

HEAVY METALS CONTENTS IN DIFFERENT TYPES OF BREAD SAMPLES AND ITS RAW MATERIALS

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ABSTRACT

The contents of Cu, Zn, pb, Cd and Hg were analyzed in raw materials used to produce bread samples i.e. (wheat flour 82% and 72%, wheat bran, tap water, salt, compressed yeast, dough and final product (shamey, Balady and bran bread samples) and different types of bread samples which collected from El-Mansoura City super market. These heavy metals were determined using atomic absorption spectrophotometry (AAS).

The results showed that;

- The concentrations of heavy metals in compressed yeast and wheat bran were higher than other raw materials.
- The amount of heavy metals were in bran higher than in whole wheat flour than wheat flour ext. 82% than wheat flour ext. 72%.
- The highest level of this heavy metals were in bran bread samples (4.944 – 5.335 mg/kg for Cu, 34.166 – 36.145 mg/kg for Zn, 1.907 – 2.076 mg/kg for pb, 0.2 – 1.10 mg/kg for Cd and 0.01 – 0.013 mg/kg for Hg).

INTRODUCTION

Bread is the major wheat based food and one of the least expensive product consumed widely throughout the world. Some countries in Europe have the highest level of bread intake, approximately 60 to 70% of the total food intake. In Egypt, bread comprises 60 to 70 % of the food intake and cereals provide 78% of calories (2347.4 calories) and 60% of protein (96.9 gm) from bread daily intake consumption. Among the poor classes about 90% total calories are derived from bread and cereal (CAPMS, 1998).

The raw material used in bakery industry is generally the wheat flour. Bread also contains all nutritious compounds in wheat but, vitamins and minerals were found in wheat grain less than in wheat embryo and outer layer, which are decreased during milling process depending on the level of refining. (Ercan, 1993).

Heavy metals are potential environmental contaminants with the capability of causing human health problems if present in excess amounts in the food we eat. They are given special attention throughout the world due to their toxic effects even at very low concentrations (Das, 1990).

Wenk et al. (1992) found that the concentration of pb, Cd, Cu, and Zn in white, mixed, brown, specially and rye breads were 56, 57, 61, 75 and 45 µg/kg; 23, 24, 30, 30 and 17 µg/kg; 2.2, 2.6, 3.4, 3.4 and 3.5 mg/kg, and 11.5, 14.6, 22, 20.4 and 19.7 mg/kg respectively. The daily intakes of about 5.3 µg pb, 2.3 µg Cd, 0.25 mg Cu and 1.5 mg Zn was estimated to provide 1.2 and 3.8% of the maximum tolerable intake for pb and Cd respectively and 6 – 13 and 10% of recommended intakes of Cu and Zn respectively.

Dabeka and Mckenzie (1995) found that the concentration of lead, cadmium, nickel and cobalt in wheat flour, bran and wheat bread were 13.8, 27.34, 135 and 13.6; 17.6, 56.51, 324..and 33.6; and 21.3, 23.96, 87 and 0.3 ng/g respectively.

Cuadrado et al. (2000) found that the concentration of lead cadmium, copper and zinc in wheat flour, white bread, whole bread, biscuits and pasta were 21.3, 35.9, 59.2, 25.6 and 18.7 µg/kg; 33.2, 16.5, 33.9, 7.91 and 50.4 µg/kg; 1.88, 1.87, 2.86, 0.99 and 3.81 mg/kg; 8.63, 9.19, 18.4, 3.95 and 14.1 mg/kg respectively.

Salah (2003) showed that, the concentration of pb; Cd and Hg in wheat flour 82% ext.; wheat bran; dough and Balady bread samples collected from some bakeries in Cairo and Giza governorate were 235 – 473; 244 – 821; 286 – 566.5 and 436 – 1003 and 3.00 – 15.25; 11.00 – 82.25; 5.25 – 17.00 and 7.25 - 19.50 and 0.128 – 1.222; 0.773 – 9.50; 0.168 – 1.564 and 0.204 - 1.991 µg/kg respectively.

So, the aim of the present study was investigate some of most common cereal products (bread) contamination with heavy metals (Cu, Zn, pb, Cd and Hg) and effect of raw materials, milling, backing and handling on their contents.

MATERIALS AND METHODS

Materials:

- Wheat grains:

Wheat grains obtained from villages near of Talkha fertilizer factory

- Talkha.

- Raw materials and product:

Wheat flour 82% ext.; wheat flour 72% ext., bran flour, water, salt, bakers yeast, dough and the product (balady, shamey, bran) bread were collected from different bakeries at El-Dakahlia governorate.

- Bread Samples:

Bread samples ie. (balady – shamey – bran) bread were collected from super market, El-Mansoura city, Egypt.

Method:

Technical Methods:

- Wheat grains milling:

The grains were cleaned thoroughly and the foreign seeds and materials were removed by hand picking followed by sieving. Milling of wheat grains was run in local milling the flour extracted from wheat was individually sieved by suitable sieves to obtain 82% ext., 72% ext. and bran flour. The flour yield was calculated as percentage of the total products according to the following formula:

$$\text{Extraction rate} = \frac{\text{flour}}{\text{flour} + \text{offals}} \times 100$$

The resulted flour was mixed well, then kept in cloth bags and stored at room temperature for homogenization.

Method of analysis:

- Determination of heavy metals:

Samples were prepared for heavy metals determination by digestion in perchloric acid and nitric acid according to (Pupsa et al., 1994).

Cadmium; lead; zinc; copper and mercury contents were determined by using atomic absorption spectrophotometer (AAS) [Perkins – Elmer, Model 2380].

Table (1):The conditions of (current lamps, wave length, slit and flame) used in the heavy metals determination by the AAS.

Element	Current lamp MA	Wave length nm	Slit nm	Flame
Cd	4	228.8	0.7	air acetylene
Pb	10	217	0.7	air acetylene
Zn	10	213.9	0.7	air acetylene
Cu	15	324.8	0.7	air acetylene
Hg	4	253.7	-	Hydrate (nitrous air)

According to (Pupsa et al., 1994).

Statistical analysis:

Data were analyzed according to statistical analysis system, SAS (1996).

RESULTS AND DISCUSSION

Results in table (2) show the level of heavy metals ie. (Cu, Zn, pb, Cd and Hg) in Balady, Shamey and Bran bread samples from El-Mansoura city super markets. The heavy metals concentrations in bran bread samples were higher than Balady and shamey bread. Where, the concentrations were 5.335, 4.945 mg/kg for Cu; 36.145, 34.166 mg/kg for Zn; 1.907, 2.076 mg/kg for pb; 1.10, 0.200 mg/kg for Cd and 0.013, 0.010mg/kg for Hg.

Table (2): Heavy metal contents (mg/kg*) for three types of bread from two different places.

Type	Place	Heavy metals content (mg/Kg sample)				
		Cu	Zn	Pb	Cd	Hg
Balady bread	1	3.612	19.091	1.418	0.257	0.009
	2	4.536	21.097	1.704	0.208	0.010
Shamey bread	1	2.591	12.166	1.011	0.060	0.005
	2	3.140	10.163	0.902	0.187	0.003
Bran bread	1	5.335	36.145	1.907	1.10	0.013
	2	4.945	34.166	2.076	0.200	0.010
Type		**	**	**	**	**
Place		*	**	**	**	**
Type *Place		**	**	N.S.	**	N.S.

-All values are means of three replicates.

*on dry weight basis.

These results showed that the level of Cu in all samples of 3 types of bread were within the permissible limits as recommended by CAC (1993) who reported that the level of Cu in cereals and cereal products was 10 mg/kg. Also, the level of Zn in all samples were within the permissible limits as recommended by USDA (2003) who reported that the level of Zn in cereals and cereal products was 50 mg/kg. But, the level of pb in all samples were higher than the permissible limits as recommended by European Commission (1997) who showed that, the level of pb in cereals was 0.1 to 0.2 mg/kg. While, the concentration of Cd were lower in shamey and Balady brean than the permissible limits as recommended by European Commission (1997) who reported that the level of Cd in cereals was 0.1 to 0.2 mg/kg, but it was higher in bran bread. Statistical analysis of the data in table (2) revealed that the effect of types were high significant for (Cu, Zn ,pb, Cd and Hg). The effect pf places were high significant for (Zn, pb, Cd and Hg) but significant for Cu. The interaction effect between types and places were high significant for (Cu, Zn and Cd) but non significant for (pb and Hg).

The reason of contamination in different types of bread with heavy metals may be due to raw materials, mixing, baking, packaging, handling, marketing and extraction rate of flour.

Data in table (3) show the heavy metals contents in whole wheat, wheat flour 82% ext., wheat flour 72% ext. and wheat bran. The concentration of heavy metals were depending on the extractions rate, where the higher levels of heavy metals were in wheat bran but the lower levels were in wheat flour 72% ext.. The obtained results illustrated the milling process was high significantly reduced the concentrations of (Cu, Zn, pb and Cd) but non significant for Hg.

Table (3): Effect of milling process on heavy metal contents (mg/kg) in wheat grains*.

Treatment	Heavy metals content (mg/Kg)				
	Cu	Zn	Pb	Cd	Hg
Whole flour	2.291	34.147	1.05	0.803	1.012
Flour 82%	1.201	19.790	0.761	0.633	0.007
Flour 72%	0.883	11.963	0.332	0.427	0.004
Bran	5.527	50.759	1.682	0.969	0.013
Treatment	**	**	**	**	**
Replicates	N.S.	N.S.	N.S.	N.S.	N.S.

-All values are means of three replicates.
*on dry weight basis.

So, wheat bran was unsafe to use for bran bread process. These results were in agreement with Abou-Raya, (1999) who reported that, the level of zinc in whole wheat, wheat flour 82% ext and wheat flour 72% ext. were 34.3, 21.4 and 12.00 mg/kg respectively. But, these results were higher than Badawy et al., (2002) and Noman (1992) who reported that, the mean levels of Pb in wheat grain, wheat bran, flour and bread were 0.155, 0.186, 0.083 and 0.111 mg/kg respectively.

Milling process significantly reduced the concentrations of all the elements. The average percent of reduction rates were 32% of Cd, 50% of Pb. (Francesco et al., 2005). Because of Cd content, in wheat grain was higher in bran and lower in albumen. So that, Cd content in flour after milling is much lower e.g. approx. 40% than that in the whole grain (Zhang et al., 1997). The level of Cu was within permissible limits as recommended by CAC (1993). And the level of Zn was within permissible limits as recommended by USDA (2003). But the level of Pb and Cd were higher than the permissible limits as recommended by European Commission (1997). These results may be attributed to the contamination of wheat grains obtained from areas near from Talkha fertilizer Factory.

The results in table (4, 5 and 6) show, the concentrations of heavy metals mg/kg in Shamey, Balady and Bran breads respectively and their components collected from different bakeries in El-Mansoura city. These results could be noticed that, wheat bran flour has higher value of heavy metals than the wheat flour 82% and 72% ext. But the level of Cu, Zn and Hg were within permissible limits as recommended by CAC (1993), USDA (2003) and Egyptian Standards (1993) respectively. The level of Pb in wheat bran flour and wheat flour 82% ext. was higher but the level of Cd was within the permissible limits as recommended by European Commission (1997).

Table (4): Heavy metals contents (mg/kg D.w) in shamey bread sample and its components*.

Components		Heavy metals content (mg/Kg)				
		Cu	Zn	Pb	Cd	Hg
Raw materials	flour	1.698	11.551	0.073	0.062	0.004
	water	ND	0.099	0.006	0.001	ND
	salt	1.624	7.996	0.476	0.215	0.001
	bakery's yeast	6.717	42.043	0.998	0.215	0.005
Processing	dough	1.803	11.757	0.164	0.092	0.004
	bread	1.952	12.304	0.201	0.100	0.004

-All values are means of three replicates.

*on dry weight basis.

- ND: Not detected by (AAS).

Table (5): Heavy metals contents (mg/kg) in balady bread sample and its components*.

Components		Heavy metals content (mg/Kg)				
		Cu	Zn	Pb	Cd	Hg
Raw materials	flour	2.035	21.330	0.494	0.090	0.007
	water	ND	0.112	ND	0.022	ND
	salt	1.448	9.076	1.090	0.361	0.002
	bakery's yeast	8.541	40.028	1.368	0.379	0.009
Processing	dough	2.579	22.137	0.525	0.107	0.008
	bread	3.016	23.049	0.562	0.162	0.009

-All values are means of three replicates.

*on dry weight basis.

- ND: Not detected by (AAS).

Table (6): Heavy metals contents (mg/kg d.w) in bran bread sample and its components*.

Components		Heavy metals content (mg/Kg)				
		Cu	Zn	Pb	Cd	Hg
Raw materials	flour	5.854	39.461	0.971	0.279	0.010
	water	0.057	0.185	0.003	0.010	ND
	salt	1.922	6.610	0.978	0.261	0.001
	bakery's yeast	9.696	41.805	1.349	0.066	0.006
Processing	dough	6.302	40.753	1.022	0.317	0.013
	bread	6.845	42.238	1.045	0.389	0.013

-All values are means of three replicates.

*on dry weight basis.

- ND: Not detected by (AAS).

Furthermore, the obtained results showed that, the contents of heavy metals in tap water were in range of 0.00 – 0.057 mg/L for Cu, 0.099 – 0.185 mg/L for Zn, 0.00 – 0.006 mg/L for pb, 0.001 – 0.022 mg/L for Cd and N.D. for Hg. The level of pb in this study was lower than Saleh (2003), Abd El-Wahab (2003) and Badawy et al., (2002). But the level of Cd was higher than Saleh (2003) and Abd El-Wahab (2003). Generally, the levels of pb, Cd and Hg in all samples were within the permissible limits as recommended by WHO (1985) and Egyptian Standards (1995). But the level of Zn in water sample from bran bread and Balady bread bakery was higher than the permissible limits as recommended by WHO (1985).

From these results, it could be clearly noticed that, the level of heavy metals in salt samples were average 1.448 – 1.922 mg/kg for Cu, 6.610 – 9.076 mg/kg for Zn, 0.476 – 1.09 mg/kg for pb, 0.215 – 0.361 mg/kg Cd and 0.001 – 0.002 mg/kg for Hg.

The levels of Cu and pb were in similar with Kassem (1996) but the level of Cd was higher. The level of Cd was lower than Abd El-Wahab (2003) who reported that, the level of Cd in salt samples were ranged from 0.5185 to 0.904 mg/kg.

Also, the level of Hg in all samples was lower than Salah (2003) and Abd El-Hady (1997) who reported that, the level of Hg in salt samples was in average of 0.10 – 0.73 mg/kg.

Generally, the levels of pb and Cd were higher but the level of Hg was lower than the limits allowed and recommended by the Egyptian Standards (1996) who reported that, the levels were 1.0 mg/kg for pb, 0.20 mg/kg for Cd and 0.5 mg/kg for Hg.

Moreover, the contents of heavy metals in compressed yeast were in average of 6.717 – 9.696 mg/kg for Cu, 40.028 – 42.043 mg/kg for Zn, 0.998 – 1.368 mg/kg for pb, 0.066 – 0.379 mg/kg for Cd and 0.005 – 0.009 mg/kg for Hg. These results were in similar with Salah (2003) who reported that, the level of Cd, Hg and pb in compressed yeast samples were 0.0095 – 0.3115 mg/kg, 0.00107 – 0.009275 mg/kg and 0.286 – 1.270 mg/kg respectively. The level of pb was in similar but level of Cd was higher than Abd El-Wahab (2003) who reported that, the level of pb and Cd were 1.059 mg/kg, 1.304 mg/kg for pb and 0.131 mg/kg, 0.19648 mg/kg for Cd.

The levels of pb and Hg in all samples were lower than the permissible limits as recommended by Egyptian Standards (2000). Also, from the results in tables (3, 4 and 5) it could be noticed that, the highest levels of heavy metals were in dough from bran bread bakery, because of the high contamination in raw materials as a main ingredient, in bread produced and transferred to dough and consequently to the produced bran bread. So, the bran bread was unsafe to eating.

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محتوى أنواع مختلفة من الخبز ومكوناتها من المعادن الثقيلة
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تم تقدير محتوى كل من النحاس والزنك والرصاص والكاميوم والزنق في المواد الخام الداخلة في تصنيع أنواع مختلفة من الخبز (دقيق قمح إستخلاص ٨٢% و ٧٢% - نخالة القمح - ماء الصنبور - الملح - الخميرة المضافة - المعينة والنتاج النهائي من الخبز الشامي والبلدي وخبز المخالة وكذلك عينات تم تجميعها من محلات مدينة المنصورة بواسطة جهاز الإمتصاص الذري.
وأظهرت النتائج:

- أن محتوى الخميرة المضافة و نخالة القمح من المعادن الثقيلة سجل اعلى قيم عن باقي المكونات الأخرى
- أن نخالة القمح سجل اعلى محتوى من المعادن الثقيلة يليها دقيق القمح الكامل ثم دقيق القمح إستخلاص ٨٢% وأخيرا دقيق القمح إستخلاص ٧٢% حيث كانت ٤,٩٤٤ - ٥,٣٣٥ ملجم/كجم نحاس و ٣٤,١٦٦ - ٣٦,١٤٥ ملجم/كجم زنك و ١,٩٠٧ - ٢,٠٧٦ ملجم/كجم رصاص و ٠,٠٢ - ١,١٠ ملجم/كجم كاميوم و ٠,٠١ - ٠,٠١٣ ملجم/كجم زنق .
- كان اعلى محتوى من المعادن الثقيلة في عينات خبز النخالة.