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Spectrophotometeric Determination of Bromate in Bread By the Oxidation of Dyes

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Abstract

Potssium bromate ($KBrO_3$) is an oxidizing agent that has been used as a food additive , mainly in the bread making process. Amethod is proposed for the determination of bromate based on the oxidation of congo red and crystal violet dyes in a hydrochloric acid medium .Application of spectroscopy for determining bromate in bread was described , fifteen samples of bread , made from flour treated with potassium bromate , was collected from different regions in Hawler, Iraq. The residual bromate level in the analyzed bread samples were in the range from 6.66mg/L to 67.45mg/L The accuracy and precision of the method are discussed.

Introduction

Potassium bromate($KBrO_3$)is a flour improver that acts as a maturing agent. It acts principally in the late dough stage giving strength to the dough during fate proofing and early baking(Kuro Kawo.etc,1990; www.Kemix.com;de Man,1990;Hirayama,etc.,1980). Bromate is dough conditioner,in bread it has tow main purposes: Aprotein called gluten is needed to trap gas and expand when the dough is proofing without good gluten breads would be thin and dense. Bromate can help a lower qulity gluten perform like a good gluten, providing a better looking loaf of bread . Another characteristic that consumers like in bread is small, uniform air cells.If you look closely at the bread you will see that there are small holes in it.Bromate helps the gluten form small uniform holes in the bread. Without it the holes would be big (www.madsci.org(1999-02)) .Potassium bromate has been evaluated for flour to be consumed by man by Joint FAO/WHO committed on food additives in 1964. In addition to its use in the treatment of flour,potassium bromate is used in treating barley in beer making and it has been used for the improvement of the quality of fish–paste products in Japan(ministry of Health and welfare, Japan,1979) (Joint FAO/WHO(1992)).The presence of bromate in bread may caus renal failure,respiratory depression,hearing loss,break down of vitamins and

cancer to humans (IPCS., 1994; Field, 2004; Akunuyili., 2004; PCHRD. Com.,2000). Bread was made by bulk fermentation and also by mechanical development from dough containing amounts of added potassium bromate ranging from(0 to 200)ppm(PCHRD.Com.,2000).when the added potassium bromate level was less than(50)ppm,the residual level was too small to be detected,at higher levels of addition increasing amount of residule potassium bromate began to appear bulk fermentation giving more than mechanical developme. Bromate in bread was analysed by gas chromatography (Atkins.,1993) . Inductively coupled plasma-mass spectrometry (Dennis.etc,1994) and spectrophotometry (OJEKA.etc,2006;J Medina-Escriche.etc,1985; J.F.van Staden, 2004). No such study has been done in our city. This study was aimed to determine the level of bromate (flour improver) in bread from Hawler city.

Experimental

Sampling:

Bread samples were bought from different outlets and bakeries in Hawler city. Representative samples were bought from south, north, western and eastern parts of Hawler city. The bread sample locations included:100 matry,Choliiminarate,Rasty,Mantkawa 92,Mantkawa 99, Badawa,Escan, Mhabad,40matry,Olma Q.,Br-ayati,Jmhuri hospital,Ateba street,60 matry and Kuran enkawa.We analysed 15 Commercial samples of bread. All samples were obtained from products that are wid-ely consumed in Hawler.Duplicate samples from each location were analysed for residual bromate level.

Reagents:

All chemicals were analytical grade reagents and distilled–deionized water was used throughout the study.The following solutions were prepared.

Potassium bromate stock solution: 0.027 M.(4.3 g of $KBrO_3$)were dissolved in 1L of water .

Potassium bromate working solution: The working standard solutions were prep-ared in the range:12,24,36,48,60,72,84 and 96 ppm respectively .

Hydrochloric acid: 2 M. (43.10 ml of concentrated HCl) were diluted to 250 ml with water.

Congo red dye solution: $5*10^{-4}$M(0.348 g of congo red) were dissolved in 1L of water.

Crystal violet solution: $5 * 10^{-4}$ M. (0.216 g of crystal violet) were dissolved in 1L of water .

Apparatus:

Spectrophotometric measurements were made on a Jenway 6305 UV–Visible spectrophotometer.The absorbance was measured at λ_{max} = 485 nm for samples containing crystal violet and 452 nm for samples containing congo red . All measurements were made at room temperature against water as reference.

Sample preparation:

A circular sample of 2 cm diameter from the center of a 15 mm thick slice of each bread sample was taken and dried in an oven for 72 hours at 55^{o}C the crust was ground to a fine powder with electrical grinter. 2.5 g of each powdered samples was weighed into 250 ml beaker, and 25 ml of water was added The mixture was centrifuged and the liquid fraction was diluted to 50 ml in volumetric flask.(Dennis.etc,1994).

Procedure:

4 ml of aliquot of each of the 15 bread samples was measured into 30 separate samples,each in 25ml calibrated flask. 5ml of $5*10^{-4}$ M solution of congo red dye or 5ml of $5*10^{-4}$ M of crystal violet dye was added separately followed by 10 ml of 2 M HCl solution.Each flask was diluted to 25ml marks with water,and shaken gently prior to colorimetric analysis.

Data Treatment:

The concentration of samples were found from equation no.1 and 2 for crystal violet and congo red respectively.

$y = 0.0047 X + 0.2267$ …1

$y = 0.0011 X + 0.5558$ …2

Were y =Absorbance and X = concentration of potassium bromate .

R^2=coefficient of determination is a measure of the fraction of the total variation in y that can be explained by the linear relationship between conc.of bromate and absorbance .

Results and Discussion

A number of case studied of acute human intoxication with potassium bromate have been reported following accidental ingestion or attempted suicide. In autopsy cases , degeneration of kidney tubules and liver parenchymal cells,and acute myocardities were the principal pathological changes observed (Paul,1966 ;Stewart,1969;Niwa et al. ,1974;Norris,1965; Quick et al.,1975).(Paul.A.H.(1966);Stewart.T.H.etc(1969); Niwa.T.Ho.T. (1974);Norris.J.A (1965);Quick.C.A.etc(1975)).level causing no

toxicological effect estimate of acceptable level of treatment of foods to be consumed by man for flour:Temporary acceptance 0-75mg/kg flour (providing bakery products prepared from such treated flour contain negligible residues of potassium bromate(Hirayama,K..etc (1980)). Calibration graphs for absorbance versus bromate concentration for crystal violet and congo red dyes showing in figs(1,2) respectively. The data in table(1)shows the concentration of potassium bromate in the studied bread samples .The precision and accuracy are reported in table(2),the data showed that the crystal violet procedure has a higher sensitivity and limit of quantification respectively,than the congo red method .A quantitative agreement between the results was observed. The oxidation of the dyes by bromate was carried out in a hydrochloric acid medium

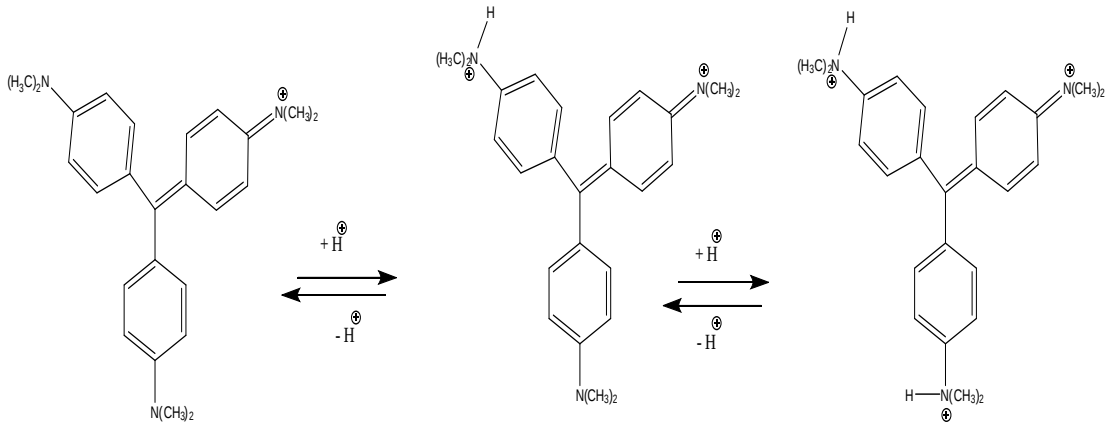
$$BrO_3^- + 6\ H^+ + 6\ e = Br^- + 3\ H_2O$$

With irreversible oxidation indicators,the quantity of bromate solution consume by the dyestuff indicator inexceedingly small and the indicator is bleached in the presence of 2M Hcl :

$$10\ Cl^- + 2\ BrO_3^- + 12\ H^+ = 5\ Cl_2 + Br_2 + 6\ H_2O$$

The red colour of congo red changed to blue.

Crystal violet is purple in weak acid solution,green in strong acid solution and finally yellow.Both dyes were water soluble because of the tow sulphuric acid groups(SO_3H)in Congo red and dimethylamino groups in crystal violet(www.byto com.com\vb\) .



Violet Blue Yellow

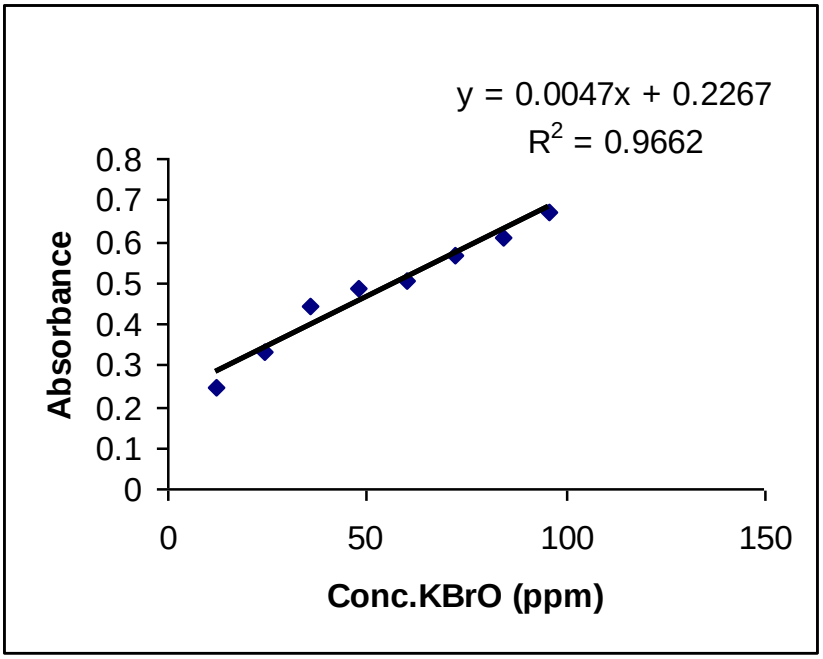


Fig.1: Calibration curve for crystal violet at ƛ $_{max}$=485nm

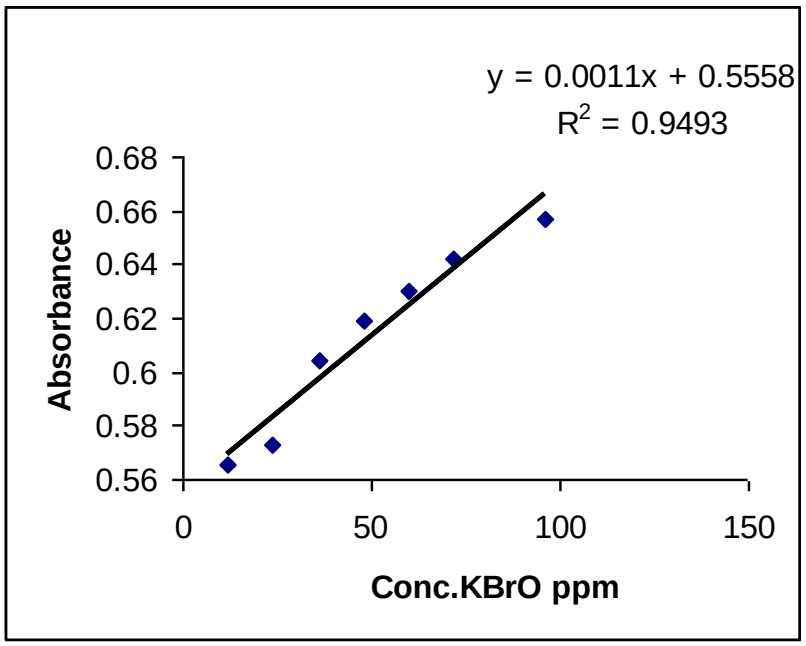


Fig.2: Calibration curve for congo red at λ_{max} = 452 nm.

Table 1:Conc.Of potassium bromate (ppm) in studied bread samples

Bread sample	Conc. of $KBrO_3$ by congo red oxdation.	Conc. of $KBrO_3$ by crystal violet oxdation
1	11.09091	6.659574
2	17.45455	15.59574
3	58.36364	52.19149
4	24.72727	20.70213
5	67.45455	65.59574
6	56.54545	51.97872
7	34.72727	33.89362
8	67.45455	63.04255
9	65.63636	64.31915
10	66.54545	64.31915
11	46.54545	46.23404
12	34.72727	33.89362
13	62	61.76596
14	56.54545	50.48936
15	57.45455	50.70213

Table (2): Analytical parameters of the proposed methods

Analytical mode	Slope (m)	Standared deviation	Error (%)	R^2
1. crystal violet Method	0.004746	0.141923	3	0.9662
2. congo red method	0.00115	0.034137	3	0.9493

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التقدير الطيفي للبرومات في الخبز بأكسدة الاصباغ

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الخلاصة

برومات البوتاسيوم عامل مؤكسد يستعمل كمادة مضافة إلى الغذاء وبشكل رئيسي في عملية صنع الخبز، الطريقة المقترحة لتقدير البرومات مستندة على أكسدة اصباغ احمر الكونغو والبنفسجية البلورية في وسط حامض هايدروكلوريك، تم وصف التحليل الطيفي لتقدير البرومات في الخبز، خمس عشرة عينة من الخبز مصنوعة من الطحين المعامل ببرومات البوتاسيوم جمعت من مناطق مختلفة من اربيل – العراق. مستوى البرومات المتبقية في عينات الخبز المحللة كانت في المدى ٦،٦٦ غم / لتر إلى ٦٧،٤٥ غم / لتر ، تم مناقشة الدقة والضبط للطريقة.