Selection of priority unintentionally present chemical contaminants based on the example of rice retailed in the Russian Federation

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Abstract

Chemicals that are not subject to hygienic standards and yet are found in rice can be classified as unintentionally present chemicals in food products. However, these chemicals can pose a potential health hazard, which requires an assessment of the risk they represent. For this purpose, it is necessary to select priority potentially dangerous unintentionally present chemicals in rice. The study included five samples of rice from Cambodia, India, and Russia. Chemical element content studies were conducted on Agilent 7900 mass spectrometer (Agilent Technologies, Japan/Singapore) with an octopole collision/reaction cell (ORS) using the semi-quantitative analysis program for the mass spectrometer. The selection of priority unintentionally present chemical contaminants in rice was conducted in three stages. The researchers applied specific criteria to include chemicals in the further assessment at each stage. As a result of the evaluation of the selection of priority unintentionally present chemicals contained in rice sold through retail chains, a potential hazard category (PHC) was established, i.e., an integral characteristic of the potential hazard of an unintentionally present chemical contained in a food product, covering the possibility of ingestion of a specific chemical and its toxicity. Thus, in accordance with the PHC, aluminum was identified as priority potentially hazardous chemical contained in rice for further risk assessment since it corresponded to category I of the potential hazard.

Keywords: *chemicals, hazard, integral index, category, risk assessment.*

1. INTRODUCTION

One of the priorities of the global concept of food security and nutrition for the period up to 2030 is to ensure food safety in relation to chemical pollution [1]. Currently, the content of many hazardous chemicals in food products is controlled using state regulatory

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instruments [2]. The state regulation means developing of hygienic standards for the content of hazard chemicals in food. However, the improvement of analytical methods and testing technologies makes it possible to detect many chemicals in food products, including in very low concentrations. At the same time, among the identified chemicals, some may be unintentionally (including naturally) present in the food product and may pose a danger to human health. The presence of these chemicals in food products may be due to the peculiarities of the production of raw materials, transportation, packaging, and, in fact, the manufacturing of these products [3-4].

In this regard, to ensure food security with respect to the content of unintentionally present chemicals, it is advisable to conduct a health risk assessment and consider the need for hygienic regulation. For this purpose, it is necessary to select priority potentially dangerous unintentionally present chemicals.

The purpose of the study was to select priority unintentionally present chemical contaminants, using the example of rice sold through retail chains to assess the health risk further.

2. MATERIALS AND METHODS

The object of the study on the content of unintentionally present chemical contaminants in food products was rice sold through retail chains in the Russian Federation. The study examined five samples of popular brands of rice available in retail chains: sample 4 of round-grain rice grown in Cambodia, sample 5 represents steamed rice from India, and other samples were from the Russian Federation. The chemicals classified as unintentionally present served as the subject of the study.

The authors conducted hazard identification of unintentionally present chemicals in rice in 3 stages: chemical and analytical identification of unintentionally present chemicals; integrated hazard assessment of chemicals using selection criteria, followed by the use of scoring and summation of points, and the final stage of categorization of chemicals with the assignment of the potential hazard categories for further assessment of health risk based on the integral index.

At the chemical and analytical identification stage, the inclusion of chemicals for an integrated hazard assessment was conducted by their presence in more than 50% of rice samples.

Rice samples were crushed to fine powder in TSM6A017C system (BOSCH, Slovenia). When preparing solutions and samples, we used extra pure HNO_3 (Sigma - Aldrich, USA). To purify hydrochloric acid (GOST 3118-77) we used Savillex distillation system (USA), model DST - 1000. We used deionized water with resistivity 18.2 Mega-ohm·cm purified in Milli-Q Integral system (Millipore SAS, France).

Preparation of rice samples was carried out by acid mineralization in a microwave system SW-4 (Berghof, Germany). We added a 0.5 g sample of rice to Teflon autoclaves (or quartz inserts) of the microwave sample preparation system, where 6.5 mL of concentrated HNO_3 and 0.5 mL of concentrated HCl were injected with a pipette. The samples were left open for 80 - 90 min. The autoclaves with the added sample were closed and placed in the microwave sample preparation system. Sample decomposition in the microwave system proceeded at 120ºC for 10 min, then at 170ºC for 5 min at 40 bar. When cooled to room temperature, the obtained solution was transferred into a 15 mL plastic tube. Prior to measurements, we added to the tubes of the automatic sampler 0.5 mL of the sample and 0.05 mL of the complex solution of the internal standard with a mass concentration of 100 $\mu g/dm^3$ of reference elements, 0.05 mL of the internal standard with a mass concentration of 100 $\mu g/dm^3$ of rhodium and 4.4 mL of deionized water. The chemical elements content studies were conducted on Agilent 7900 mass spectrometer (Agilent Technologies, Japan/Singapore) with an octopole collision/reaction cell (ORS) using the semi-quantitative analysis program for the mass spectrometer. The results are presented in Table 3 as the arithmetic mean of the four measurements.

The accuracy of the results was confirmed by the analysis of solutions with the certified content of the determined chemicals. The certified reference material of rice flour SRM 1568b (NIST USA) was used as a standard sample. The obtained mass concentration values for 22 elements corresponded to the certified values.

The concentrations of chemicals classified as naturally present in the food product, in turn, should be compared with the average values of natural levels of their content in rice (based on literature data) to avoid an overestimation of their potential danger. If it does not exceed the values set for the food product, it is advisable to exclude it from the integral assessment and categorization.

At the stage of the integral assessment, the prioritization of hazardous unintentionally present chemicals found in rice was conducted based on an integral index, which was calculated using scoring according to the toxicity criterion, which largely determines their potential danger. In addition, when calculating the integral index, the authors applied the criteria that characterized the possibility of the intake of potentially hazardous chemicals during the manufacturing and sale of products.

The scoring was conducted by the toxicity class of the chemical adopted in the Oxford "Handbook of Hazardous Chemicals" according to LD_{50} when administered orally [5] (Table 1).

Table 1. *The score depending on the toxicity class of chemicals established by the LD_{50} value (rats, intragastric, mg/kg).*

LD_{50}	***TC***	***Description***	***Point***
≤ 1	I	Highly toxic	6
1 - 50	II	Highly toxic	5
50 - 500	III	Moderately toxic	4
500 - 5,000	IV	Low-toxic	3
5,000 - 15,000	V	Almost non-toxic	2
> 15,000	VI	Relatively harmless	1

TC - toxicity class

Toxicity data (LD_{50} value) were obtained using relevant information sources, such as PubMed, PubChem, and US EPA databases.

When assessing the priority of unintentionally present chemical chemicals, the authors used additional criteria that take into account the possibility of migration during the preparation of food for consumption (yes - 1 point; no - 0 points), the possibility of migration from packaging, containers, storage tanks, etc. (yes - 1 point; no - 0 points), the likelihood of their entry into the food product with the raw material (yes - 1 point; no - 0 points).

The result of the integral evaluation stage is the development of an integral indicator by formula 1. The maximum value of this indicator in accordance with the proposed criteria was 9 points.

$$II=\Sigma_{n\ 1+ n\ 4}, \text{ where} \qquad (1)$$

II is an integral index;

n1...n4 - the number of points according to the criteria.

At the categorization stage, depending on the value of the integral index, a Potential Hazard Category (PHC) of unintentionally present chemicals was determined, i.e., an integral characteristic of the potential hazard of a chemical contained in a food product, covering the possibility of a particular chemical and its toxicity. PHC is the basis for making decisions on the selection of priority chemicals to assess the health risk and their possible regulation (Table 2).

Table 2. *Categories of potential hazards of unintentionally present chemicals for health risk assessment and possible regulation*

PHC	***Integral index value***	***Characteristics of potential hazard***
III	≤ 2	Low
II	3 - 5	Medium
I	6 - 9	High

Under the PHC, category III included chemicals that did not require risk assessment and subsequent regulation. Category II (medium) included chemicals, the potential hazard of which required confirmation by additional studies. Category I (high) included chemicals requiring risk assessment and possible regulation.

3. RESULTS AND DISCUSSIONS

Certain researchers [6-7] in studies of the chemical composition of rice identified chemicals that do not have developed hygienic standards and thus can be classified as unintentionally present.

According to chemical and analytical identification, 36 chemicals were found in rice sold through retail chains (Table 3), two of which were excluded from further evaluation since their occurrence in the samples was lower than 50% (Figure 1).

Table 3. *Concentrations of chemicals in samples of rice sold through retail chains, mg/kg*

No	Chemicals	Concentrations in rice samples					Frequency of occurrence, %
		1	2	3	4	5	
1	Li	undefined	undefined	0,0050	0,0347	0,0745	60
2	To	1.52	1.76	1.08	1.83	5.51	100
3	Na	20.91	undefined	1.55	3.21	123.78	80
4	Mg	329.13	194.56	434.31	506.26	309.11	100
5	Al	2.11	0.41	2.14	1.26	4.66	100
6	Si	9.25	18.15	6.75	8.21	15.50	100
7	P	840.43	0.86	1189.26	1455.11	1304.39	100
8	S	2794.00	4525.26	3014.89	3279.77	3291.62	100
9	K	1090.26	905.80	1436.66	1780.96	2368.62	100
10	Ca	9.51	7.05	7.69	10.08	5.22	100
11	Ti	undefined	undefined	0.0060	0.0015	0.0301	60
12	V	0.0054	0.0020	undefined	0.0032	0.0060	80
13	Cr	undefined	undefined	undefined	undefined	0.0972	20
14	Mn	20.32	8.72	15.71	16.02	4.05	100
15	Fe	6.29	10.37	6.20	6.72	12.17	100
16	Co	0.0039	0.0208	0.0069	0.0067	0.0749	100
17	Ni	0.051	0.152	0.062	0.070	0.678	100
18	Cu	2.95	1.50	2.70	2.53	4.46	100
19	Zn	11.37	13.40	12.23	9.61	5.64	100
20	As	0.175	0.124	0.183	0.132	0.091	100
21	Se	0.0239	undefined	0.0035	0.0003	0.0900	80

No	Chemicals	Concentrations in rice samples					Frequency of occurrence, %
		1	2	3	4	5	
22	Br	0.631	undefined	0.118	0.147	18.733	80
23	Sr	0.185	0.141	0.218	0.212	0.335	100
24	Mo	0.341	0.455	0.405	0.403	0.472	100
25	Ag	0.0018	0.0015	0.0025	0.0013	0.0022	100
26	Sn	undefined	undefined	0.0050	0.0025	0.0120	60
27	Sb	0.00045	0.00108	0.00072	0.00050	undefined	80
28	Ba	0.045	0.085	0.075	0.052	0.142	100
29	W	0.00044	0.00001	0.00057	0.00013	0.00085	100
30	Pt	undefined	0.00001	undefined	0.00013	undefined	40
31	Au	0.00002	0.00020	0.00001	0.00001	0.00001	100
32	Hg	0.00249	0.00150	0.00214	0.00322	0.00343	100
33	Cd	0.0062	0.0192	0.0061	0.0076	0.008	100
34	Hg	0.0025	0.0015	0.0021	0.0032	0.0034	100
35	Pb	undefined	undefined	undefined	undefined	undefined	0

**undefined - the chemical was not detected*

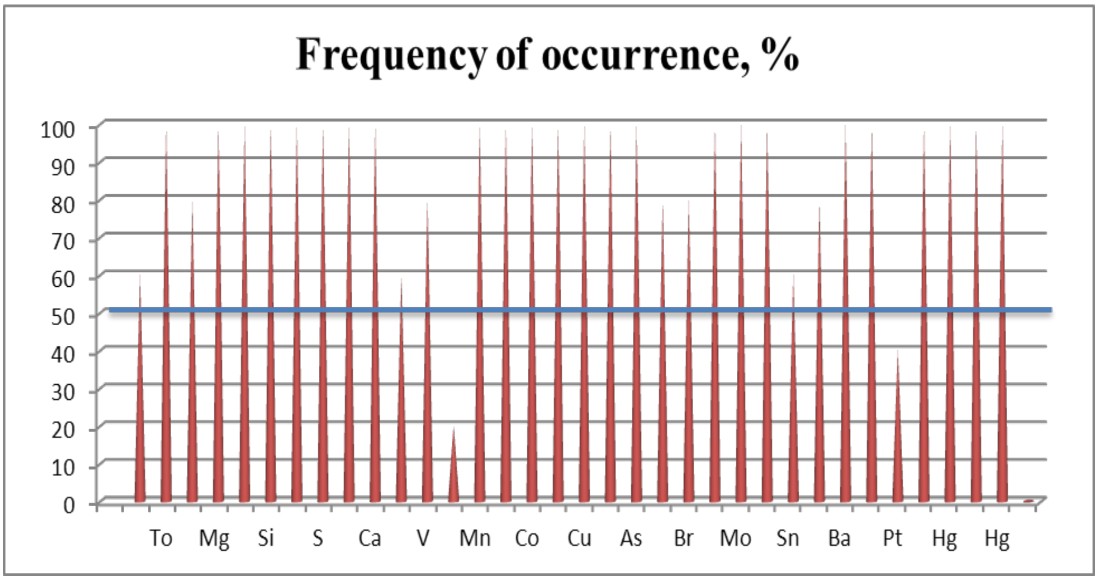

Figure 1. *Frequency of occurrence of chemicals in samples of rice sold through retail chains, % (the chemicals below the line are excluded from the assessment)*

The content of arsenic, cadmium, mercury in all samples of rice did not exceed the maximum permissible concentrations permitted in the Russian Federation according to the Technical Regulation of the Custom Union No. 021-2011 "About food safety" (arsenic (As) - 0.2 mg/kg; mercury (Hg) - 0.03 mg/kg; cadmium (Cd) - 0.1 mg/kg). The chemicals that were regulated by the hygienic standards and corresponded to them were also excluded from the study.

The obtained concentrations of chemicals were compared with the average values of their natural content in rice, which made it possible to include in the assessment of potential hazard chemicals whose actual content exceeded the average content was established according to literature data, in this product (Table 4) [8].

Table 4. *Actual and average content (according to literature data) of naturally present chemical chemicals in rice samples*

No	The name of a naturally present chemical in rice	The average actual content in rice samples (mg/kg)	The average content in rice according to literature data (mg/kg)
1	K	1,516.5	3,140
2	Ca	7.9	400
3	Si	11.6	12,400
4	Mg	354.7	1,160
5	Na	29.9	300
6	S	3,381.1	600
7	P	958.0	3,200
8	B	2.3	0.2
9	V	0.003	0.4
10	Fe	8.4	21
11	Co	0.02	0.07
12	Mn	12.9	36.3
13	Cu	2.8	5.6
14	Mo	0.4	0.3
15	Ni	0.2	0.5
16	Se	0.02	0.2
17	Zn	10.5	18

According to the comparison results, three chemicals (sulfur, bromine, and molybdenum) exceeded their natural content in rice. Consequently, 13 chemicals were included to obtain an integral indicator to establish the priority of unintentionally present chemicals contained in rice.

As a result of evaluating the probability criteria for the presence of detectable chemicals in rice and the level of toxicity (LD_{50}), the authors of the study calculated an integral index and established the categories of the potential hazard of unintentionally present chemicals for health risk assessment (Table 5).

Table 5. *Results of the selection of unintentionally present hazardous chemicals contained in rice, taking into account the category of the potential hazard for further health risk assessment.*

No	Name of the chemical	CAS	Assessment of the probability of presence in the product (points) (Yes – 1 No – 0)			Toxicity assessment				Integral index	PHC
			Migration to raw materials	The probability of migration from packaging, containers, etc.	The probability of migration of chemicals during the preparation of a food product for consumption	LD_{50}, mg/kg	Reference	TC	Points		
1	Al	7429-90-5	1	1	1	2000	[9]	IV	3	6	I
2	Ag	7440-22-4	1	0	0	280	[10]	III	4	5	II
3	Ba	7440-39-3	1	0	0	300	[11]	III	4	5	II
4	Li	7439-95-2	1	0	0	1165	[12]	IV	3	4	II
5	Ti	7440-32-6	1	0	0	1200	[13]	IV	3	4	II
6	Br	7726–95–6	1	0	0	1750	[14]	IV	3	4	II
7	Sn	7440–31–5	1	0	1	2000	[15]	IV	3	5	II
8	Mo	7439-98-7	1	0	0	2000	[16]	IV	3	4	II
9	Sb	7440-36-0	1	0	0	2000	[17]	IV	3	4	II
10	W	7440-33-7	1	0	0	2000	[18]	IV	3	4	II
11	Sr	7440–24–6	1	0	0	2350	[19]	IV	3	4	II
12	S	7704-34-9	1	0	0	n/a		-	0	1	III
13	Au	7440-57-5	1	0	0	n/a		-	0	1	III

Thus, in accordance with the potential hazard category of unintentionally present chemicals, further health risk assessment included chemicals belonging to category I (mercury, arsenic, and aluminum).

4. CONCLUSION

As part of a systematic approach, the study involved the identification of the hazards of unintentionally present chemicals in rice in 3 stages. At each stage, the authors applied the criteria for the inclusion of chemicals in the further assessment. Therefore, at the chemical and analytical identification stage, 29 out of 36 chemicals were included for further evaluation. At the stage of establishing an integral index based on a criterion assessment, 15 chemicals were included in the final assessment. At the final stage, as a result of the evaluation of the selection of priority unintentionally present chemicals contained in rice sold through retail chains, a category of potential hazard was established. Aluminum, in accordance with the PHC, was assigned to category I (high potential hazard). As a result of the selection of priority potentially dangerous unintentionally present chemicals in rice, aluminum requires further assessment of the risk to public health with a view to possible regulation.

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Lựa chọn mức độ ưu tiên sự tồn tại của hóa chất ô nhiễm ngẫu nhiên có mặt trong các mẫu gạo bán lẻ ở Liên bang Nga

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Tóm tắt

Những hóa chất chưa được nhắc tới trong các quy định vệ sinh được tìm thấy trong gạo có thể được xếp vào nhóm hóa chất ngẫu nhiên có mặt trong thực phẩm. Tuy nhiên, những hóa chất này tiềm ẩn mối nguy hiểm cho sức khỏe, điều này cần phải có đánh giá mức độ rủi ro của sự có mặt các hóa chất trên.Vì vậy, cần có sự lựa chọn ưu tiên các hóa chất ngẫu nhiên có mặt trong gạo dựa trên nguy cơ tiềm ẩn của chúng. Nghiên cứu bao gồm năm mẫu gạo từ Campuchia, Ấn Độ, và Nga. Các nghiên cứu về hàm lượng các nguyên tố hóa học được thực hiện trên thiết bị khối phổ Agilent 7900 Agilent Technologies, Japan/Singapore) với buồng phản ứng tám cực (ORS) và chương trình phân tích bán định lượng cho thiết bị khối phổ. Việc lựa chọn ưu tiên các hóa chất ngẫu nhiên có mặt trong gạo được thực hiện trong ba giai đoạn. Nhóm nghiên cứu đã áp dụng các tiêu chí cụ thể để đưa các hóa chất vào đánh giá thêm ở mỗi giai đoạn. Kết quả của việc đánh giá sự lựa chọn ưu tiên các hóa chất ngẫu nhiên có mặt trong các mẫu gạo bán lẻ cho thấy một loại mối nguy tiềm ẩn (PHC) đã được thiết lập. Tức là, một đặc điểm tổng hợp của mối nguy của một hóa chất ngẫu nhiên có mặt trong thực phẩm, bao gồm khả năng nuốt phải một hóa chất cụ thể và độc tính của nó. Do đó, theo PHC, nhôm được xác định là hóa chất nguy hiểm tiềm ẩn chứa trong gạo ưu tiên để đánh giá rủi ro thêm vì nó tương ứng với loại I của mối nguy tiềm ẩn.

Từ khóa: *hóa chất, nguy cơ, chỉ số tích hợp, danh mục, đánh giá rủi ro.*

[+] **Ghi chú/Note:** Tiêu đề và tóm tắt tiếng Việt do Ban Biên tập biên dịch với sự đồng ý của tác giả / *The Vietnamese title and abstract is translated by the Editorial Board with the agreement of the Author.*