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Evaluating heavy metal contamination in paper-based packaging for bakery products: a HACCP approach

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ABSTRACT

Food quality and safety are among the most important aspects of the food industry. The object of this study was packaging materials intended for packaging bakery products. One of the key factors for food safety is provided by packaging. The increase in food packaging materials creates a demand for promoting products and brands that are safe for consumption. Food spoilage due to poor-quality packaging causes huge losses not only to businesses but also to consumers. Despite the effectiveness of existing practices, retailers still face many challenges, including the materials used and their possible interaction with food. In addition, the transfer of harmful materials from packaging to food is still an issue. This study presents the results of an assessment of the migration of heavy metals used in different types of food packaging in the Republic of Kazakhstan. Determination of heavy metal migration was carried out in aqueous extract by atomic absorption spectrometry. The practical value of the above research is to study the content of lead, zinc and chromium in the composition of various types of paper food packaging. The assessment of the average migration level of heavy metals following the current requirements revealed that all types of paper contain significant amounts of lead and zinc, which do not meet the requirements for paper intended for food packaging. Thus, specific samples should be considered a potential risk to human health if reused without pre-treatment as a source of recycled cellulose fibre for producing packaging used in direct contact with foodstuffs.

Keywords: food packaging, food safety, food shelf life, heavy metals, permissible migration of heavy metals

INTRODUCTION

Safe food is a major determinant of human health. Access to safe, nutritious, healthy food is a basic human right. To guarantee this right, public policy ensures that available food meets safety standards. This is not an easy task, as developments in food production, management, delivery, and consumption have rapidly improved in various ways over the last two decades **[1]**. These factors call for a new global approach to improving food safety and strengthening national food safety systems while improving national and international cooperation **[2]**. The baking industry is one of the leading food industries in the Republic of Kazakhstan's agro-industrial complex. It fulfils the task of producing products of prime necessity for the following reasons: availability, nutritional value, convenience, etc. Accordingly, their sales in packaged form are increasing. According to the statistics of the Republic of Kazakhstan for January-June 2024, the main share in the structure of the manufacturing industry is the production of flour (37%) and about 16% production of bread and bakery products **[3]**. Of all the packaging materials for bakery products, paper packaging is the most common and best option. However, since bakery products, compared to other foodstuffs, have a relatively high moisture content and low pH level, as well as the increasing tendency for the packaged realisation of this type of product, it is of great importance to investigate the permissible migration of heavy metals into the food product. Like all food products, bakery products are a complex matrix; therefore, the analysis of migrating substances can cause analytical difficulties. Therefore, test media (food simulants) that reflect the basic physicochemical properties of food products are used. Specific migration tests can sometimes be performed directly in food, but general migration cannot be tested in food. Packaging and materials for direct food contact must meet various food safety requirements. Materials and articles must not transfer their components to food in quantities that may endanger human health and/or unacceptably alter food composition or cause deterioration of bakery products' colour, taste or odour. Packaging plays an important role in ensuring the quality and safety of food products. Packaging usually performs basic functions such as protecting, containing and informing. In addition to these functions, the food packaging process needs to guarantee the transportation of food products. The chemical indicator of the quality of a product during its shelf life is mainly determined by contaminants and toxic components, whose presence in certain quantities makes it possible to assess the current quality of the product or, more preferably, to estimate its shelf life. For an organism to be suitable for use as such an indicator, it must meet the following requirements as much as possible (Figure 1):

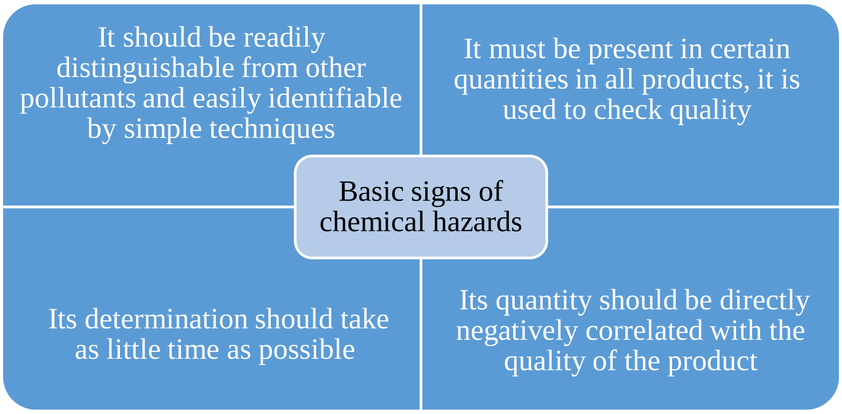


Figure 1 Basic signs of chemical hazards.

Packaging materials include packaging for direct contact with food substances, for which contaminants and toxic components mustn't migrate into the product during contact **[4]**. Paper, cardboard, and corrugated board are considered traditional packaging materials for bakery products, processed by different operations, and have different properties depending on their application. Let's analyse the sources of chemical contaminants. We can assume that the structure of the paper is formed from pulp, which, during production, goes through processes such as bleaching and adding dyes, pigments, and chemicals that strengthen the paper **[5]**. To improve paper's strength and other properties, recycled paper is produced using chemical additives **[6]**. In addition, during these processes, the inclusion of chemical components of printing inks is allowed, which increases the amount of contaminants and toxic components in food paper and cardboard packages **[7]**. Food packaging also provides easy handling and transportation by preventing chemical contamination and extending shelf life, providing consumers convenience **[8]**. The increase in food packaging materials creates a demand for promoting products and brands that are environmentally friendly **[9]**. Despite the effectiveness of existing practices, retailers still face many challenges, including the materials used and their possible interaction with food. The transfer of harmful materials from packaging to food is still an issue, especially when reusing food-grade plastic **[10]**. A significant issue is reusability, including how much packaging waste is recyclable (disposal). To reduce the toxicity of packaging waste, it is necessary to reduce the content of heavy metals in the packaging and/or ensure that such substances are not released into the environment, including the food product. Reusing organic materials for food contact is undesirable because of the difficulty in controlling the constituents present in such materials due to other types of materials other than packaging materials. Several carcinogenic and non-carcinogenic diseases may occur due to exposure to heavy metals above the safety limit **[11]**. Therefore, European legislation sets quality standards for food contact packaging materials and emphasises that materials used for food should not pose a risk to human health. According to the RASFF report, 219 notifications of food contact materials were transmitted in 2022, about half involving the migration of a wide range of substances. Most concern primary aromatic amines, followed by formaldehyde and lead **[12]**. In the Republic of Kazakhstan, there is a Register of products that do not comply with the requirements of normative legal acts in the sphere of sanitary and epidemiological well-being of the population. The grounds for inclusion of products in the Register are:

1) results of sampling and sanitary-epidemiological examination of products in cases revealing violations of the requirements of the legislation of the Republic of Kazakhstan in the sphere of sanitary-epidemiological well-being of the population poses a threat to life, human health and habitat;

2) results of sampling and sanitary-epidemiological examination of products, confirming information

from international organisations, from member states of the Eurasian Economic Union or third countries on the detection of products controlled by the state sanitary and epidemiological supervision (control), which do not meet the requirements of technical regulations **[13]**. According to the available data of the register, there was no information on violations of food contact materials.

In Europe, paper fibre has recycled an average of 3.5 times, but up to 7 cycles is technically feasible. Recycled material is often preferable to paper and board made from fresh fibres because recycling reduces waste and saves raw materials and energy. For successful recycling, separate collection systems for paper and cardboard have been created to prevent contamination by, for example, food waste. However, unlike some types of plastic, it is not customary to fractionate the collected material into food-grade and non-food-grade streams before recycling. Safety limit values set by different international standards are listed in Table 1 **[14]**.

Table 1 Variation of heavy metal concentrations among three different types of recycled papers (mg/kg).

Controlled indicators	**EPA, 2012 paper-based food packaging regulations**	**Metal Content Directive 2002/72/EC limited values**	**Council of Europe specific release limits (SRLs) for food packaging**
Lead (Pb)	3	2	0.01
Zinc (Zn)	50	100	5
Chromium (Cr)	3.05	1	0.250

On the territory of the Republic of Kazakhstan, there is Technical Regulation (hereinafter TR) 005/2011, "On the safety of packaging", which specifies sanitary and hygienic safety indicators and standards of substances emitted from packaging (closures) in contact with food products. According to this Regulation, the permissible migration quantity (hereinafter called DCM) of heavy metals is indicated in Table 2 **[15]**.

Table 2 Permissible migration amount (PMA, mg/l) of heavy metals, according to TR TS 005/2011 "On the safety of packaging".

Product material name	**Controlled indicators**	**PMA, mg/L**	**Hazard class**
Paper	Lead (Pb)	0.030	2
	Zinc (Zn)	1.000	3
	Chromium (Cr3+)	Total 0.100	3
	Chromium (Cr6+)		3
Cardboard	Lead (Pb)	0.030	2
	Zinc (Zn)	1.000	3
	Chromium (Cr3+)	Total 0.100	3
	Chromium (Cr6+)		3
Paraffinized paper and cardboard	Lead (Pb)	0.030	2
	Zinc (Zn)	1.000	3
	Chromium (Cr3+)	Total 0.100	3
	Chromium (Cr6+)		3

The study of heavy metal migration in paper food packaging makes it possible to assess their compliance with the requirements established by current legislation, thus developing a monitoring system for enterprises. Also, the scientific novelty of this study is the approbation of the method based on the measurement of resonance absorption of light by free atoms of the determined metal during the passage of light through the atomic pair of the sample under study, formed in electrothermal atomisation for the determination of heavy metals in food packaging used in the process of packaging bakery products.

Scientific Hypothesis

The main scientific hypothesis of the study is that paper-based packaging materials used for the production of bakery products exhibit varying levels of heavy metal migration, with some types likely to exceed the permissible limits set by current requirements for the safety of packaging materials. This assumption is based on the fact that paper fibre is recycled on average 3.5 times, but technically feasible up to 7 cycles, in turn recycling can increase the level of potentially hazardous chemicals in packaging and – after migration – In food.

MATERIAL AND METHODOLOGY

Samples

The samples were obtained from the manufacturer prior to certification that they conformed with the Republic of Kazakhstan's packaging safety legislation. The samples were paper bags for bakery products, laminated cardboard sheets and boxes for confectionery products, cardboard boxes, and pizza corners. Table 3 shows samples of packaging paper intended for contact with food products.

Table 3 Samples of packaging paper intended for contact with food products.

Sample code	Type of packaging paper material
1	White paper bag for bakery products.
2	Brown paper bag for bakery products.
3	White paper bag for confectionery products.
4	Brown paper bag for confectionery products.
5	Laminated white cardboard box for confectionery products.
6	Laminated brown cardboard box for confectionery products.
7	White cardboard with lamination for cakes
8	Brown cardboard with cake lamination
9	White cardboard corner for pizza
10	Brown cardboard corner for pizzas
11	White cardboard pizza box
12	Brown cardboard pizza box

Chemicals

The research utilised 65% nitric acid of EMSURE® Reag. Ph Eur, ISO.

Animals, Plants and Biological Materials

This study did not use any biological or animal components.

Instruments

Experimental studies were carried out using the atomic absorption spectrometer KVANT-Z.ETA (KORTEK LLC, Russia) The instrumental parameters of the methods are given in Table 4, while the description of the thermal programs followed for the determination of each single metal is reported in Table 5, Table 6 and Table 7.

Table 4 Instrumental Parameters of atomic absorption spectrometer KVANT-Z.ETA.

Metal	Wavelength (nm)	Slit Width (mm)	Lamp Current (mA)
Zn	307.6	0.5	20
Cr	357.9	0.5	25
Pb	283.3	0.5	10

Table 5 Graphite Furnace program for the determination of Zn.

Step	Temperature (°C)	Ramp (s)	Hold (s)
1	100	3	5
2	120	3	5
3	300	3	5
4*	2000	0	1
5	2600	0	2

Note: *The atomization occurs at step 4.

Table 6 Graphite Furnace program for the determination of Cr.

Step	Temperature (°C)	Ramp (s)	Hold (s)
1	100	3	5
2	120	3	5
3	600	3	5
4*	2400	0	1
5	2650	0	2

Note: *The atomization occurs at step 4.

Table 7 Graphite Furnace program for the determination of Pb.

Step	Temperature (°C)	Ramp (s)	Hold (s)
1	100	3	5
2	120	3	5
3	300	3	5
4*	1900	0	1
5	2600	0	2.2

Note: *The atomisation occurs at step 4.

Table 8 Calibration curve information and detection limits of atomic absorption spectrometer KVANT-Z.ETA.

Metal	Concentrateion (µg/L)	Number of calibration points	Curve type	Detection Limits (mg/dm^3)
Zn	30	3	non-linear	0.04 - 2
Cr	5	7	non-linear	0.02 - 10
Pb	5	3	non-linear	0.02 - 0,5

Calibration of atomic absorption spectrometer KVANT-Z.ETA was carried out following the operating instructions. The wavelength and slit width are selected according to the recommendations of the manufacturer of a particular model of a spectrophotometer, and the gas flow rate and spraying speed are optimized for each individual instrument, and the metal to be detected.

Laboratory Methods

The migration levels of heavy metals from food packaging materials were analysed according to ST RK 1788 1-2008 "Packaging. Requirements for measuring and identifying four heavy metals and other hazardous substances in the package and their entry into the environment. Part 1. Requirements for measuring and identifying four heavy metals in package" **[16]**.

Description of the Experiment

Sample preparation: Samples of food packaging paper were purchased from local dealers, cut into samples and stored at 24 °C (humidity: 50-55%). Experimental studies were conducted under repeatable conditions, at 22 °C; humidity 69% and atmospheric pressure 93.0 kPa, 5 series of measurements were obtained, 3 blank samples and 2 repetitions were run for each analyzed parameter to ensure accuracy and precision.

Number of samples analyzed: 12

Number of repeated analyses: 5

Number of experiment replications: 2

Design of the experiment: The studies were carried out by measuring the resonance absorption of light by free atoms of the determined metal when light passes through the atomic pair of the sample under study, formed in electrothermal atomisation. Preparation of the main calibration solution. The main calibration solution (solution A) of the metals to be determined is prepared from the corresponding Standard Reference Materials (SSR) of aqueous solutions of metal ions following the recommendation of their instructions for use. Carefully transfer a pipette 5 cm^3 of SSR into a 50 cm^3 measuring flask, bring the volume to the mark with 5% (v/v) nitric acid solution and mix. The main graded solution A contains 100 mg/dm^3 metal. The shelf life of solution A is 2 months at a temperature of 2-10 °C. Preparation of working calibration solution with a concentration of 10 mg/dm^3 (solution B). 10 cm^3 of solution A is transferred with a pipette into a measuring flask with a capacity of 100 cm^3, brought to the mark with 5% (v/v) nitric acid solution and mixed. The metal concentration in the resulting calibration solution B is 10 mg/dm^3. Preparation of working calibration solution with a concentration of 1 mg/dm^3 (solution C). 10 cm^3 of solution B with a concentration of 10 mg/dm^3 is transferred into a measuring flask with a capacity of 100 cm^3, bring the volume to the mark with 5% (v/v) nitric acid solution and stir. The resulting calibration solution C contains 1 mg/dm^3 of metal. A series of calibration solutions of the metals to be determined is prepared by adding the volumes of working calibration solutions to 100 cm^3 measuring flasks and bringing to the mark with 5% (v/v) nitric acid solution. Preparation of aqueous extract from the sample using nitric acid. The package samples weighing 30 g, weighed with an error of no more than 0.001 g, were placed in conical flasks (Figure 2).To the samples, pour 99 cm^3 of distilled water into a pipette or cylinder. The sample with water is stirred for 3 min, after adding 1 cm^3 of nitric acid (65%) by pipette and left for 24 hours. Prepared samples were decanted and filtered through a fritted-glass filter with porosity 4 (nom. size 90).

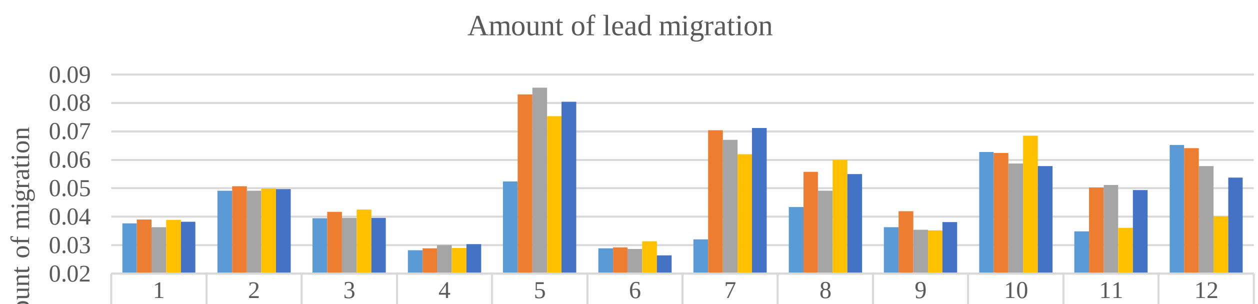
Figure 2 Samples of samples after preparation in aqueous fume hood.

Statistical Analysis

Statistical analysis was performed to evaluate the amount of migration of lead, chromium and zinc by one-way ANOVA and Tukey HSD as post hoc tests using Excel and SPSS for Windows V27.0.1.0 software (SPSS, Inc., Chicago, IL, USA, 2020). Results were considered statistically significant at a p-level equal to or less than 0.05 ($p \leq 0.05$).

RESULTS AND DISCUSSION

Low cost, lightweight, availability, printability and durability make paper and paperboard products popular as food packaging materials worldwide **[17]**. However, a limitation of using paper and paperboard as food packaging material is its permeability to moisture, which can promote the migration of undesirable compounds from paper and paperboard packaging into food products. The study **[18]** shows that heavy metals in food products are water soluble, and the heavy metal content of food products will decrease if the products are handled or cooked with water. In addition, it is pointed out that it is necessary to determine the migration rate in other cooked foods and to evaluate the risk of heavy metals in concentrations calculated from the migration rate. In this work, the migration of zinc and its effect on the functionality of the nanocomposite film has been studied. In contrast, the migration of zinc from paper packaging materials for food contact still needs to be studied. Natural pigments are the main source of lead in paper and board **[19]**. Lead content should be no more than 0.050 mg/L and can be found in paper and cardboard, especially those intended for use in the printing industry. Lead content in paper and cardboard intended for packaging will be reduced to 0.020 mg/L **[20]**. The results of the study of lead migration during water extraction are presented in Figure 3.



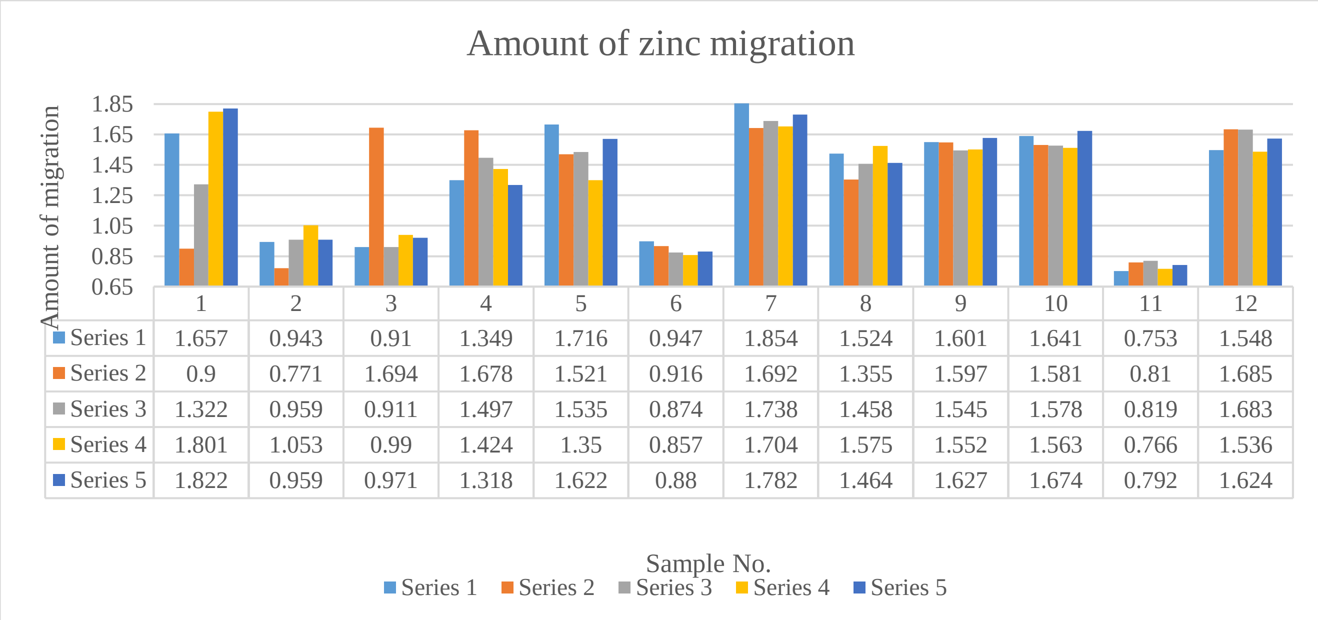
	1	2	3	4	5	6	7	8	9	10	11	12
Series 1	0.03765	0.0491	0.03943	0.02819	0.0524	0.02885	0.032	0.0434	0.03634	0.06274	0.03482	0.06526
Series 2	0.03902	0.05069	0.04171	0.02892	0.083	0.02921	0.0704	0.0558	0.04192	0.06244	0.05022	0.06408
Series 3	0.03632	0.04911	0.03959	0.02999	0.0854	0.02867	0.067	0.0492	0.03546	0.05876	0.0512	0.05782
Series 4	0.03895	0.0499	0.04253	0.02895	0.0754	0.0314	0.062	0.06	0.03518	0.06852	0.03608	0.04012
Series 5	0.03822	0.04971	0.03959	0.03032	0.0804	0.02642	0.0712	0.055	0.03808	0.05784	0.04942	0.05376

Sample No.

Series 1 Series 2 Series 3 Series 4 Series 5

Figure 3 Results on the study of the amount of lead migration.

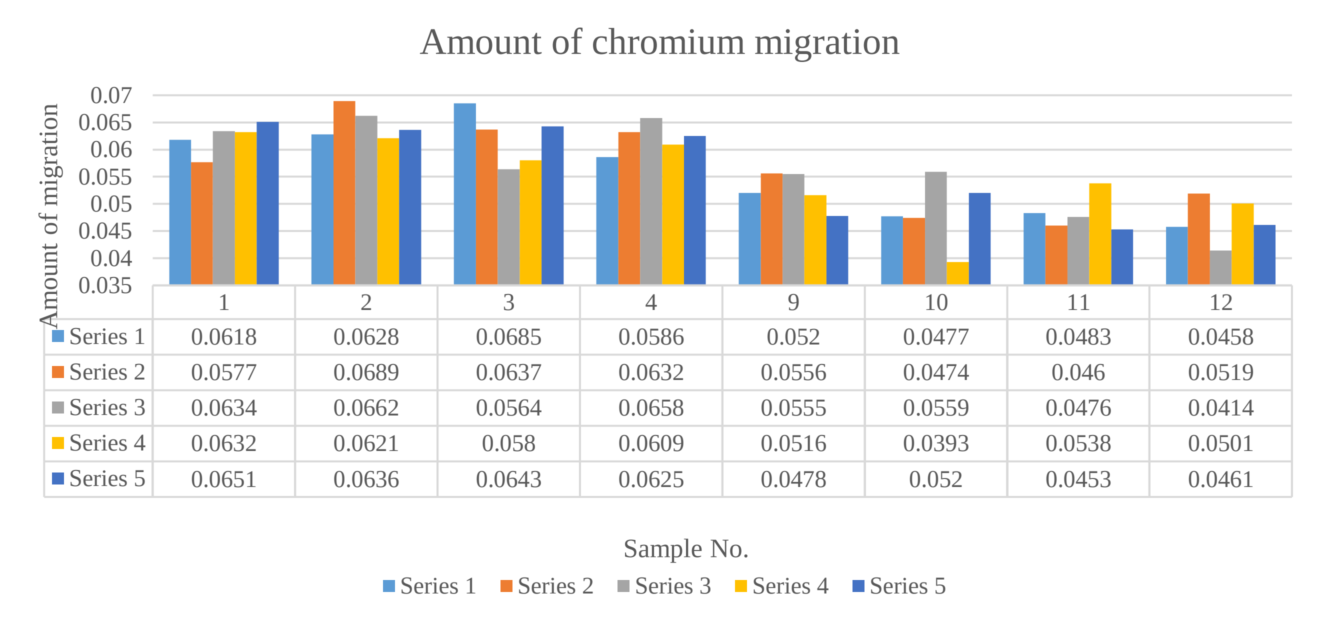
The main reason for high migration rates is using various synthetic and natural pigments, which contain various heavy metal compounds transferred to paper and cardboard packaging **[14]**. The use of recycling is also one of the important reasons for the formation of large amounts of heavy metal compounds. Sood and Sharma used an inductively coupled plasma-optical emission spectrometry technique to determine the content of various metals in paper food packages. They found high lead levels in similar packages **[21]**. These results indicate the lead content problem and potential lead migrations into food products. Interest in incorporating nanoparticles into food contact materials is growing due to their attractive functions, such as ultraviolet (UV) blocking and antimicrobial activity **[11]**. When using nanoparticles, it should be considered that heavy metal migration affects food packaging, especially acidic foods, as Zn is likely to migrate. Hence, their UV blocking and antimicrobial functions may no longer be effective. Zinc oxide or zinc sulfate compounds are sometimes added to paper and are used to increase opacity and to produce copying and packaging paper **[22]**. In the final product, these compounds, including food, can migrate into the environment. The results of the study of zinc migration during aqueous extraction are presented in Figure 4.



	1	2	3	4	5	6	7	8	9	10	11	12
Series 1	1.657	0.943	0.91	1.349	1.716	0.947	1.854	1.524	1.601	1.641	0.753	1.548
Series 2	0.9	0.771	1.694	1.678	1.521	0.916	1.692	1.355	1.597	1.581	0.81	1.685
Series 3	1.322	0.959	0.911	1.497	1.535	0.874	1.738	1.458	1.545	1.578	0.819	1.683
Series 4	1.801	1.053	0.99	1.424	1.35	0.857	1.704	1.575	1.552	1.563	0.766	1.536
Series 5	1.822	0.959	0.971	1.318	1.622	0.88	1.782	1.464	1.627	1.674	0.792	1.624

Figure 4 Results on the study of the amount of zinc migration.

Zinc oxide and zinc sulfate are used in papermaking to increase the opacity of speciality papers. According to Erkan and Malayoglu, when strong mineral acids were used as food simulants, the paper's maximum, minimum and average values of Zn content were below the limit values compared to the EC requirements. In addition, it was observed that the colour of paper packaging has an important role in zinc content, especially red and blue colours affected zinc formation at about the same rate **[23]**. Due to recycling, hexavalent chromium cannot be present in paper or cardboard as it is immediately converted to trivalent chromium. The chromium content should be a maximum of 0.1 mg/L **[23]**. The source is mainly natural white pigments (kaolin, clay, calcium carbonate, etc.) used as paper-making fillers and surface coating to improve printing quality **[24]**. The amount of chromium migration was not detected in samples No. 5-8. The results of the chromium migration study in water extraction are presented in Figure 5.



	1	2	3	4	9	10	11	12
Series 1	0.0618	0.0628	0.0685	0.0586	0.052	0.0477	0.0483	0.0458
Series 2	0.0577	0.0689	0.0637	0.0632	0.0556	0.0474	0.046	0.0519
Series 3	0.0634	0.0662	0.0564	0.0658	0.0555	0.0559	0.0476	0.0414
Series 4	0.0632	0.0621	0.058	0.0609	0.0516	0.0393	0.0538	0.0501
Series 5	0.0651	0.0636	0.0643	0.0625	0.0478	0.052	0.0453	0.0461

Figure 5 Results of the study of the amount of chromium migration.

The results of this study suggest that laminated surface treatment of paper packaging helps reduce chromium migration in the aqueous extract. High chromium content was found in confectionery boxes in paper food packaging in India. In addition, chromium ingestion is suspected to be caused by printing inks and wood treated with chromate copper arsenate as a preservative **[21]**. Compared to the above studies, the method used in this work provides a more stable process for obtaining results from aqueous extracts by using an atomic absorption spectrometer. The authors **[25]** used drying food packages after preparing an aqueous extract to measure the total migration of heavy metals. The main difference of this work is the possibility of determining different types of heavy metals and the possibility of application in other types of packaging materials. The limitation of this study is the dependence of the results on the detection limits of the atomic absorption spectrometer, which may affect the study of the content of small amounts of compounds in food packages. Assessment of heavy metal migration results according to sanitary-hygienic requirements for food packages in the Republic of Kazakhstan. Material properties such as mechanical and other physical properties, permeability, sealing and migration of substances in contact with food determine food quality, shelf life and safety. Therefore, food packaging materials need to be tested to ensure that they have the correct properties in terms of permeability to gases, water vapour, contaminants, mechanical and other physical properties, and thickness of the main components and coating layers **[26]**. In investigating plastic-based food contact materials **[24]**, the paper showed that plastic-based materials potentially threaten the environment and public health by releasing toxic heavy metals. This study aimed to identify the types of plastic commonly used as food contact materials (FCM) in Bangladesh and assess the migration of heavy metals from these FCMs. As the study shows that paper packaging material is also a potential threat to public health if a certain level of migration is not controlled. The average amount of metal migration plays a major role in food safety. The levels of similarity and/or difference, as well as the significance level between the groups of samples studied, were identified for each requirement of sanitary and hygienic safety indicators and standards of substances emitted from food contact packaging. The average amount of heavy metal migration from food packages intended for contact with food products is shown in Table 9.

The study showed that in all types of paper, there was a significant amount of heavy metals, which did not meet the requirements established by the Technical Regulation for paper intended for food packaging. In the study of the amount of zinc values close to the limits established by TR CU 005/2011. As a result of the evaluation of the presence of heavy metals: zinc (Zn), chromium (Cr) and lead (Pb) in different recycled papers, the variation of the mean value with standard deviations of the different heavy metals present in each type of paper and the safety limits set by different international standards are shown in Table 1. Compliance of the research results with the requirement of sanitary and hygienic safety indicators and norms of substances migrating from the packaging is an important factor for regulating the safety level of food packaging in the countries that have adopted this Technical Regulation. Compliance with the safety requirement of the average amount of migration of heavy metals for each sample of food packages, according to TR TS 005/2011 "On the safety of packaging", is shown in Figure 6.

Table 9 Average amount of heavy metal migration from food packages.

Sample	Amount of migration		
	Pb	**Cr**	**Zn**
1	0.0380 ±0.00111[ab]	0.0525 ±0.00323[a]	1.5004 ±0.39071[b]
2	0.0497 ±0.00066[bc]	0.0485 ±0.00620[a]	0.9370 ±0.10249[a]
3	0.0406 ±0.00145[ab]	0.0482 ±0.00335[a]	1.0952 ±0.33663[a]
4	0.0293 ±0.00087[a]	0.0471 ±0.00410[a]	1.4532 ±0.14356[b]
5	0.0753 ±0.01334[d]	Not detected	1.5488 ±0.13583[b]
6	0.0289 ±0.00177[a]	Not detected	0.8948 ±0.03624[a]
7	0.0605 ±0.01635[c]	Not detected	1.7540 ±0.06592[b]
8	0.0527 ±0.00646[bc]	Not detected	1.4752 ±0.08248[b]
9	0.0374 ±0.00277[ab]	0.0622 ±0.00280[b]	1.5844 ±0.03483[b]
10	0.0621 ±0.00421[c]	0.0647 ±0.00281[b]	1.6074 ±0.04769[b]
11	0.0443 ±0.00816[ab]	0.0622 ±0.00494[b]	0.7880 ±0.02815[a]
12	0.0562 ±0.01014[bc]	0.0622 ±0.00268[b]	1.6152 ±0.07130[b]

Effect of types of packaging materials on migration of heavy metals from packaging		
Sanitary and hygienic safety indicators	***F***	***p***
Pb	17.313	<0.001
Cr	384.415	<0.001
Zn	64.967	<0.001

Note: Data are expressed as mean (n = 5) ± standard deviation (SD). The effect of type of packaging material on migration of heavy metals from packaging is significant at $p \leq 0.05$. [a-b] Mean values in the column with different letters are significantly different ($p \leq 0.05$).

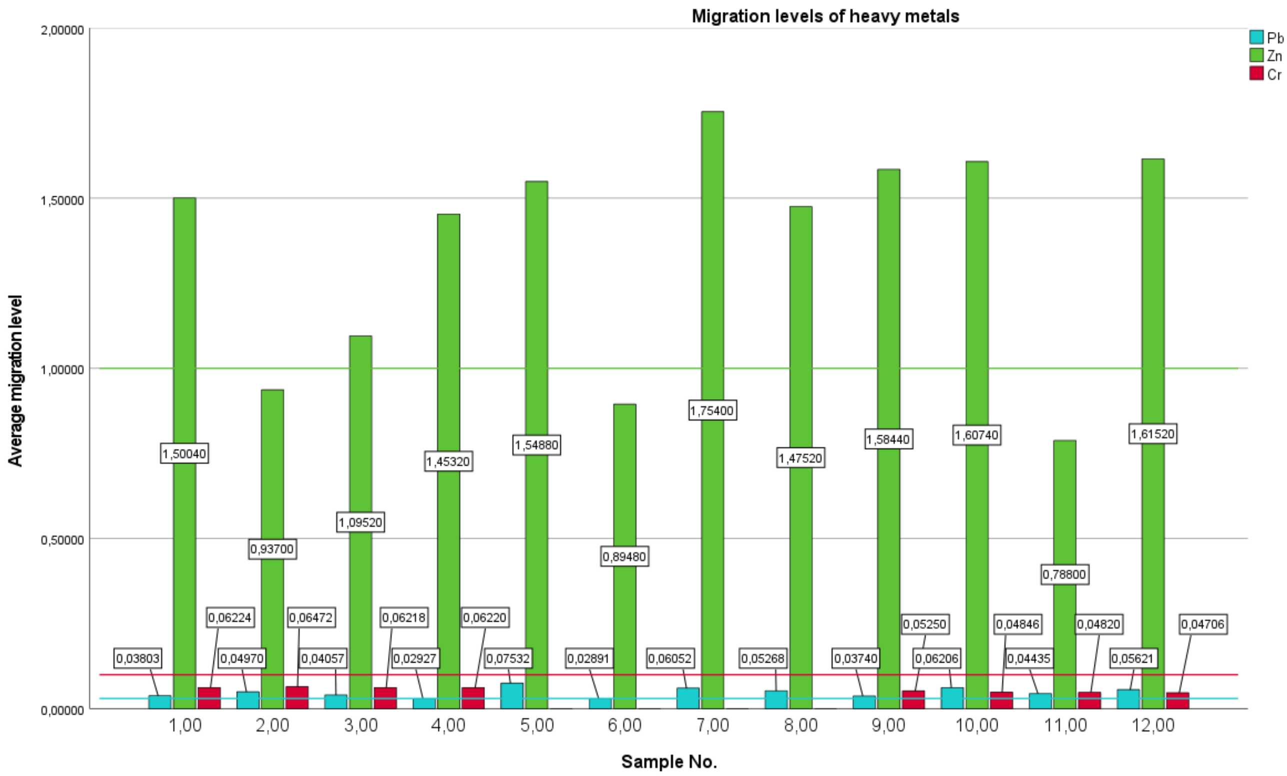


Figure 6 Average migration level of heavy metals according to the requirement of TR TS 005/2011 “On the safety of packaging”.

A study **[27]** analysed heavy metals, including lead (Pb), cadmium (Cd), arsenic (As) and aluminium (Al) in oilseeds, noodles, tea leaves and their processed or cooked products to study the effect of food processing methods on the migration of heavy metals. The paper indicates ways to reduce heavy metals naturally present in food products. Recycling is currently seen as an important measure to manage packaging waste. However, recycling can increase potentially hazardous chemicals in packaging and - after migration – In food **[28]**. Chemicals of various origins are commonly present in recovered paper and may eventually end up in the recycled product. The paper shows that these include additives introduced during manufacturing and often intended to be retained in the paper product, such as fillers, retention agents, adhesives, coatings, biocides and synthetic binders. In addition, paper is typically printed, dyed, glued or labeled, resulting in printing inks, adhesives, photoinitiators, solvents, plasticisers, surfactants and pigments in the wastepaper. Contaminants can also be introduced during the use or waste disposal process, as paper and paperboard tend to absorb chemicals. Thus, recycled paper and paperboard used as primary or secondary food packaging is usually derived from rather uncertain sources. A study **[29]** examined food contact materials, items of any type intended to come into contact with food, thus representing a potential source of human exposure to chemicals. The authors point out that information on chemical constituents and potential human health effects remains scarce for materials made from paper and cardboard, making safety assessment difficult. The paper describes a guided exposure strategy for identifying and characterising new chemicals for paper and paperboard. That is, practical regulation remains unlearned.

Recommended interim production control measures

Food safety is considered in European legislation within the framework of an integrated approach based on the principle "from the field (stall) to the table" as a single continuous chain that starts with the production of animal feed includes (but is not limited to) the production of primary products, processing, packaging, transportation and marketing, and ends with the consumption of the food product by the final consumer **[30]**. The international document **[31]** states that food business operators must ensure that food contact materials and articles are used in the production or preparation, storage and distribution of food in a manner that does not compromise compliance with applicable Council of Europe Technical Guidelines, EU and Member State legislation or recommendations on food contact materials and articles.

In the production of bakery products, there are significant critical control points such as baking and cooling processes **[32]**. Naturally, every food processing plant has a certificate of conformity check when purchasing packaging materials. It is proposed that purchasing packaging materials should be included as a control point **[33]**. A control point is any point in a particular food system where loss of control does not result in an unacceptable health risk **[34]**. To these intermediate control processes, according to the results of this study, monitoring the procurement process of the packaging can be added as a control point, as shown in Table 10.

Table 10 Recommended monitoring activities for the implementation of interim production control.

	No. CP	CP No. 3 – procurement process for packaging materials
The monitoring procedure	**Dangerous factor**	Chemical Hazard Factor - absence of a certificate of conformity if the requirements for evaluating the choice of packaging materials for contact with bakery products are not met. Permissible migration amount (PMA) of heavy metals, according to TR TS 005/2011 "On the safety of packaging".
	Procedure (what will be measured, how, how often)	Compliance with the requirements for evaluating the choice of packaging materials for contact with bakery products.
	Frequency (how often)	Once a year, an independent examination by an accredited testing laboratory is recommended.
	Responsible	Technologist
	Correction, corrective actions	Product inspection, rejection, isolation and disposal if necessary. Additional staff training on purchasing of packaging materials
	HACCP records	Records in the logbook of control of technological parameters test protocols of packaging materials. Records of confirmation of competence and responsibility of personnel

Chemical hazards in food products usually result from unintentionally including certain ingredients during food production **[35]**. A scientific paper **[36]** presents the results of studies on the kinetics of food deterioration. The paper provides an in-depth study of shelf life and various evaluations of approaches to determining the shelf life of finished products. Based on the nature of food products as physically, chemically and biologically active systems, food quality is a dynamic state constantly changing at ever lower levels **[37]**. In general, the overall quality of food products is better described by organoleptic evaluation. Consequently, for each product, there is a certain finite time from the moment of its production, during which, under given storage conditions, it retains the required level of organoleptic properties **[38]**. Metals and alloys are used in food contact materials and articles, food-processing equipment, containers, household utensils, and foil used to wrap food. These materials are frequently used as a safety barrier between the food and the environment. They are often covered by a coating to reduce ion release into foods. Metal ions can be released from materials and put into food. They may endanger the health of the 89 consumers if the intake exceeds the toxicological reference value or may unacceptably alter the 90 composition of the food or its organoleptic characteristics. Consequently, it was decided to establish 91 technical guidance in this area **[39]**. The results of this study indicate the importance of regulating the safety levels of food packaging at the level of technical documents, as the obtained data exceeded/complied close to the maximum permissible requirements of TR TS 005/2011. Thus, these samples should be considered as a potential risk to human health if they can be reused without any pre-treatment as a source of recycled cellulose fibre for the production of packaging to be used in direct contact with food. One tonne of recycled newspapers will save one tonne of wood while recycling printing or copy paper will save more than 2 tonnes **[40]**.

This finding presents authorities with a dilemma: recycling is supported for the sustainable use of materials, but based on current toxicological assessments, migration often goes far beyond what is acceptable **[41]**. Using recycled cardboard and corrugated cardboard for food packaging is in the interest of resource sustainability, but in most cases, food must be protected from contamination by these materials **[42]**. Due to increased consumer health awareness, the importance of transferring harmful materials from packaging to food is of great concern **[43]**. Chemical compounds incorporated into packaging materials to improve functionality can interact with food components during processing or storage and migrate into the food. Food quality and safety can be jeopardised once these compounds reach a certain limit **[44]**.

In general, it is necessary to identify and restrict the amount of migrating chemicals from the coating into food to a level that does not present risks to human health. An evaluation of starting substances can serve as a basis for the safety assessment of coatings, provided that the evaluation considers the foreseeable reactions that may occur during the manufacturing process **[45]**. Ideally, the evaluation should consider both the starting material AND the type of process to guarantee that the use of such material will always lead to the same reaction or degradation products (evaluated as of no safety concern when the substance was assessed) **[46]**.

According to the study's results, we can conclude that the main scientific hypothesis is confirmed. Paper-based packaging materials used for the production of bakery products show different levels of heavy metal migration, and some types exceed the permissible limits established by the requirements for the safety of packaging materials.

CONCLUSION

1. Heavy metals in food packages used in bakery products were determined by atomic absorption spectrometry: zinc migration (13.6% less than PMA for sample No. 9, 9.8% less than PMA for sample No. 10, 11.3% less than PMA for sample No. 11, 12.9% less than PMA for sample No. 12, respectively). Samples No. 1 to No. 8 had no significant difference, with the lowest zinc content in sample No. 8 (45.1% less than PMA).

a) Lead. As a result of the study, the average amount of lead migration from food packaging was below the PMA specified in TR/TC 005 2011 'On the safety of packaging' in samples No. 4 and No. 6 (2.42% less than the PMA for sample No. 4 and 3.63% less than the PMA for sample No. 6, respectively). The results of the remaining samples exceeded the permissible migration level. The highest amount of lead was detected in samples No. 5 (151.06% more than the permissible level), No. 7 (101.73% more than the permissible level), No. 8 and No. 10 (75.6% and 106.86% more than the PMA, respectively).

b) Zinc. The average amount of zinc migration from samples No. 2, No. 6, and No. 11 met the acceptable migration level specified in the Technical Regulations (6.3% less than the PMA for sample No. 2, 10.52% less than the PMA for sample No. 6, and 21.2% less than the PMA for sample No. 11, respectively). On average, the other samples exceeded the PMA by 1.5 times. The highest amount of zinc migration was found in samples No. 5, No. 7, No. 9, No. 10, and No. 12 (54.9% more than the PMA for sample No. 5, 75.4% more than the PMA for sample No. 7, 58.4% more than the PMA for sample No. 9, 60.7% more than the PMA for sample No. 10, 61.5% more than the PMA for sample No. 12, respectively).

c) Chromium. No chromium content was detected in the laminated cartons. The values of the other samples were within the permissible limits of the Technical Regulations. The average amount of chromium migration in paper packages and cartons was significantly different, with the highest value in sample No. 1 for paper packages and in sample No. 10 for cartons (47.5 per cent less than the PMA for sample No. 1 and 35.3 per cent less than the PMA for sample No. 10, respectively).

2. According to the results of the assessment of the average migration level of heavy metals according to the requirement of TR TS 005/2011 'On the safety of packaging' (Figure 2), it can be concluded that in all types of paper, there is a significant amount of lead and zinc, the level of which did not meet the requirements established by the Technical Regulations for paper intended for food packaging. In the study of the amount of zinc, values were found to be close to the limits set by TR CU 005/2011. Thus, these particular samples should be considered as a potential risk to human health in case they can be reused without any pre-treatment as a source of recycled cellulose fibre for the production of packaging to be used in direct contact with food products.

Further research is needed to study in more depth the influence of food simulator parameters such as temperature and acidity, as well as the effect of storage time, on the degree of migration of heavy metals directly to the food product.

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