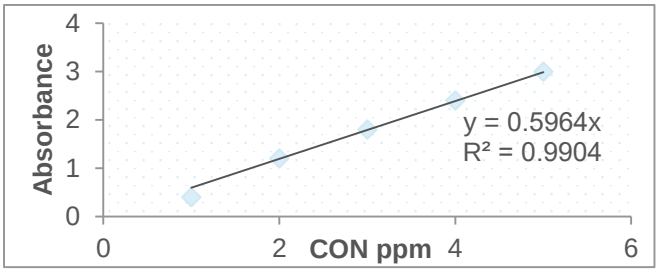

Fig 2: .Calibration curve of Fe

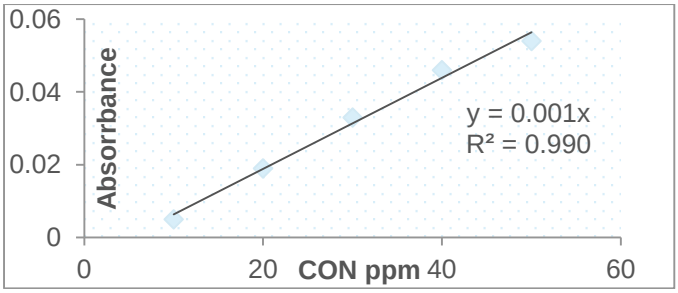

Fig 3: .Calibration curve of Cu

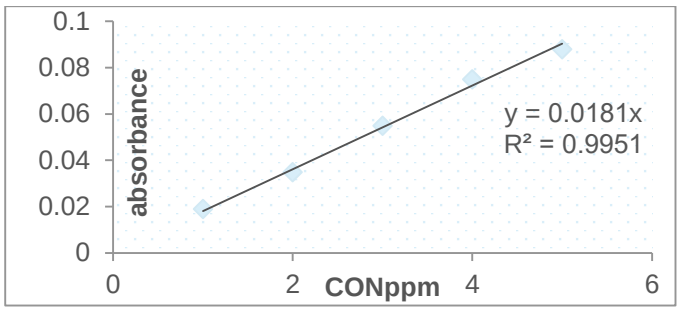

Fig 4: .Calibration curve of Ni

Table (3) : Shows absorbance and concentration of potassium bromate in different samples

sample	absorbance	Concentration ppm
1	0.455	2.78
2	0.708	4.41
3	0.644	4.00
4	1.390	8.81
5	1.244	7.85
6	1.469	9.32
7	0.580	3.59
8	1.007	6.34
9	2.150	13.72
10	0.0825	0.38

Table (4) : Shows absorbance and concentration of Fe in different samples

sample	Absorbance	Concentration ppm
1	0.002	0.0035
2	0..007	0.0117
3	0.022	0.036
4	0.002	0.0035
5	0.005	0.0083
6	0.006	0.0100
7	-	0
8	0.01	0.0167
9	-	0
10	-	0

Table (5) : Shows absorbance and concentration of Cu content in different samples

sample	Absorbance	Concentration ppm
1	0.011	11
2	0.015	15
3	0.041	41
4	0.005	5
5	0.006	6
6	0.0184	18.4
7	0.014	14
8	0.006	6
9	0.012	12

Table (6) : Shows the concentration of Ni content in the studied samples.

Sample	Absorbance	Concentration ppm
1	0.024	1.32
2	0.037	2.044
3	0.036	1.98
4	0.012	0.66
5	0.024	1.32
6	0.032	1.76
7	0.049	2.70
8	0.029	1.60
9	0.013	0.71

Table (7) : Statistics values of KBO_3 , Fe, Ni and Cu content in different samples

Statistics value	Ni	Cu	Fe	KBO_3
Mean	1.5194	14.1400	.0090	6.1200
Std. Error of Mean	.19985	3.28661	.00350	1.23018
Median	1.4600	12.5000	.0059	5.3750
Mode	1.32	6.00	.00	.38a
Std. Deviation	.63199	10.39318	.01106	3.89016
Variance	.399	108.018	.000	15.133
Skewness	.356	2.174	1.822	.565
Std. Error of Skewness	.687	.687	.687	.687
Kurtosis	-.131-	5.700	3.814	.218
Std. Error of Kurtosis	1.334	1.334	1.334	1.334
Range	2.04	36.00	.04	13.34
Minimum	.66	5.00	.00	.38
Maximum	2.70	41.00	.04	13.72
SUMA	15.19	141.40	.09	61.20

linearity of the strategy was performed during a range 1-5 ppm of KBO_3 and therefore the method showed good linearity regression (R^2 = 0.97) with y=0.157x , 10 – 50 ppm of Cu (R^2 = 0.99), with y = 0.001 x , 1- 5 ppm of Ni, with y = 0.018 x and (R^2 = 0.99) , 1-5 ppm of Fe with y= 0 . 59 x and (R^2 = 0.99) and Which is showing good linearity, precision, accuracy and sensitivity, which might be used for determination heavy metals .

The amount of potassium bromate bread samples ranged from 0.38 to 13.72 ppm and the amount of Ni in bread ranged from 0.66 to 2. 7 ppm the amount of Cu ranged from 5 to 41 ppm and the amount of Fe 0.003 ppm to 0.03 ppm , the values showed in tables **3** , **4** , **5** and **6** .

In addition to the fact that a large amount of potassium bromate was found in the bread samples analyzed, coupled with the fact that bread is the staple food consumed by the residents of Guaguvarada (regardless of their socioeconomic status), we can conclude that Guaguvarada's diet Residents exposed to high levels absorb potassium bromate through bread consumption. In addition, the workers in the bakery that bake these breads also face the additional risk of inhaling bromate. Therefore, the community may experience carcinogenicity and other symptoms related to long-term exposure to high concentrations of potassium bromate in the future. The presence of bromate in bread samples also means that NAFDAC has poor compliance with the ban on the use of potassium bromate in bread, and regulatory agencies need to strengthen supervision and enforcement of this rule. Potassium bromate added to bread is harmful to bread consumers because it is related to nerve and nephrotoxicity,
ototoxicity (Diachenko, et al.,2002), and it poses additional risk to the health of bakery workers as potassium bromide, a heat decomposition product of potassium bromate, is additionally toxic (Giesecke, et al.,2000). additionally, potassium bromate reduces the nutritional quality of bread by degrading essential vitamins like A, B and E (Joint FAO/WHO, 1992). in sight of the various adverse effects of $KBrO_3$, other oxidizing agents, like ascorbic acid, that's non toxic and equally enhances the standard and value of bread is employed in place of $KBrO_3$. Also enzymes like hemicelluloses (volume enhancing), glutathione oxidase (protein strengthening) and exo-peptidase (improves color and flavor) can equally be used. The maximum amount of potassium bromate allowed in bread by the FDA is 0.02 ppm (Ekop, et al.,2008) . All the samples analysed in this study had potassium bromate in excess of the allowed concentration. Similar Studies by (Emeje, et al.,2010) carried out revealed similar findings. The presence such levels of potassium bromate in bread is highly undesirable considering its deleterious effects.

These heavy metals are also implicated in carcinogenesis, mutagenesis and teratogens. The highest concentration of Ni was observed for sample 7 (2.7 ppm) while the lowest was for sample 4 (0.66 ppm).

The concentration of Cu in the different bread brands ranged from 5-41 mg/kg. These concentrations are far above the permissible level of Cu in foods (10 ppm) (Salama, et al.,2005). The samples can therefore be considered have Cu contamination.

It's all about the Iron is a trace element that is required by all living things. It is necessary for the creation of haem proteins and numerous enzyme systems in humans. The requirements for iron vary by gender (male, female, children, pregnant,), and iron insufficiency is one of the most prevalent dietary deficiencies among children, women and pregnant women. Except in cases of chronic bleeding, it is uncommon in adult men. The concentrations of Fe in the bread samples studied ranged from 0.003-0.03ppm . The permissible limit for Fe in food is in the range of 2.5-5.0 ppm depending on the food stuff.

Samples had iron concentrations below the permissible level. However, in human, acute toxicity of iron ingested from normal dietary sources has not been reported.

Metal containers used for kneading of dough during bread making may be responsible for high levels of such metals
. Atmospheric deposition from urban and industrial areas may result in contamination of agricultural produce with heavy metals which are in turn transferred to the finished products (Codex Alimentarius Commission((CAC), 2003) .

Conclusion

With compounds that are commonly present as contaminants, the spectrophotometric method has been found to be selective, sensitive, simple, and straightforward to use. The method validation showed the accuracy and precision of low-level potassium bromate and heavy metals determination in a daily application.

The concentrations of heavy metals in bread samples under study , Ni in bread ranged from 0.66 to 2. 7 ppm the amount of Cu ranged from 5 to 41 ppm and the amount of Fe 0.003 ppm to 0.03 ppm .

The amount of potassium bromate bread samples ranged from 0.38 to 13.72 ppm. The results obtained for analysis of potassium bromate and heavy metals within the studied samples using UV-Visible Spectrophotometer showed that there are differences of the concentrations in these samples and also the methods employed.

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