Janusz Ryszard RAK

Faculty of Civil and Environmental Engineering
Rzeszów University of Technology
Rzeszów

QUALITY CONTROL OF NATURAL MINERAL WATERS FROM THE HEALTH SAFETY SIDE

KONTROLA JAKOŚCI NATURALNYCH WÓD MINERALNYCH W ASPEKCIE BEZPIECZEŃSTWA ZDROWOTNEGO

Rynek wód mineralnych rozwija się bardzo dynamicznie w tempie 12% rocznie. Stało się to przyczynkiem do stworzenia procedur związanych z produkcją i kontrolą jakości wód mineralnych. W pracy szczegółowo omówiono system analizy i zagrożeń w krytycznych punktach kontroli HACCP). Przedstawiono zasady związane z wdrażaniem systemu HACCP w firmach produkujących wody mineralne. Zaprezentowano maksymalne i minimalne limity jakościowe składników mikrobiologicznych, chemicznych i fizycznych wód mineralnych, które obowiązują przy monitoringu w ramach systemu HACCP.

The mineral water market is growing rapidly at a rate of 12 % a year. This fact was the contribution of mineral water production and quality control procedures creation. The system of hazard analysis concerning critical control points (HACCP) has been described. The rules of HACCP system introduction into mineral water factories have been shown. The maximum and minimum HACCP system quality limits concerning the content of microbiological, chemical and physical elements of mineral waters have been presented.

1. Introduction

The known ancient Greek thinker Thales of Miletos (624 BC – 546 BC) stated in such a concise way "Water is the first principle of all things. For from this all things come, and to it they all return". His statement, regarded as one of the first scientific theories, stood over 25 centuries and did not loose its reality till today.

The ancient Romans delighted in drinking the first bottle water and attributed to the water brought from the Alps in amphoras the curative properties. The first firm started to

produce carbonated bottle water in Sweden in 1776. In 1863 the emperor Napoleon's III decree allowed to sell the bottle natural mineral water Perrier. In XIX century bottle water was available only for the high society, however, in XX century it became a mass product. In 1968 the sale of French water Vittel in plastic bottles started and in the mid 1980s the sale of water in disposable recycled PET bottles started.

In 2005 every average Pole drank already 50 dm^3/year of mineral water (the Italians 160 dm^3/year, the French 120 dm^3/year). In Poland the best selling are the following brands of mineral waters: Żywiec Zdrój (belongs to Danone concern) – 23%, Nałęczowianka (belongs to Nestle concern) – 10% and Kropla Beskidu (belongs to Coca Cola concern) – 8% of the domestic market.. The mineral waters world market is growing rapidly at a rate of 12 % a year [1]. At present its value is 50 mld USD. According to the consulting firms in 2011 it will equal the soft drinks market.

With regard to health still water is considered as safer than carbonated water. Rapid water drinking causes that human body immediately excretes it through kidneys and skin. It is recommended to drink water in little portions, at some time intervals and the best way is to do it 30 minutes after a meal.

Modern firm manufacturing mineral water diligently protects its bore holes using cameras and security service. Water from water bearing deposit is poured into bottle in sterile conditions. Production lines belonging to the so called clean zone are computer controlled , workers supervising production are wearing protective clothes and have to have suitable health certificates. Bottles moulded in temperature 200^0C are washed with a special stream of water before filling. Technological air used to pneumatic control of the production line is cleaned in three different types of filters which guarantees its sterility. The quality of water from the bore hole and the final product are examined by the factory laboratory.

The purpose of the work is to present the rules of natural mineral waters quality control from the health safety side connected with water consumption.

2. Water in human body

Water volume (V) in human body can be preliminarily estimated according to the Fris-Hansen formula [2]

$$V = 0.55 \cdot \text{weight [kg]} + 0.5\ dm^3 \quad (1)$$

Proportional portion of water in human body depends on age and gender. At young women it is 50%, and at men 60%. At people over 60 the proportional portions are, respectively, 45% and 50%. Brain and muscles at adult person contain about 75% and blood about 87% of water. Twenty four hour's water requirement in human body is from 2.0 up to 3.5 dm^3, depending on the physical activity and ambient temperature. In twenty four hour's balance one should take into account the metabolism processes which produce 0.2 up to 0.6 dm^3 of water. For example, while 1g of protein is burnt $0.41\ 10^{-3}$ dm^3 of water is produced, 1g of fat – $1.07 \cdot 10^{-3}$ dm^3, and 1g of carbohydrate – $0.6 \cdot 10^{-3}$ dm^3 [2] .

With regard to consumers feelings the organoleptic properties of water, such as: taste, colour, transparency and smell are subject to estimation. [3]. The specific taste of mineral waters is caused by a significant concentration of their components: Thus:

- sour - considerable content of carbon dioxide,

- salt - large content of sodium chloride,
- bitter – magnesium or sodium sulphate,
- metallic – ferrous and sodium compounds,
- alkaline – sodium bicarbonate.

3. Quality systems in mineral waters production and trade

Guarantees and safety of mineral waters consumers can be assured by the following quality systems [4]:

- management in order to achieve quality - Quality Management- QM
- analysis of threats in critical control points -Hazard Analysis Critical Control Points - HACCP
- risk analysis and biocontamination control - Risk Analysis Biocontamination Control - RABC
- good hygienic practice - GHP
- good manufacturing practice – GMP
- early warning about dangerous food - Rapid Alert System for Food – RASF

The rules of GHP and GMP are implemented before HACCP is introduced [4].

Quality systems concerning mineral waters production and trade define the mentioned below terms in the following way:

- threat – biological, chemical or physical factors which can occur in mineral waters and cause the negative consequences for human health [5],
- monitoring – system of processed observations, measures and studies having a specified aim, performed on the representative samples ,
- risk – danger that the negative severe consequences for human health will occur as a result of mineral waters drinking,
- risk analysis – procedure consisted of three interconnected elements including risk assessment, risk management and information about risk,
- risk estimate – scientifically aided process consisting of three stages containing threat identification, characteristic of danger, hazard assessment and risk characteristic,
- risk management – action undertaken by the suitable body supervising safety of using mineral waters that establishes the ways to prevent risk and to control risk, based on the risk estimate and binding requirements regarding sanitary and hygienic safety at production and trade of mineral waters,
- information about risk – it means to exchange information and opinions regarding threats and risk as well as factors connected with risk, during risk analysis, among those who estimate risk, manage risk, consumers, producers, traders and scientists,
- procedure – it is an established way of action – description of operations allowing to perform some task,
- instruction - it is an operational procedure of lower order – it gives detailed actions in logical sequence of execution, describes step by step the task connected with the given position, explains the way of carrying out.

4. The HACCP system methodology

As results from the rules of the HACCP system, it is a proceedings which aim is to ensure mineral waters safety by the identification and the evaluation of a threat scale, from the point of view of a curative quality and risk of threats, during the course of all production stages and trade of mineral waters. The purpose of this system is also to determine the methods to reduce threats and to establish corrective actions.

The HACCP system regarding food control came to existence in the USA in the late 1960s, ordered by NASA (National Aeronautics and Space Administration). The origin of HACCP was related to the scientific research on production of food without pathogenic microorganisms for the astronauts. [4].

In 1971 Pollsburgy company presented this system at the American National Conference for Food Protection. The HACCP system has been accepted by World Health Organization (WHO) and International Commission on Microbiological Specifications for Foods (ICMSF).

As a result of the fact that Poland joined the European Union the sector dealing with mineral waters production and distribution has been obliged to use the HACCP system. It is regarded as the most efficient tool which guarantees that water as a foodstuff will not be polluted or contaminated and will be safe for consumers health. The HACCCP system is created individually for every production line and distribution type, taking into account the specific character of the given activity.

The main rules are the following:

- the identification of the possible biological, chemical and physical threats and the methods of counteractions,
- the prevention, in form of a control of the particular phases of mineral waters production process and distribution, not the final product only,
- it is used in the whole production cycle: from water intake, then bottling plant, warehouse, distribution, delivery to consumers in stores and restaurants.

There are seven basic stages connected with the HACCP system implementation [4].

Stage 1. Threats analysis.

It consists in:

- the identification of the potential threats in the categories of occurrence: biological, chemical, physical. The medical reports indicate that 90% of sicknesses resulting from bad quality water consumption is caused by its microbiological contaminations,
- the establishment of a source and a reason, as well as the preventive activities,
  - the general procedures,
  - the direct actions.
- the assessment of risk of threat [6],
  - a frequency of occurrence (f),
  - a magnitude of consequences (C),
  - the determination of risk indicator $r = f \cdot C$,
  - the establishment of a priority list.

Stage 2. The establishment of critical control points (CCP).

It enables to achieve the purpose of the system by being in control of mineral water sanitary safety . The condition of CCP determination is the possibility of their monitor-

ing and the possibility of real threat controlling. To determine CCP one can use a decision tree method. It allows to determine CCP by the logical series of questions and answers concerning the possibility of eliminating the threat in a given point or reducing it to the acceptable level. Below you can see the example of decision tree questions, according to Dutch procedures [4].

Question 1

Are there any preventive means regarding to the given threat ?

Yes: go to question 2 No: go to question 1a

Question 1a

Are the preventive means necessary as regard to health safety ?

Yes: go to question 1b No: it is not CCP

Question 1b

Is the threat controlled by means of the standard procedures?

Yes: it is not CCP No: modify the process or/and preventive means

Question 2

Does the given protective means eliminate or reduce the threat to the acceptable level?

Yes: go to question 4 No: go to question 3

Question 3

Can the contamination by the identified threat reach the unacceptable level or can it increase to the unacceptable level ?

Yes: go to question 4 No: it is not CCP

Question 4

Can the threat be eliminated in the further process or can it be limited to the tolerable level?

Yes: it is not CCP No: it is CCP

Stage 3. The establishment of the critical limits for every control point

After the CCP designation one should determine one or more indicators of contamination which will be controlled and the desirable values, the limits of tolerance and the unacceptable critical value. [7] The criterion for the choice of the indicator should be speed and easiness of measurement and the possibility of monitoring. In case of difficulties one should use the visual and/or sensor assessment. In tab.1 the maximum concentration of mineral waters components that can create a risk for human health is presented. [8]

Tab. 1. Components, maximum limits which, if exceeded, are a risk for human health and requirements concerning the measurement methods.

Type of component	Acceptable concentration mg/dm^3	Requirements concerning the measurement		
		Accuracy [%]	Precision [%]	Limit of detection [%]
Antimony	0,005	25	25	25
Arsenic	0,01(total)	10	10	10
Nitrates	50,0	10	10	10
Nitrites	0,1	10	10	10
Barium	1,0	25	25	25
Cyanides	0,07	10	10	10
Chromium	0,05	10	10	10
Fluorides	5,0	10	10	10
Cadmium	0,003	10	10	10
Manganese	0,5	10	10	10
Copper	1,0	10	10	10
Nickel	0,02	10	10	10
Lead	0,01	10	10	10
Mercury	0,001	20	10	20
Selenium	0,01	10	10	10
Radioactivity				
α = 0,1 Bq/dm^3 ; β = 1,0 Bq/dm^3 ; Tritium 100,0 Bq/dm^3				

The microbiological examination and the examination of sanitary and hygienic state of water at its intake and in the consumer package are conducted to ascertain [8]:

- lack of parasites and pathogenic microorganisms,
- lack of Escherichia coli and other forms of coli bacteria in 250 cm^3 in temperature 37 ^{0}C and 44.5 ^{0}C,
- lack of streptococcus faecalis in 250 cm^3,
- lack of Clostridium reducing sulphates in 50 cm^3,
- lack of Pseudomonas aeruginosa in 250 cm^3,
- total amount of bacterial colonies growing from 1 cm^3 of water:
  - in temperature 20-22 ^{0}C during 72 hours in agar or in the mixture of agar and gelatine is not higher than 5,
  - in temperature 37^{0}C during 24 hours in agar is not higher than 20.

Stage 4. The establishment of CCP monitoring procedures

The CCP monitoring is a base of the HACCP operating. The results obtained from the monitoring have to be recorded. For monitoring procedures one should determine:

- a method of monitoring,
- a character, constant or periodical,

- a periodical monitoring frequency,
- a way of supervision,
- the rules of measuring device control and calibration.

In tab.2 the range of mineral waters quality examination within the framework of CCP monitoring during production is presented .

Tab. 2. The range of mineral waters quality examination within the framework of CCP monitoring

Type of water quality rating	Range of monitoring
Organoleptic rating	smell taste turbidity colour
Physical and chemical rating	conductivity pH
Undesirable components in excessive concentration	nitrites nitrates ammonia nitrogen iron ChZT
Basic components	Characteristic components mentioned in water marking

The microbiological, physical and chemical determination of water quality in 5 bottles randomly taken from different production batches are performed within twenty four hours. The so called keeping quality examination that determines water quality before its consumption expiry date is also performed.[10]

In tab.1 the requirements concerning the measurements connected with mineral waters monitoring are tabulated. The particular parameters are defined in the following way:

accuracy – it is a systematic error that is a difference between a mean value and an accurate value,

precision – it is an accidental error expressed by a standard deviation (permissible precision is equal double relative standard deviation),

limit of detection – it is triple or fivefold relative standard deviation.

Stage 5. The establishment of corrective actions

Corrective activities have to be undertaken when monitoring shows the trend to exceed permissible values of cleanliness rating or such values are exceeded. The possibility of stop in mineral water production process should be predicted, in order to eliminate the causes of the necessity of the corrective actions.

In tab.3 the maximum concentrations of chosen mineral waters components, when their quality is corrected by permissible process of water ozonization, are presented.

Tab..3. Maximum limits for components that remain or are created during aeration of natural mineral water and spring water by ozone enriched air .

Kind of component	Maximum limits $\mu g/dm^3$
Dissolved ozone	50
Bromate	3
Bromoform	1

In order to regard water as curative the clinical and pharmacological examinations, according to the scientific methods, which estimate natural mineral water properties and its impact on human body, such as: diuresis, stomach and bowel functions, balance in mineral elements, should be carried out. In natural waters having components good for health the general water properties resulting from quantity proportions between macro and micro elements are essential. As an example one can give the desirable proportion of the contents of calcium to magnesium: 2:1.

Stage 6. The establishment of system verification procedures

Verifications are performed after the HACCP system is implemented as its first evaluation. Then a frequency of next verifications should be established, verification is always performed after the changes in the technological production process are made and also when the undesirable events occur.

Effectiveness of the HACCP system can be verify by means of external and internal audits . There is the possibility to achieve HACCP certificate which definitely increases confidence of the present and the future consumers of the given mineral water brand.

Stage7. The creation of documentation

System documents should contain a plan of HACCP and the records testifying system operation. The way of documents drawing up, storage and supervision must be establish.

5. Conclusions

- The HACCP system is one of the systems to ensure mineral waters quality and curative values. The implementation of the system increases the confidence among the particular participants of mineral waters market. The beneficiaries of the effects of the HACCP system introduction are producers, sellers, supervisor service, and, most of all, mineral water consumers. The efficient HACCP system allows to avoid the groundless complains, protects against the loss of customers and credibility of the firm on the market.
- The external benefits of the HACCP introduction for mineral waters producer are the following:
  - the increase of consumers confidence,

  - the opportunity of sale in the European Union markets,
  - the improvement in product competitiveness,
  - the improvement in firm image,
  - the increase of confidence at official inspection units.
- The HACCP system means a change in the way of evaluation of mineral waters quality as a product. The evaluation of the conditions of high quality mineral waters production, instead of the control of the final product only, ensures the increase of health safety connected with their consumption.
- There are some possibilities to develop the method to assess the risk of threat, based on the three and four parameter matrix for risk analysis and evaluation. [6]

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