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# THE LEVEL OF ARSENIC IN WATER FROM MINERAL WATER SPRING GAJDOVKA IN KOŠICE AND THE ASSOCIATED HEALTH RISKS

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## ABSTRACT

**In the recreation area Anička in Košice, there is a mineral spring that inhabitants call Gajdovka. It has been used with several breaks since the 19th century. Mineral water from this spring is specific by the presence of arsenic the concentration of which often exceeds the permitted limit level. This study focused on the analysis of the mineral composition of the spring water. Chemical and microbiological analysis was made in the years 2013—2015. In 2014, the mineral water Gajdovka was regularly monitored throughout the year with respect to the concentrations of arsenic, iron and hydrogen sulphide levels and water levels in the nearby river. The following mean concentrations were determined: total arsenic 0.063 mg.dm$^{-3}$; iron 0.275 mg.dm$^{-3}$; hydrogen sulfide 4.608 mg.dm$^{-3}$. The concentration of iron was below the limit, while the limit for As(III) was exceeded in 2014 for 7 months. The statistical analysis showed that the season affects significantly the level of H2S and Fe and the water levels in the nearby river.**

**Key words: arsenic; atomic absorption spectrometry; hydrogen sulphide; iron; mineral water**

## INTRODUCTION

Water in nature is subjected to constant circulation resulting in changes in its physical and chemical properties. It is enriched by various mineral substances and saturated by gases that change its microbiological properties, pH and temperature. Of natural waters the mineral water with healing powers is important for humans. Water from many mineral springs have physiological and therapeutic effects and, therefore, they are used for treatments. Slovakia is a country that ranks among the most significant world countries in terms of quantity, capacity and chemical composition of mineral waters. Nowadays, there are more than 1600 sources of mineral and thermal waters of various chemical composition, capacity and temperature in the Slovak territory. In particular regions there are also less known springs used by local residents [2].

One of these lesser known springs is a mineral spring located in the area of Košice in a suburban park named Anička, nearby the river Hornad, which inhabitants call "Gajdovka". It has been known since 1881 when a spa was established at this location. During the First World War it started to become dilapidated. It was restored again later in 1923 and named Gajdove kúpele (Gajda spa) in honour of general Gajda [8, 24]. In the 1960s, the spa and the source of mineral water were closed for hygienic reasons.

In 1995 a new 30-m-deep mineral water well was drilled in this location. This well is used to this day and the spring is very popular with the residents of Košice concerning its availability. Some of them drink the mineral water sporadically during walks in the park. Others, mostly older people, take larger amounts of water home and use it for cooking. The spring is now managed by the Administration of urban green areas in Košice. The monitoring of the quality of this mineral water is executed four times a year by the Regional Public Health Authority based in Košice. This institution monitors the indicators of quality defined by the decree of the Ministry of Agriculture and Rural Development of the Slovak Republic No. 51, of 15 March 2004, as issued in the 25th chapter of the Food Code of the Slovak Republic. The Annex No. 1 of this material defines the microbiological, biological, physical and chemical indicators and demands on mineral water quality [29]. The spring water is also known for the fact that the level of arsenic in this mineral water often exceeds the limit value of arsenic determined by the relevant regulation [4, 5].

Arsenic belongs among the most significant contaminants of the environment with a high potential to harm human health. Arsenic is present in nature in many oxidation states (V, III, 0, -III). In natural waters it is mostly in the As(III) form, as an arsenite anion typical for ground waters with shortage of oxygen. As(V) dominates in surface water in the form of arsenate anions [32]. The less stable As(III) form oxidises easily. In nature, the activity of microorganisms may contribute to changes of inorganic forms of As to volatile or non-volatile organic forms [28]. Some studies reported that the natural background level of arsenic in ground water is 5 mg.dm$^{-3}$ [25]. The most significant factors affecting particular forms of arsenic in the water environment are pH and the oxidation-reduction potential of the environment (Eh) [20, 21].

Inorganic forms of As are more toxic to humans than organic forms [10]. As(III) is organically bound and chemically or biochemically oxidizes to As(V). The As(V) form is more stable under aerobic condition; As(III) is more toxic, it causes chronic diseases and belongs to inhibitors of biochemical oxidation. Many mammals methylate inorganic arsenic to dimethylarsinic acid. This substance causes organ-specific toxicity and acts as a promoter of genesis of tumours in many organs [12]. The International Agency for Research on Cancer (I. A. R. C.) classified arsenic as a Group 1 human carcinogen. This element has carcinogenic, mutagenic and teratogenic effects on humans. Long-term exposure to arsenic can cause severe damage to an organism [19]. Due to its chemical structure, it has similar biochemical properties as phosphorus and can replace it in a certain way. It affects perniciously almost at the DNA level and destroys enzymes and proteins. Many epidemiological studies conducted throughout the world have demonstrated that the human intake of arsenic exceeding the limit value causes degenerative changes in optic and acoustic nerves, painful periphery polyneuropathy, encephalopathy, anaemia and pernicious tumours mainly of skin, kidneys, liver and lungs, leukaemogenesis and lymphoma [1]. Arsenic accumulates in bones, hair and nails. Permanent concentration of arsenic of 100 mg.dm$^{-3}$ is related to 1 : 200 lifelong possibility of the development of tumours that exceeds the annual probability of death due to a tumour disease. An acute toxicity was recorded after drinking water from a well with the arsenic content 1.3—20 mg.dm$^{-3}$ [14].

There are no published expert studies that would give more complex information on the properties of the mineral water from Gajdovka. Arsenic concentrations have been lately sporadically monitored. Moreover, there exists no overview of arsenic levels during the year, nor of potential effects of the seasonal changes, its relationship to particular components of mineral water, or its dependency on water levels in the nearby river Hornád.

This study focused on the determination of selected characteristics of the mineral water "Gajdovka" relevant to the health of its consumers.

## CHARACTERISTICS OF THE SPRING

On the basis of the Slovak technical standard STN 86 8000, valid up to 2005, the mineral water from the spring Gajdovka was classified as "natural, low-mineralized, hydrogen carbonate-chloride, calcium-sodium-magnesite, carbonate, sulfuric water, hypotonic, cold (temperature approximately 13 °C) water" [5].

A new well with designation G-5, 30 m deep, of capacity 0.3 dm3.s$^{-1}$ was drilled in 1995. On the basis of the analysis of its chemical composition and other properties, mineral water from this well was characterised as mineral water with deep circulation and long-term retention, metamorphosed, with significant influence of neogene sediments from which the chloride-sodium component of the water is supported. Its mineralisation is related to the solution of sedimentary carbonate rocks. These rocks also contain some iron minerals, such as pyrite ($FeS_2$) and arsenopyrite (FeAsS). Significant amounts of iron and arsenic comes from the hydrolytic decomposition of the mentioned minerals while free hydrogen sulfide is created. From the facts presented above, it shows that the component influencing the water quality the most is arsenic. After leaving the reduction environment of an original thermodynamic conditions, the contact of mineral water of deep circulation with air starts to eliminate amorphous ferrous sulphides (FeS and Fe2S3) that have adverse effect on the sensorial properties of the water. The listed properties classed the mineral water as healing waters with modified mode of use [13].

The spring is protected by a protective fence to prevent the possibility of its direct pollution and the water is pumped by a submersible pump. The original aroma of fresh water persists for twelve hours after sampling. Unaltered mineral water acquires earthy — petroleum odour 24 hours after sampling. This odour is caused by bacterial strains that survive in deep-circulation mineral waters and are hygienically harmless. Potential turbidity can be caused by the presence of iron in water that does not hinder its consumption [5].

## MATERIALS AND METHODS

### Sampling and processing of samples

Samples of mineral water for determination of basic indicators according to the Food Code [29] were taken in the years 2013—2015, always in October, and were analysed at the Geoanalytical Laboratory of the State Geological Institute of Dionýz Štúr in Spišská Nová Ves, Slovakia. All sampling vessels were provided by this laboratory.

All vessels intended for collection of samples were thoroughly washed and dried before use. The sample for the determination of mercury was collected in a glass vessel of volume 100 cm$^3$ containing 1.25 cm$^3$ of concentrated $HNO_3$. The sample for the determination of other metals was collected to a polyethylene vessel of volume 250 cm$^3$ containing 1.25 cm$^3$ of concentrated $HNO_3$. For the determination of $H_2S$, 250 cm$^3$ of water was collected to a glass vessel that contained 2.5 cm$^3$ of cadmium acetate of concentration 100 g.dm$^{-3}$ and 1.25 cm$^3$ of 25 % w/w NaOH solution. To determine the relevant cations and anions, 2 dm$^3$ of water were collected in a glass vessel. Sample for the determination of the total mineralization of the water was collected in 1 dm3 vessel. Water samples for microbiologic analysis were collected in sterile glass vessels of volume 1 dm$^3$.

For regular monitoring of the concentrations of arsenic, iron and hydrogen sulfide in mineral water conducted in 2014, the samples were taken once per week, always on Wednesdays in the morning, stabilised and examined after transfer to a laboratory. In total, 51 samples of mineral water were taken and analysed.

To determine the overall mineralisation of water in 2014, 2 separate samples were collected in glass vessels with a volume of 1 dm$^3$. One sample (1 dm$^3$) was evaporated in a porcelain dish on a water bath (Sample 1) and another was allowed to evaporate freely at room temperature (Sample 2). The residues (fine crystalline matter) were then used for X-ray diffraction analysis and IR spectrometry.

### Analytical methods

The analysis of the chemical composition of mineral water was made at an accredited Geoanalytical Laboratory of the State Geological Institute of Dionýz Štúr in Spišská Nová Ves, according to internal regulations of this laboratory.

X-ray diffraction powder analysis was made with a diffractometer XRD D2 PHASER (Bruker, Germany), using

CuK(α) radiation generated at 10 mA and 30 kV. The measurement was made in a range of 10—90 ° 2 Theta and evaluated by software Diffrac.EVA v. 2.1. To identify the phase, the database ICDD PDF (ICDD PDF-2 Release 2009) was used. Measurement conditions were the same for all samples.

For analysis of the infrared spectra of powder samples, an Alpha FT-IR Spectrometer ALPHA's Platinum ATR single reflection diamond ATR module (Bruker, Germany) was used. To determine particular metals, the methods of atomic emission spectrometry with inductively coupled plasma (AES-ICP), atomic absorption spectrometry with hydride technique (AAS-HG) and atomic absorption spectrometry with mercury analyser (AAS-AMA) were used.

Chlorides and sulphates were determined by ion chromatography (IC), carbonates by volumetric analysis and hydrogen sulfide by photometry.

The monitoring of arsenic and iron concentration during the year 2014 was conducted by the method of atomic absorption spectrometry with an electrothermic atomizer (AAS-ETA) using a SpektrAA 220 (Varian), with Zeeman background correction.

The hydrogen sulfide content in samples was determined by volumetric analysis with iodometric titration. The determination was carried out in triplicate.

The residues after evaporation of two 1 dm3 samples of water (Samples 1 and 2), obtained at determination of mineralization were subjected to X-ray diffraction analysis and IR spectrometry with the collaboration of the Department of Environmental Engineering, Faculty of Civil Engineering, Technical University of Košice.

Microbiological analysis involving 14 parameters was carried out in a microbiological laboratory of the Section of Microbiology and Environmental Biology of the Regional Authority of Public Health in Košice. The methods of membrane filtration and cultivation complied with relevant technical standards.

Information on the level of water in the river Hornád were obtained from the Slovak Water Management Company in Banská Štiavnica, Slovakia [27].

### Statistical evaluation

One-way analysis of variance (ANOVA) was used for statistical evaluation of the results. The calculation was performed using Excel. The likelihood of the first type error, referred to as "P-value", was calculated by ANOVA. The effect of the season on the monitored parameters, namely the concentration of arsenic, iron, hydrogen sulphide, and level of water in the Hornad River were evaluated. Correlation between individual parameters was investigated. $P < 0.05$ was considered significant.

## RESULTS

The analysis of residues after evaporation of 1 dm$^3$ of water on water bath and at room temperature (Samples. 1 and 2) showed that the composition of both samples was almost identical. In samples there were identified compounds of $CaCO_3$ (aragonite), NaCl (halite) and $Na_2SO_4$ (thenardite). In sample 2 also $MgCa(CO_3)_2$ (dolomite) was identified. The results of X-ray powder analysis, completed through the measurement of IR spectra of these samples in the range from 4000 cm$^{-1}$ to 600 cm$^{-1}$ confirmed the presence of anions $CO_3^{2-}$ and $SO_4^{2-}$ appertaining to compounds determined through the previous method in the analysed samples. Repetency assignment of particular absorption bands to inorganic anions was made on the basis of the literature [23]. Typical infrared absorption frequencies characterizing the presence of $(CO_3)^{2-}$ and $(SO_4)^{2-}$ anions in the samples are shown in Table 1.

The results of the analysis of the particular indicators determined at the Geoanalytical Laboratory of the State geological Institute of Dionýz Štúr in Spišská Nová Ves are presented in Table 2.

**Table 1. Infrared absorption frequencies**

| **Wavenumber** [cm$^{-1}$] | | **Assignment** |
|---|---|---|
| **Sample No. 1** | **Sample No. 2** | |
| 1480.43 s | 1480.15 s | $CO3^{2-}$ |
| 1421.24 vs | 1424.64 vs | $CO3^{2-}$ |
| 1113.57 s | 1111.27 s | $SO4^{2-}$ |
| 881.87 w | 877.03 w | $CO3^{2-}$ |
| 853.17 vw | 855.00 sp | $CO3^{2-}$ |
| 667.5 vw | 668.29 vw | $SO4^{2-}$ |
| | 638.41 sp | $SO4^{2-}$ |
| 615.71s | 614.76 s | $SO4^{2-}$ |

vw — very weak; w — weak; s — strong; vs — very strong; sp — sharp

**Table 2. Determination of inorganic indicators in mineral water "Gajdovka" in the period of 2013—2015**

| Indicator | Limit [29] [mg.dm$^{-3}$] | Concentration [mg.dm$^{-3}$] | | | LOQ [mg.dm$^{-3}$] | Method |
|---|---|---|---|---|---|---|
| | | 2013 | 2014 | 2015 | | |
| **Na** | **800.0** | 379 ± 37.9 | 364 ± 36.4 | 260 ± 26 | 0.05 | AES-ICP |
| **K** | **–** | 27.0 ± 2.7 | 25.4 ± 2.54 | 30.5 ± 3.05 | 0.1 | AES-ICP |
| **Ca** | **≥ 20.0** | 284 ± 19.9 | 264 ± 18.5 | 264 ± 18.5 | 0.2 | AES-ICP |
| **Mg** | **200.0** | 143 ± 10.0 | 115 ± 8.0 | 116 ± 8.12 | 0.2 | AES-ICP |
| **Fe** | **10.0** | 0.210 ± 0.021 | 0. 114 ± 0. 011 | 0.255 ± 0.026 | 0.007 | AES-ICP |
| **Mn** | **2.0** | 0.267 ± 0.04 | 0.250 ± 0.038 | 0.249 ± 0.037 | 0.002 | AES-ICP |
| **Al** | **0.4** | 0.04 ± 0.008 | 0. 0 ± 0.02 | 0.05 ± 0.01 | 0.02 | AES-ICP |
| **Cu** | **2.0** | < 0.002 | < 2.0 | < 2.0 | 2.0 | AES-ICP |
| **Zn** | **5.0** | 0.003 ± 0.0006 | < 0.002 | < 0.002 | 0.002 | AES-ICP |
| **As (total)** | **0.05 As(III)** | 0.089 ± 0.009 | 0.073 ± 0.007 | 0.071 ± 0007 | 0.001 | AAS |
| **Cd** | **0.003** | < 0.0003 | < 0.0003 | < 0.0003 | 0.0003 | AES-ICP |
| **Pb** | **0.01** | < 0.005 | < 0.005 | < 0,005 | 0.005 | AES-ICP |
| **Cr** | **0.05** | < 0.002 | < 0.002 | < 0.002 | 0.002 | AES-ICP |
| **Hg** | **0.001** | < 0.0001 | < 0,0001 | < 0.0001 | < 0.0001 | AAS |
| **H2S** | **–** | 4.39 ± 0.88 | 4.20 ± 0.84 | 5.27±1.05 | 0.01 | P |
| **Cl-** | **500.0** | 415 ± 20.8 | 406 ± 20.3 | 302 ± 15.1 | 1.0 | IC |
| **(CO3)2-** | **–** | < 0.3 | < 0.3 | < 0.3 | 0.3 | OA |
| **(SO4)2-** | **1 400.0** | 255 ± 12.8 | 214 ± 10.7 | 218 ± 10.9 | 2.0 | IC |

LOQ — limit of quantification; IC — ion chromatography; AES-ICP — atomic emission spectrometry with inductively coupled plasma
AAS — atomic absorption spectrometry; OA — volumetric analysis; P — photometry

The determination of the total mineralization of water showed that the residue after evaporation in individual years was as follows: 2013: 2.548 g.dm$^{-3}$; 2014: 2.653 g.dm$^{-3}$ and 2015: 2.629 g.dm$^{-3}$. The average weight of the residue was 2.610 g.

Microbiological analysis that focused on 14 indicators showed an absence of pathogenic microorganisms and indicators of faecal contamination. The water complied with relevant requirements. The monitored indicators, type of the method used (standard) and relevant results are summarised in Table 3.

The monitoring of the concentrations of arsenic, iron and hydrogen sulphide conducted throughout the year 2014 was conducted to determine variations in arsenic concentrations in mineral water throughout the year and to investigate the potential relationship between the concentrations of arsenic, iron and hydrogen sulfide. The levels of the river Hornád was monitored as another factor with possible influence on arsenic concentration in mineral water "Gajdovka". The results are presented in Tables 4a and 4b.

The minimal, maximal and average values of the concentrations of the analytes are presented in Table 5.

The average concentrations of arsenic in mineral water in particular months are presented in Table 6.

## DISCUSSION

Arsenic usually gets into the environment in a natural way as the product of decomposition of minerals that

**Table 3. Microbiological analysis of mineral water "Gajdovka" in 2014**

| Indicator | Unit/volume tested | Result | Type of method | Technical standard |
|---|---|---|---|---|
| Pathogenic microorganisms | | not present | MF | STN ISO 6340 |
| Escherichia coli | CFU/250 ml | 0 | MF | STN EN ISO 9308-1 |
| Coliform bacteria | CFU/250 ml | 0 | MF | STN EN ISO 9308-1 |
| Enterococci | CFU/250 ml | 0 | MF | STN EN ISO 7899-2 |
| Pseudomonas aeruginosa | CFU/250 ml | 0 | MF | STN EN ISO 16266 |
| Sporebearing sulphites reducing the anaerobic bacteria | CFU/50 ml | 0 | MF | STN EN 26461-2 |
| Microorganisms cultivable at 21 °C ± 1 °C | CFU/1 ml | 0 | C | STN EN ISO 6222 |
| Microorganisms cultivable at 37 °C ± 1 °C | CFU/1 ml | 0 | C | STN EN ISO 6222 |
| Living organisms | individuals/ml | 0 | M | STN 757711 |
| Dead organisms | individuals/ml | 0 | M | STN 757711 |
| Ferrous and manganese bacteria | % coverage of the field of view | 0 | M | STN 757711 |
| Ferrous and manganese bacteria | CFU/30 ml | not present | C | |
| Sulphur green bacteria | CFU/30 ml | not present | C | |
| Microscopic fungi (micromycetes) | individuals/ml | 0 | M | |

C — cultivation method; MF — membrane filtration; M — microscopic method; CFU — colony forming unit

contain it, or through emissions from coal combustion, ore processing, extracts from sludge beds, mining piles and old mines. The most significant source of the contamination of ground water by arsenic are pit water flowing out of old mining works or water flowing from mining piles [31]. In the case of weathering of arsenopyrite containing mining mullock, the concentrations of arsenic in ground water may result in high local levels. As an example, we can mention the abandoned mine deposit Poproč, located near Košice. In this location the important source of contamination is the pit water from swamps named Agnes with a high concentration of arsenic (2.4 mg.dm$^{-3}$) and antimony (0.6 mg.dm$^{-3}$) [7]. Loredo et al. [22] stated that the concentration found in one mining location in Spain ranged from 4.1 to 5.6 mg.dm$^{-3}$ of As. Arsenic is also part of some insecticides, phosphate fertilizers and detergents [6].

Nowadays, great attention is given to the issue of arsenic presence mainly in connection with contamination of drinking water and its sources [26]. In the past, the allowable arsenic concentration in drinking water was 50 mg.dm$^{-3}$. In 1993, WHO decreased this value to 10 mg.dm$^{-3}$ on the basis of long-tern epidemiological studies. In Slovakia, the Regulation of the Government of the Slovak Republic No. 354/2006 of the Collection defines the requirements for water intended for human consumption and for quality check of this water. According to this regulation, the limit value of arsenic in drinking water is 10 mg.dm$^{-3}$. Observation of this limit can cause problems in some regions of Slovakia. It concerns especially the locations where the public water supplies are ground sources with higher content of arsenic that comes from the geological background. This results in the increased level of arsenic in drinking water, e. g. in Pohronský Bukovec in 2009 [15], in artesian wells in districts Nové Zámky and Šaľa in 2010 [11] and, unexpectedly, also in municipality Brehov in the district of Trebišov in 2015 [16]. In the last case, increased arsenic in ground water was probably related to andesite mining in this area.

Higher concentrations of arsenic in spring and min-

**Table 4a. Levels of hydrogen sulfide, total arsenic and iron in mineral water in the period of January — June, 2014**

| Date of sampling month/day | $H_2S$ [mg.dm$^{-3}$] | As (total) [mg.dm$^{-3}$] | Fe [mg.dm$^{-3}$] | Height of the river Hornád (cm) |
|---|---|---|---|---|
| 1/18 | 5.49 ± 0.66 | 0.031 ± 0. 008 | 0.34 ± 0.04 | 103 |
| 1/15 | 4.61 ± 0.55 | 0.052 ± 0.013 | 0.45 ± 0.05 | 97 |
| 1/22 | 5.83 ± 0.70 | 0.120 ± 0.030 | 0.36 ± 0.04 | 112 |
| 1/29 | 5.03 ± 0.60 | 0.110 ± 0.028 | 0.49 ± 0.06 | 111 |
| 2/5 | 4.52 ± 0.54 | 0.032 ± 0.008 | 0.41 ± 0.05 | 111 |
| 2/12 | 6.43 ± 0.77 | 0.053 ± 0.013 | 0.42 ± 0.05 | 119 |
| 2/19 | 4.10 ± 0.49 | 0.057 ± 0.014 | 0.40 ± 0.05 | 139 |
| 2/26 | 5.14 ± 0.62 | 0.140 ± 0.035 | 0.32 ± 0.04 | 120 |
| 3/5 | 5.97 ± 0.72 | 0.056 ± 0.014 | 1.19 ± 0.12 | 113 |
| 3/12 | 5.70 ± 0.68 | 0.081 ± 0.020 | 0.28 ± 0.04 | 104 |
| 3/19 | 5.75 ± 0.69 | 0.089 ± 0.022 | 0.22 ± 0.03 | 112 |
| 3/26 | 5.41 ± 0.65 | 0.041 ± 0.010 | 0.24 ± 0.03 | 110 |
| 4/2 | 5.39 ± 0.65 | 0.049 ± 0.012 | 0.26 ± 0.03 | 108 |
| 4/9 | 5.19 ± 0.62 | 0.061 ± 0.015 | 0.20 ± 0.03 | 112 |
| 4/16 | 5.06 ± 0.61 | 0.062 ± 0.015 | 0.25 ± 0.03 | 110 |
| 4/23 | 4.87 ± 0.58 | 0.039 ± 0.009 | 0.17 ± 0.02 | 106 |
| 4/30 | 4.90 ± 0.59 | 0.043 ± 0.011 | 0.23 ± 0.03 | 118 |
| 5/7 | 4.64 ± 0.56 | 0.063 ± 0.016 | 0.25 ± 0.03 | 114 |
| 5/14 | 5.20 ± 0.62 | 0.055 ± 0.014 | 0.24 ± 0.03 | 188 |
| 5/21 | 6.92 ± 0.83 | 0.058 ± 0.015 | 0.23 ± 0.03 | 184 |
| 5/28 | 5.94 ± 0.71 | 0.058 ± 0.015 | 0.23 ± 0.03 | 188 |
| 6/4 | 4.25 ± 0.51 | 0.052 ± 0.013 | 0.35 ± 0.04 | 117 |
| 6/11 | 2.31 ± 0.28 | 0.050 ± 0.013 | 0.14 ± 0.02 | 113 |
| 6/18 | 1.13 ± 0.14 | 0.053 ± 0.013 | 0.24 ± 0.03 | 104 |
| 6/25 | 3.18 ± 0.36 | 0.061 ± 0.015 | 0.44 ± 0.05 | 106 |

eral waters do not occur frequently. Water considered to be mineral water is defined in Chapter 25 of the Food Code as clear, colourless to yellowy water, with mild silt content, free of mechanical impurities. It cannot have atypical sensory properties and must have stable chemical composition and stable physical properties [29]. Mineral water must meet the microbiological, biological, physical and chemical indicators of quality listed in the Food Code. In this material the highest limit values (HLV) for particular indicators are listed. HLV for As(III) in mineral water is 0.05 mg.dm$^{-3}$.

Mineral water Gajdovka was subject to chemical and microbiological analysis in accredited laboratories in the years 2013 to 2015, always in October. The average overall mineralisation was 2.610 g.dm$^{-3}$. This value is very close to the level of 2.646 g.dm$^{-3}$ determined in 1996 [13]. Regarding the concentrations of particular indicators involved in mineralisation (Na, K, Ca, Mg, Fe, $Cl^-$, $SO_4^{2-}$), the biggest changes were observed in the levels of sodium (379 mg.dm$^{-3}$ in 2013; 364 mg.dm$^{-3}$ in 2014; 260 mg.dm$^{-3}$ in 2015), iron (0.210; 0.114; 0.255 mg dm$^{-3}$) and chlorides (415; 406;

**Table 4b. Levels of hydrogen sulfide, total arsenic and iron in mineral water in the period of July — December, 2014**

| Date of sampling month/day | $H_2S$ [$mg.dm^{-3}$] | As (total) [$mg.dm^{-3}$] | Fe [$mg.dm^{-3}$] | Height of the river Hornád [cm] |
|---|---|---|---|---|
| 7/2 | 2.92 ± 0.35 | 0.038 ± 0.010 | 0.22 ± 0.03 | 125 |
| 7/9 | 3.35 ± 0.40 | 0.050 ± 0.013 | 0.21 ± 0.03 | 145 |
| 7/16 | 4.39 ± 0.53 | 0.052 ± 0.013 | 0.18 ± 0.03 | 160 |
| 7/23 | 4.92 ± 0.59 | 0.040 ± 0.010 | 0.15 ± 0.02 | 145 |
| 7/30 | 4.53 ± 0.54 | 0.064 ± 0.016 | 0.09 ± 0.01 | 156 |
| 7/31 | 5.69 ± 0.68 | 0.040 ± 0.010 | 0.10 ± 0.01 | 154 |
| 8/6 | 4.80 ± 0.58 | 0.060 ± 0.015 | 0.15 ± 0.02 | 122 |
| 8/13 | 4.17 ± 0.50 | 0.066 ± 0.017 | 0.15 ± 0.02 | 138 |
| 8/20 | 3.93 ± 0.47 | 0.064 ± 0.016 | 0.15 ± 0.02 | 136 |
| 8/27 | 4.21 ± 0.50 | 0.064 ± 0.016 | 0.14 ± 0.02 | 125 |
| 9/3 | 4.62 ± 0.55 | 0.066 ± 0.017 | 0.18 ± 0.03 | 132 |
| 9/10 | 3.94 ± 0.47 | 0.041 ± 0.010 | 0.29 ± 0.04 | 133 |
| 9/17 | 4.20 ± 0.50 | 0.047 ± 0.011 | 0.30 ± 0.04 | 114 |
| 9/24 | 5.14 ± 0.62 | 0.062 ± 0.016 | 0.23 ± 0.03 | 115 |
| 9/30 | 4.00 ± 0.48 | 0.052 ± 0.013 | 0.18 ± 0.03 | 104 |
| 10/1 | 4.20 ± 0.50 | 0.055 ± 0.014 | 0.14 ± 0.02 | 104 |
| 10/8 | 3.55 ± 0.43 | 0.094 ± 0.024 | 0.19 ± 0.03 | 112 |
| 10/15 | 3.87 ± 0.46 | 0.055 ± 0.014 | 0.18 ± 0.03 | 99 |
| 10/22 | 3.66 ± 0.44 | 0.058 ± 0.015 | 0.18 ± 0.03 | 132 |
| 10/29 | 3.59 ± 0.43 | 0.067 ± 0.017 | 0.28 ± 0 04 | 135 |
| 11/5 | 4.51 ± 0.54 | 0.063 ± 0.016 | 0.19 ± 0.03 | 133 |
| 11/12 | 4.02 ± 0.48 | 0.100 ± 0.025 | 0.20 ± 0.03 | 118 |
| 11/19 | 5.03 ± 0.60 | 0.098 ± 0.024 | 0.30 ± 0.04 | 112 |
| 11/26 | 4.88 ± 0.59 | 0.052 ± 0.013 | 0.33 ± 0.05 | 116 |
| 12/3 | 4.99 ± 0.60 | 0.081 ± 0.020 | 0.46 ± 0.06 | 113 |
| 12/10 | 4.93 ± 0.59 | 0.140 ± 0.035 | 0.˝53 ± 0.06 | 109 |

**Table 5. Minimal, maximal and average values of the indicators monitored in 2014**

| Indicator | Unit | Value | | |
|---|---|---|---|---|
| | | Minimal | Maximal | Average |
| Arsenic (As) (total) | $mg.dm^{-3}$ | 0.031 | 0.140 | 0.063 |
| Iron (Fe) | $mg.dm^{-3}$ | 0.090 | 1.190 | 0.275 |
| Hydrogen sulfide ($H_2S$) | $mg.dm^{-3}$ | 1.130 | 6.920 | 4.608 |

**Table 6. Average concentrations of total arsenic and calculated concentration of As(III) in the particular months of 2014 and comparison with the limit value (0.05 mg.dm-3)**

| Month | Average value total As [mg.dm$^{-3}$] | 80—90 % As(III) [mg.dm$^{-3}$] | Limit overload [%] |
|---|---|---|---|
| January | 0.078 | 0.063—0.070 | 26—40 |
| February | 0.071 | 0.057—0.064 | 14—28 |
| March | 0.067 | 0.054—0.060 | 8—20 |
| April | 0.051 | 0.041—0.046 | < limit |
| May | 0.059 | 0.047—0.053 | 0—6 |
| June | 0.054 | 0.043—0.049 | < limit |
| July | 0.047 | 0.038—0.042 | < limit |
| August | 0.064 | 0.052—0.058 | 4—16 |
| September | 0.054 | 0.043—0.049 | < limit |
| October | 0.066 | 0.053—0.059 | 6—18 |
| November | 0.078 | 0.062—0.070 | 24—40 |
| December | 0.110 | 0.088—0.099 | 76—98 |

302 mg.dm$^{-3}$). Relatively little changes were observed in the case of calcium, magnesium, arsenic and sulphates (Table 2). Table 2 presents also the limit values for individual inorganic parameters. Except for arsenic, neither indicator exceeded the limit value set by the Food Code [27].

The results of microbiological analysis presented in Table 3 showed an absence of any determined pathogenic microorganisms in the mineral water in the monitored years.

The relevant Food Code (Third part, Chapter 25, Annex No. 1: Quality indicators for table water, infant water and mineral water) states that the limit value for arsenic content in mineral water is 0.05 mg.dm$^{-3}$ As(III) and this is not the value of overall arsenic. The concern is obvious — As(III) is 25 to 60 times more toxic than As(V) [9]. The AAS method used for determination of As can be used only for determination of total arsenic in water samples. Thus, the results obtained in this study characterise the concentration of total arsenic in mineral water. Under anaerobic conditions of ground mineral water, the form As(III) prevails. Under aerobic or oxidising conditions, the As(III) form oxidizes easily to As(V). The analyses of ground water showed that the share of As(III) is 80 to 90 % in overall content of arsenic [11]. When we used this proportion to calculate As(III) from total arsenic, the limit value was exceeded during seven months of the year 2014, i. e. during January to March, August, and October to December (Table 6). Thus, the mineral water met the prescribed limit value for arsenic content during 5 months in the year. These months were mostly the summer months. The arsenic content of mineral water determined in the Geoanalytical Laboratory in 2013—2015, converted to As (III), also indicated that the limit value was exceeded (2013—0.071; 2014—0.058; 2015—0.057 mg. dm$^{-3}$).

The influence of the seasons on the monitored parameters ($H_2S$, arsenic, iron and the level of river Hornád) was investigated by one-way ANOVA. The results were divided into four groups according to four seasons, to be specific January—March, April—June, July—September, October—December. Significant differences between seasons were observed for parameters $H_2S$, Fe and the level of river Hornád ($P < 0.05$ for $H_2S$ and the level of river; $P < 0.001$ for Fe). No significant differences were observed for arsenic. No correlation between particular indicators were detected.

Except for some periods of different length, the mineral spring Gajdovka was used from the second half of the 19th century to 1920s. The spring was often closed because the water did not comply with the hygiene criteria. The modern history of this spring started in 1995 when 30-metres deep new well, designated G-5, was drilled. This well with capacity of 0.3 litres per second is used up to this day.

The problem with arsenic in mineral water persisted until 2006 when technology based on sorbent BAYOXIDE E33 was introduced. The arsenic content was decreased significantly but the water quality was also changed. The average concentration of overall arsenic in finished water was 0.0108 mg dm$^{-3}$ in 2006—2008 [5]. However, water was became excessively enriched with iron and precipitation of its oxides and hydroxides occurred. The characteristic hydrogen sulfide smell disappeared. This was the reason why this technology was abandoned in 2009 [5]. Due to the interest of the public in the spring, the mineral water was treated by mixing mineral water with drinking water. The drinking water source is located in the gravel floodplains of the river Hornad near the Gajdovka spring [13]. Chemical composition of this drinking water shows that it is the basic calcium-magnesium-hydrogen carbonate type. Mineral water and drinking water are mixed at a ratio 1 : 1 (v/v). This way diluted mineral water is supplied to the public.

However, the problems with exceeding the limit value of arsenic content in mineral water still persist. Dietzová et al. [5] estimated the health hazard for children and adults presented by mineral water containing arsenic. Model calculations were made according to the methodology US EPA [30]. The daily consumption of 0.3 dm$^3$ by children and 1 dm$^3$ by adults do not lead to exceeding the recommended reference dose of arsenic (RfD: $3.0 \times 10^{-4}$ mg.kg$^{-1}$ of mass per day). The risk of consumption of arsenic in mineral water from Gajdovka spring is thus acceptable when the water is consumed irregularly and the volume consumed does not exceed the recommended amount [5]. Spring visitors are informed about the recommended amounts of consumed mineral water by means of information tables located near the withdrawal point.

There are only few mineral waters in Slovakia with chemical composition and properties similar to "Gajdovka". The arsenic problem is relevant also to other springs. The springs in Gánovce (Filice), Hôrka and Čenčice in district Poprad belong among the mineral springs with repeatedly determined excess arsenic values [17]. Water in these locations can be used in small amounts. The problem with arsenic can arise when water from these springs are commonly used for drinking.

The presence of arsenic in ground water in the Košice surroundings is not rare. Three geothermal wells with designation GTD-1 to 3 were made near the municipality of Ďurkov in the years 1998—1999. These wells are 2252 m, more than 3210 and 3151 metres deep. The temperature at well head in particular wells is 123—125 °C. Geothermal water of the structure Ďurkov is a complex water-steam-solid phase system. The value of its mineralisation ranges from 25 to 32.dm$^{-3}$. This geothermal water has distinct characteristics of Na-Cl type with low representation of substance Na-$HCO_3$. Of all trace metals arsenic is found in the highest concentration in geothermal water. The maximal concentration was determined to be 36 mg.dm$^{-3}$. The main source of the high level of arsenic is considered to be the neovulcanites of mountain range Slánske vrchy. At convenient geochemical conditions, arsenic is able to pass to water solution from arsenopyrite at the presence of pyrite, as salty water is capable of dissolving these minerals, it is even by solving of these minerals by salt water [3]. High content of arsenic in geothermal water presents a big risk of environmental contamination.

The most known mineral water containing arsenic in the Czech Republic is "Bělovesská kyselka" near Náchod that was very popular in the past and was known under the name of "IDA". Arsenic concentration in water from this spring reached 1 mg.dm$^{-3}$ [18]. Unlike the spring Gajdovka, its mineralisation is lower (950 mg.dm$^{-3}$) and it has a balanced concentration of Na, Mg, Ca and sulphates, with low content of iron and, on the contrary, high content of $CO_2$. Considering the high content of arsenic, this mineral water is not suitable for permanent consumption. The analyses of water in 2015 showed that concentration of arsenic in source IDA was 0.479 mg.dm$^{-3}$. After the water was treated by means of a device for elimination of arsenic, the mineral water IDA used today contains less than 0.01 mg.dm$^{-3}$ of arsenic. Near Náchod, in Hronov, there are another two arsenic containing mineral springs. These springs are similar to Gajdovka in many aspects. The water is strongly mineralised (2 g.dm$^{-3}$) with a high content of $CO_2$ and with significant share of iron and hydrogen sulfide. The springs in Náchod and Hronov are the only arsenic containing mineral waters in the Czech Republic [18].

## CONCLUSIONS

Mineral water Gajdovka is very popular among the inhabitants of Košice. Therefore, the monitoring of its quality is important. Particularly problematic is the content of arsenic, which is one of the toxic elements and can endanger human health when consumed regularly. The results of the determination of arsenic in mineral water throughout the year 2014 confirmed that its concentration changes during a calendar year and is often at or above the limit set by relevant regulations. When calculating the As(III) form from the total arsenic it was found that the limit value was exceeded during seven months of the monitored year, i.e. in January to March, August, and October to December. The limit concentration for the iron content, which influences the sensory quality of mineral water, was not exceeded during this year. Statistical analysis of the monitored parameters, namely the concentration of arsenic, iron and hydrogen sulphide and the level of the river Hornad, showed that the season influences the content of iron, hydrogen sulfide and the level of the river Hornad but not the level of arsenic. No correlation between the individual monitored parameters was observed. With regard to the arsenic content, the Regional Public Health Authority based in Košice adopted certain rules for the consumption of mineral water Gajdovka. These rules are posted at the delivery point and indicate the recommendations for the use of this mineral water.


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## REFERENCES


1. **ATSDR — Agency for Toxic Substances and Disease Registry, 2007:** Toxicological profile for arsenic. *U. S. Department of Health and Human Services Public Health Service*. Division of Toxicology and Environmental Medicine/Applied Toxicology Branch 1600, Clifton Road NE Mailstop F-32 Atlanta, Georgia, 30333.
2. **Bodiš, D., Kordík, J., Slaninka, I., Malík, P., Liščák, P., Panák, D., et al., 2010:** Mineral waters in Slovakia — evaluation of chemical composition stability using both historical records and the most recent data. *Journal of Geochemical Exploration*, 107, 382—390.
3. **Bodiš, D., Vranovská, A., 2012:** Genesis of anomalous arsenic content in the Ďurkov hydro-geothermal structure (In Slovak). *Podzemná voda* (Groundwater), 18, 123—136.
4. **Dietzová, Z., Bratská, Z., 2010:** Estimation of health risk from water consumption from the freely accessible spring water in Košice (In Slovak). In *Environment and Health*. Proceedings of Scientific Work, Bratislava, 25—30.
5. **Dietzová, Z., Labancová, J., Bratská, Z., 2012:** Is the health risk from arsenic in a freely accessible mineral spring in Kosice acceptable? (In Slovak). *Using Experimental Methods to Protect the Health of the Population and the Environment*. Reviewed Proceedings of Scientific Works, Košice, 32—37.
6. **Ďurža, O., Khun, M., 2002:** *Environmental Geochemistry of Heavy Metals* (In Slovak). Faculty of Natural Sciences, UK Bratislava, 116 pp.
7. **Fľaková, R., Ženišová, Z., Jašová, I., Krčmář, D., 2009:** Water contamination with arsenic and antimony in abandoned deposit Poproč (In Slovak). *Podzemná voda* (Groundwater), 15, 132—148.
8. **Gajda spa:** http://gajdovka.webnode.sk/gajdove-kupele/www.cassovia.sk/zony/anicka.php3. (In Slovak). Accessed Nov. 15, 2017).
9. **Gürkan, R., Kir, U., Altunay, N., 2015:** Development of a simple, sensitive and inexpensive ion — pairing cloud point extraction approach for the determination of trace inorganic arsenic species in spring water, beverage and rice samples by UV-Vis spectrophotometry. *Food Chemistry*, doi:10.1016/j.foodchem.2015.01.142. Accessed Feb. 2, 2018.
10. **Hagarová, I., Žemberyová, M., 2005:** Determination of arsenic in biological and environmental samples by AAS techniques (In Slovak). *Chemické Listy* (Chemical Letters), 99, 578—584.
11. **Hegedűsová, A., Pavlík, V., Hegedűs O., 2010:** The occurrence of arsenic in artesian wells of selected sites (In Slovak). *Acta Universitatis Matthiae Bell*i, Ser. Chem., 12, 81—86.
12. **Hughes, M. F., Razo, L. M., Kenyon, N. E. M., 2000:** Dose dependent effects on tissue distribution and metabolism of dimethylarsinic acid in the mouse after intravenous administration. *Toxicology*, 143, 155—166.
13. **Hydrogeochemical report, 1996:** Košice-Anicka-hydrogeochemical evaluation min. water in G-5 borehole. 035/96. Geoconzult a.s.
14. https://euroclean.sk/slovnik-sk/arsen-ve-vode-jeho-odstraneni/ (In Slovak). Accessed Feb. 2, 2018.
15. http://www.topky.sk/cl/10/568940/V-pitnej-vode-v-Pohronskom-Bukovci-nasli-arzen (In Slovak). Accessed Feb. 2, 2018.
16. http://vysetrenie.zoznam.sk/cl/1000663/1470313/Slovaci-v-ohrozeni--Zakazane-pitie-vody-z-vodovodu--obsahuje-nebezpecny-arzen (In Slovak). Accessed Feb. 2, 2018.

17. https://spis.korzar.sme.sk/c/5596015/pramene-v-okoli-ganoviec-maju-vyssi-obsah-arzenu.html. (In Slovak). Accessed Feb. 2, 2018.

18. http://www.putujici.cz/?p=p_354&sName=Prameny-plne-arzenu. (In Slovak). Accessed Feb. 2, 2018.

19. **IARC—International Agency for Research on Cancer, 1980:** IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans, Vol. 20, *Some Metals and Metallic Compounds*, IARC Lyon, 39—140.

20. **Jurkovič, Ľ., Hiller, E., Slaninka, I., Kordík, J., Majzlan, J., 2006:** *Geochemical Study of Contaminated River Sediments and Surface Waters and Experimental Assessment of Mobility As* (the catchment area of the Kyjov and Ondava stream, Poša wasteland, eastern Slovakia) (In Slovak). Workshop BO. http://www.banskeodpady.sk/files/Jurkovic%20et%20al%20 2006_Worshop%20BO. pdf. Accessed Nov. 15, 2017.

21. **Jurkovič, L., Kordik, J., Slaninka, I., 2006:** Geochemical study of arsenic mobility insecondarily influenced Kyjov Brook and Ondava River (Eastern Slovakia). *Slovak Geological Magazine*, 12, 31—38.

22. **Loredo, J., Ordóñez, A., Baldo, C. and García-Iglesias, J., 2003:** Arsenic mobilization from waste piles of the El Terronal mine, Asturias, Spain. *J. Geochemistry: Exploration, Environment, Analysis*, 3, 229—237.

23. **Milata, V., Segľa, P., Gatial, A., Šima, J., Kováčik, V., 2009:** *Spectral Tables for Solving Problems and Problems in Molecular Spectroscopy* (In Slovak). STU, Bratislava, 90 pp. http://www.banskeodpady.sk/files/Jurkovic%20et%20al%20 2006_Worshop%20BO.pdf. Accessed Nov. 15, 2017.

24. **Piroš, A., 1999:** Was Anna the pub owner ? *Cassovia.sk:* http://www.cassovia.sk/zony/anicka.php3. Accessed Nov. 15, 2017.

25. **Pitter, P., 1999:** *Hydrochemie* (In Czech). 3rd rev., Prague, Higher School of Chemical Technology, 568 pp.

26. **Rapant, S., Krčmová, K., 2006:** Potential health risk of arsenic contamination of groundwater of the Slovak. *Mineralia Slovaca*, 38, 29—36.

27. **Slovak Water Management Company, 2014:** *Measured Curve, Water Hornad-Kysak, Water Conditions 2014* (In Slovak). Banská Šiavnica.

28. **Ševc, J., Čerňanský, S., 2003:** Microbial methylation as a part of transformation processes and migration of arsenic under natural conditions. *Phytopedon* (Bratislava), 2, 60—68.

29. **State Veterinary and Food Administration SR:** Table: Water quality indicators, infant water and mineral water. In *Food Code* (updated on Jan. 31, 2017). Part III, Chapter 25, Appendix No. 1. http://www.svssr.sk/legislativa/kodex_03_25_01 asp. Accessed Nov. 15, 2017.

30. **US EPA Integrated Risk Information** *System, 1998: Risk Assesment-Multipathway Exposure*. Risksoft 2,0 /software/.

31. **Ženišová, Z., Fľaková, R., Jašová, I. Cicmanová, S., 2009:** Antimony and arsenic in waters affected by mining activities in selected areas of Slovakia (In Slovak). *Podzemná voda* (Groundwater), 15, 100—117. https://doi.org/10.1144/1467-7873/03-003. Accessed Nov. 15, 2017.

32. **Žemberyová, M., Chromá, O., Shearman, A., Hagarová, I., 2007:** Speciation of chromium and inorganic arsenic in waters using solid phase extraction and atomic absorption spectrometry (In Slovak). *Chemické Listy* (Chemical Letters), 101, 303—309.


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